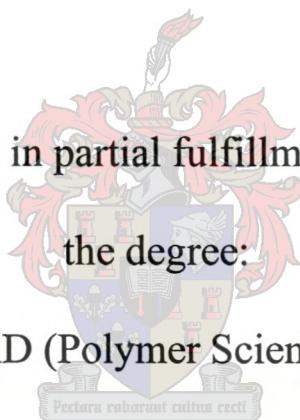


***Reversible Addition-Fragmentation
Transfer Polymerization in
Heterogeneous Aqueous Media***

Dissertation presented in partial fulfillment of requirements for

the degree:

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by

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Declaration

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

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Abstract

The study presented in this dissertation had as primary aim to develop pathways to heterogeneous aqueous polymerizations that had living characteristics. To this end, the reversible addition fragmentation chain transfer (RAFT) process was investigated in pre-dispersed and *ab initio* emulsions as well as homogeneous media.

The synthesis of RAFT agents was carried out. The compounds prepared provided varied behaviour in reaction. *In situ* ^1H nuclear magnetic resonance (NMR) increased understanding of homogeneous RAFT mediated polymerizations. The early behaviour of RAFT mediated polymerizations led to the definition of initialization; a period before pre-equilibrium in a polymerization where degenerate behaviour occurs.

Stable miniemulsion preparation methods were developed that provided living polymer latexes using high surfactant concentrations. The effect of surfactant concentration on particle size and latex stability was investigated. Living polymer characteristics were shown by the use of size exclusion chromatography, and 2-dimensional chromatography conclusively showed block polymer formation. *In situ* NMR spectroscopy of emulsions in deuterated water was used to provide evidence on the role of initiator solubility in polymerization.

Secondary nucleation in high surfactant concentration miniemulsions systems was investigated using both particle size and molar mass analysis techniques and a means of eliminating secondary particle nucleation was shown through the use of aqueous phase radical traps. The role of the RAFT agent used in the polymerization was shown to be significant in determining the extent to which multiple polymer distributions formed in the polymerization in that radical exit from particles was affected.

Finally, a new form of emulsion polymerization, which has been termed proto-seeded emulsion, has been developed. The proto-seed latex is formed by using a monomer whose polymer has chain length dependent water solubility. This process allows *ab initio* RAFT mediated emulsion polymerization to be conducted successfully without transport of RAFT agents in heterogeneous media.

Opsomming

Die primerê doel in hierdie dissertasie is die ontwikkeling van roetes na heterogene water-gebaseerde polimerisasies met lewende eienskappe. Om hierdie doel te bereik is die omkeerbare addisie fragmentasie ketting oordrag proses (*eng* reversible addition fragmentation chain transfer (RAFT)) ondersoek in vooraf verspreide en direkte emulsies sowel as homogene media.

Die sintese van RAFT agente is uitgevoer. Die verbindings wat voorberei is het verskillende eienskappe in reaksies getoon. *In situ* ^1H kern magnetiese resonansie (KMR) het die kennis en begrip van homogene RAFT polimerisasies uitgebrei. Die vroeë gedrag van RAFT polimerisasies het tot die definisie van inisialisasie gelei; 'n periode voor die pre-ekwilibrium in 'n polimerisasie waartydens "degenerate" gedrag plaasvind.

Stabiele miniemulsie voorbereidings metodes is ontwikkel wat lewende polimeer latekse verskaf het met gebruik van hoë seep konsentrasies. Die effek van seep konsentrasie op partikel grootte en lateks stabiliteit is ondersoek. Lewende polimeer eienskappe is bewys deur gebruik te maak van grootte-uitsluiting vloeistof chromatografie, en 2-dimensionele chromatografie het duidelik blok-polimeer vorming gewys. *In situ* KMR spektroskopie van emulsies in gedeutereerde water is gebruik om bewys te lewer van die rol van initieerder-oplosbaarheid in polimerisasie.

Sekondêre nukleasie in hoë seep konsentrasie miniemulsie sisteme is ondersoek met die gebruik van beide partikel grootte sowel as molêre massa analise tegnieke. 'n Metode om sekondêre partikels te verhoed is verskaf deur gebruik te maak van water-fase radikaal lokvalle. Die rol van die RAFT agent in die polimeerisasie is beduidend in die graad van vorming van meer as een polimeer distribusie in die sin dat radikaal uitgang van partikels beïnvloed was.

Ten slotte is 'n nuwe vorm van emulsie polimeerisasie ontwikkel wat proto-gesaaide emulsie genoem is. Die proto-gesaaide lateks is gevorm deur gebruik te maak van 'n monomeer waarvan die polimeer water-oplosbaarheid afhanklik is van die ketting-

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lengte. Die proses laat *ab initio* RAFT emulsie polimerisasie toe om suksesvol uitgevoer te word sonder die vervoer van RAFT agente in heterogene media.

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List of Symbols

ε	The reduced super saturation
χ	Interaction parameter
γ	The interfacial tension
μ	Chemical Potential
π	Mathematical constant
θ	Degree of surface coverage
ρ	Density of a substance
\bar{n}	The average number of radicals per particle
Φ	Volume fraction
Γ	Surfactant absorption per particle area
\bar{M}_n	Number average molar mass
\bar{M}_w	Weight average molar mass
$\bar{M}_{n, \text{theory}}$	Calculated number average molar mass
$[I]_0$	Initial concentration of the initiator
$[M]_0$	Initial concentration of the monomer
$[RAFT]_0$	Initial concentration of the RAFT agent
FW_M	Molar mass of a monomer unit
FW_{RAFT}	Molar mass of RAFT agent
σ	Surface tension of the liquid-liquid interface
η	Viscosity
v_b	Volume of a single molecule
$\Delta\mu$	Difference in chemical potential
f_i	Initiator efficiency
k_β	Rate coefficient
k_B	Boltzmann's constant
k_d	Decomposition rate coefficient for the initiator
k_p	Propagation rate coefficient
r	Radius of the droplet
x	Fractional conversion.

μ_b	Chemical potential of bulk material
μ_d	Chemical potential of droplet material

List of Acronyms

AD	Cyano isopropyl dithiobenzoate
ADme	Cyano isopropyl paramethoxy dithiobenzoate
AIBN	2,2-azobis(isobutyronitrile)
ATRP	Atom Transfer Radical Polymerization
BA	Butyl acrylate
CD	Cumyl dithiobenzoate
CDta	Cumyl phenyl dithioacetate
CMC	Critical Micelle Concentration
DMSO	Dimethyl sulfoxide
DP	Degree of polymerization
ESR	Electron Spin Resonance
HD	Hexadecane
KPS	Potassium persulfate
MMA	Methyl methacrylate
PMMA	Poly(methyl methacrylate)
PS	Poly(styrene)
PLP	Pulsed laser polymerization
RAFT	Reversible Addition Fragmentation Chain Transfer
SEC	Size exclusion chromatography
SFRP	Stable Free Radical Polymerization
STY	Styrene
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy free radical
THF	Tetrahydrofuran

Chapter 1: Introduction and Aims

Abstract

A short introduction to the dissertation is presented to allow the reader to understand the context of each chapter as well as the general aims of the research presented here.

1.1 Introduction

This dissertation is presented as a sum of parts. Each part is vital to the understanding of the whole. A doctoral investigation consists of many different aspects much the same as the dissertation presented here. To conduct the work presented in this dissertation, different aspects of the research process have been encountered and overcome. These include technical and managerial issues. From a laboratory point of view, it has been necessary to revise and develop new methods. From a scientist's viewpoint it has been necessary to evolve new techniques in data analysis.

I hope that the reader will enjoy their journey through the parts of this dissertation as much as I have enjoyed the different aspects that have been encountered in the process of conducting the work presented here. To start this dissertation it seems logical to discuss polymer science from a reference point that requires no chemical background.

1.2 Plastic

Most people are familiar with the term "plastic", the word commonly used to describe materials that are synthetic in nature. However, in many cases these materials do not display plastic behaviour in the scientific sense of the word. "Plastic" materials are scientifically referred to as being polymeric, the word polymer being derived from the Greek "poly" and "meros" loosely translated as many parts. In practical terms, this means that they are assembled from large arrays of small molecules that have been chemically bonded to form a macromolecule.

Polymers are an integral part of our daily lives. The questions may well be asked: why? What is it about these molecules that make them so remarkable? Firstly the sheer size of the molecules is quite impressive, secondly the whole is greater than the sum of the parts (monomer units) the reason being that the molecules gain macroscopic properties as the polymer chains increase in length. This is mostly due to intermolecular interactions, either physical or chemical, between the chains.

The first polymeric materials that mankind made use of were modified natural polymers which were used to make leather, paper and fabric. This was the beginning of a very special relationship that humans have with macromolecules. By the time that the human genome began to be understood, and deoxyribonucleic acid (DNA), the

fundamental building block of life, was known to be an advanced double helix polymer,^{1,2} researchers had long since begun to take baby steps into the vast and confusing realm of the macromolecule.

The science of polymers is an actively developing field. There is a large amount of fundamental research that still needs to be undertaken to understand all the variables that can be tuned in macromolecular design. The chemical characteristics that are required to provide specific macromolecular properties are still being investigated and the ability to tailor polymers for a specific purpose is a field that generates significant amounts of interest from the scientific community. The reasons for the interest in mastering polymeric materials are the vast number of potential applications that could change the life of the average person on the street.

Polymers can be divided into two groups, thermosets and thermoplastics. Thermosets are resins that are chemically bonded into a single form and do not have the ability to deform plastically. Thermoplastic materials however consist of lengthy single polymer chains, which, if given the opportunity, are capable of movement. Polymeric materials exhibit temperature dependent transitions, which influence the types of movement that are possible in a polymer system. The most important of these is known as the glass transition. The temperature at which this transition occurs is referred to as the glass transition temperature (T_g). This temperature is used as a guideline to the material properties of a polymeric material: polymers at temperatures below their specific T_g are referred to as glassy materials while polymers above their T_g exhibit rubbery characteristics.

1.3 Polymerization

Polymerization is typically broken down into two superclasses, namely step and chain polymerization. Step polymerization is a process by which the polymer grows in “steps” an example is polycondensation, which is typically used to create polymers such as polyesters and polyamides. A good example of a product of step polymerization is Nylon 6,6, a polyamide produced by the condensation of adipic acid and hexamethylene diamine, ubiquitously referred to as Nylon. Du Pont used this material, which has a vast number of applications, to revolutionize the production of ladies’ stockings prior to 1940 and up to the 1960’s.

Chain polymerization is a process in which polymer chains are created by stringing together monomer units to create a macromolecule. The monomers that are typically used for chain polymerization are olefinic, although some processes, such as group transfer and the polymerization of cyclic monomers, do not require olefinic units. Anionic, cationic and radical mechanisms are among the most common means of chain polymerization. Transition metal catalyzed polymerization first developed by Ziegler³ and Natta,⁴ with the two groups focusing on different aspects of the polymerizations, has however become of significant commercial importance. It is ironic to note that the stereospecific transition metal catalyzed polymerizations were developed at the same time as the double helix theory for DNA.

This dissertation is concerned with an older chain polymerization process, radical polymerization. For that reason we shall restrict detailed systemic descriptions to this single technique.

1.4 Radical Polymerization

Radical polymerization is one of the oldest chain growth techniques available for the creation of polymers. There are numerous advantages associated with radical polymerization: it is robust, being tolerant to many impurities including water; it can be conducted at moderate temperatures and pressures; and it requires very little specialized equipment.

There are however a large number of problems inherent to the radical polymerization technique. Radicals are extremely reactive, and side reactions that do not involve chain growth are common. Broad molecular weight distributions are the norm, and predicting polymerization behaviour is not elementary.⁵ To understand the difficulty in the modeling of radical systems it is important to have a deeper look at the kinetic events in radical polymerizations. This will be done in chapter two.

1.5 Dissertation

This dissertation contains an investigation into the living radical polymerization technique known as **Reversible Addition Fragmentation Transfer (RAFT)** with specific emphasis on its application in heterogeneous aqueous media. The dissertation does however contain a substantial amount of homogeneous media research. The reason for this is the simplicity of homogeneous systems, which enable us to examine

specific polymerization aspects without the complications of a heterogeneous environment.

1.6 Outline

Chapter 1-Introduction and Aim

A short outline of the dissertation, some general aims and a short introduction are presented in chapter one.

Chapter 2-Historical and Theory

Chapter two gives an introduction to radical kinetics, heterogeneous aqueous polymerizations and the RAFT process that is discussed in the dissertation, specifically highlighting areas that are given the majority of attention, but not ignoring the framework in which the investigation lies.

Chapter 3-Synthesis of RAFT agents

Chapter three addresses the organic synthesis that was required for this study. It is important to realize that the proliferation of the RAFT technique was initially slowed by the synthetic techniques and preparation of agents that are not normally associated with polymer chemistry. The RAFT agents and routes that were used are discussed.

Chapter 4-Homogeneous studies

Chapter four addresses some of the fundamental issues that play a role in the process of a RAFT mediated polymerization. Homogeneous media were used as a tool to allow insight into heterogeneous systems. Specific discoveries are presented and the mechanism of RAFT is discussed. The use of *in situ* NMR as a kinetic tool is highlighted.

Chapter 5-Heterogeneous studies

RAFT mediated miniemulsion polymerization is considered in the context of literature studies in the field. The stability of emulsions is discussed in terms of superswelling. Stable recipes were developed and the products were analyzed, showing living radical behaviour. 2-Dimensional chromatography was used as a tool for polymer analysis.

Chapter 6-Secondary particle formation

An important emulsion phenomenon is examined. Secondary particle nucleation in the presence of RAFT highlights many of the issues that are still under investigation in the process of heterogeneous aqueous polymerization. Double detector techniques and deconvolution were used to provide more insight into the results obtained by size exclusion and capillary hydrodynamic fractionation.

Chapter 7-Protoseeded *Ab initio* Emulsion

Chapter seven discusses an emulsion technique that has been patented and shows significant early promise. The use of monomers with specific properties that allow their polymers to change their aqueous phase solubility in a temperature dependent fashion provided a new route to RAFT mediated *ab initio* emulsion polymerization.

Conclusions and Recommendations

Some general conclusions and recommendations for future study are highlighted.

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Chapter Two: Historical and Theory

Chapter 2: Historical and Theory

Abstract

An introduction to radical kinetics and emulsions as relevant to the study of reversible addition fragmentation in heterogeneous aqueous media is given. Living radical polymerization is introduced. The RAFT process as described in the literature is discussed to provide a basis for the mechanistic development that is discussed in chapter four.

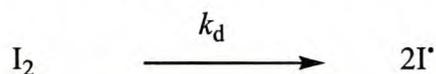


2.1 Radical Kinetics

The kinetics of radical polymerization are complex and are affected by a number of factors. There are various different, yet potentially interrelated, events that affect the concentration of radical species in a radical polymerization. There are also a number of different radical species that can be active in each system. To understand the rate of polymerization and the change in the molecular weight distribution with time in a polymerization reaction, a detailed understanding of initiation, propagation, termination and chain transfer steps is required.

2.1.1 Initiation

For a radical polymerization to occur, radicals need to be generated. This process is known as initiation. The initiation process can be driven by autoinitiation, i.e. generation of radicals by the polymerizable moiety, or initiation can be started by the use of a radical-generating source, e.g. Cobalt 60.^{1,2} The most common means of radical generation is by using a compound often termed a radical initiator, which forms radicals on decomposition. If an initiator molecular is described as I_2 then:



Scheme 2.1 Initiation, I_2 is a compound capable of fragmenting into two initiating radicals I^{\cdot} .

The rate at which the initiating compound decomposes is dependent on the mechanism of decomposition, i.e. thermal, photochemical, etc. In most cases, a decomposition rate coefficient can be defined which is dependent on the conditions under which decomposition is occurring. This coefficient is termed k_d . There are numerous classes of initiator compounds. The only attribute that they have in common is the ability to release radical species on decomposition. One common example is the azo compounds, which decompose to release molecular nitrogen as illustrated in scheme 2.2 by the decomposition of azo-bisisobutyronitrile (AIBN).

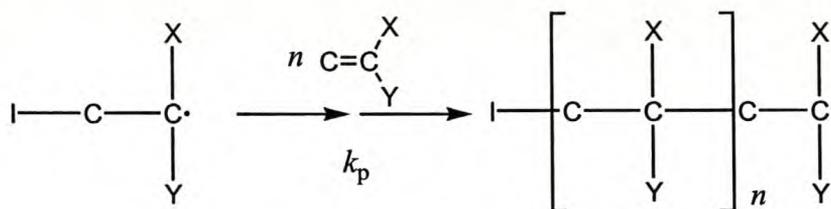
From equation 2.3 it is elementary to derive that at a certain time t the initiator concentration will be given by:

$$[I] = [I]_0 \cdot e^{-k_d t} \quad (2.2)$$

Where $[I]_0$ represents the initial initiator concentration and $[I]$ represents the initiator concentration at some time t . The radical species that is generated by the initiation process requires certain characteristics to be useful in a radical polymerization. It needs to be able to add to an olefinic monomer unit. The olefinic monomer unit is typically activated by one or two substituents, which we shall refer to as the X and Y groups (see scheme 2.4), at least one of which is typically electron withdrawing. The initiator-derived radical also needs to be formed at a rate that is suitable for the monomer in question, i.e. the decomposition of the initiating species should ideally occur fast enough that it is finished prior to complete monomer conversion, and the initiator decomposition should be slow enough that there are sufficient radicals in the system for the target conversion to be reached.

2.1.2 Propagation

This brings us to the growth of the polymer chain, which is also known as propagation. This propagation process occurs via multiple additions of monomer units to a chain.



Scheme 2.4 Propagation of a radical species by the addition of monomer units

The propagation process occurs very rapidly in a conventional polymerization, leading to chain lengths that often exceed 10^3 monomer units. The substituents X and Y play very important roles in determining both the reactivity of the monomer and the reactivity of the radical species in a polymerization reaction. This behaviour will be discussed in more detail in chapter four. Highly stabilized radicals are less reactive than radicals that are not supported by electron-accepting groups, but monomers that are capable of stabilizing a radical are more reactive for polymerization. The varied radical reactivities result in classes of vinyl monomers having rate coefficients that

can differ by orders of magnitude. For example styrene at 30°C has a propagation rate coefficient of 106 mol.L⁻¹.s⁻¹, while for acrylates values of 11600-18800 mol.L⁻¹.s⁻¹ have been reported at 20 °C.³

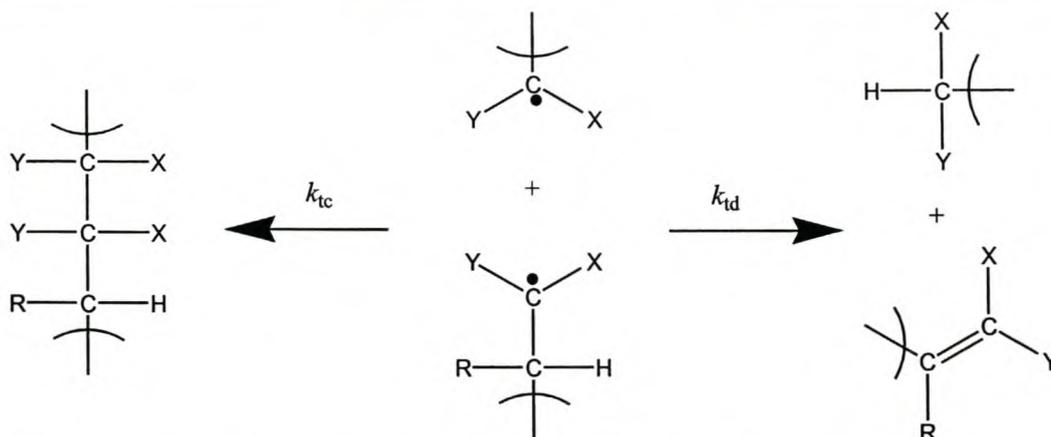
The rate coefficient for propagation (k_p) is chain length dependent for a number of reasons, the first of which is that the initiator fragment exerts an influence on a chain's ability to support a radical. This effect is significant for a small number of monomer additions to the initiator fragment. A second reason for chain length dependence is the steric influence of the growing chain, which decreases the local concentration of the monomer at the radical site.⁴ The ability of short chains to diffuse can also play a substantial role in glassy systems and as the volume of activation for propagation is non-zero, the propagation reaction is as a result pressure dependent. One of the disadvantages of the radical process is that the radical addition is typically not enantiotopic face specific leading to stereochemical heterogeneity in the polymer produced. There are a number of exceptions to the lack of stereospecificity,^{5,6} but most involve coordination of the monomer in such a way as to limit access to a specific enantiotopic face. To describe propagation in its simplified form (i.e. independent of chain length) equation 2.3 can be used:

$$-\frac{d[M]}{dt} = k_p[M^*][M] \quad (2.3)$$

Where M^* is a growing chain with a radical endgroup and M is monomer.

2.1.3 Termination

The process of radical polymerization is plagued by the sheer reactivity of radicals. Radical-radical reactions are typically diffusion-controlled and irreversible, which means that radical interactions in a polymerization process invariably lead to the loss of radical species. In a conventional radical polymerization, this process, which is called chain termination, occurs via a number of mechanisms. Termination by radical disproportionation and radical combination are the two bimolecular processes that commonly dominate in a radical polymerization.



Scheme 2.5 Termination via combination or termination via disproportionation

Termination is known to be a chain length dependent process.⁷⁻¹⁰ Diffusion is dependent on the size and shape of a molecule, and in the case of polymers, which are very large molecules, there is very little difference between very long chains, but there are significant differences in diffusion rate coefficients at short chain lengths. Autoacceleration (the Tromssdorff-Norissch gel effect) results from the increase in viscosity that occurs at higher conversions in specific polymerizations. Autoacceleration occurs because of a radical build up due to decreased termination in the reaction. To describe termination we need two rate coefficients, the rate coefficient for disproportionation (k_{td}) and the rate coefficient for combination (k_{tc}) as illustrated in scheme 2.5:

$$k_t = k_{td} + k_{tc} \quad (2.4)$$

The rate of termination in the reaction (ignoring chain length effects) is therefore:

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

Initiation and termination are competing events and because two radical species are being formed by each initiation decomposition step, we can say that:

$$\frac{d[M^\bullet]}{dt} = 2f \cdot k_d[I] \quad (2.6)$$

Where f is the efficiency with which propagating radicals are formed. The efficiency factor will be discussed in more detail later in chapter four.

When the polymerization reaches a point at which the rate of radical loss and generation are equal then the polymerization is said to be under steady-state conditions and by combining equations 2.5 and 2.6 we can state that:

$$[M^*] = \left(\frac{f \cdot k_d [I]}{k_t} \right)^{0.5} \quad (2.7)$$

Combination of equations 2.3 and 2.7 lead us to a general description for the rate of a thermal free radical polymerization, which is:

$$-\frac{d[M]}{dt} = k_p \left(\frac{f \cdot k_d}{k_t} \right)^{0.5} [M][I]^{0.5} \quad (2.8)$$

This expression, when integrated against time assuming that $\frac{d[I]}{dt}$ is very small, leads us to equation 2.9:

$$\ln \left(\frac{[M]_0}{[M]_t} \right) = k_p \left(\frac{f \cdot k_d}{k_t} \right)^{0.5} [I]^{0.5} \cdot t \quad (2.9)$$

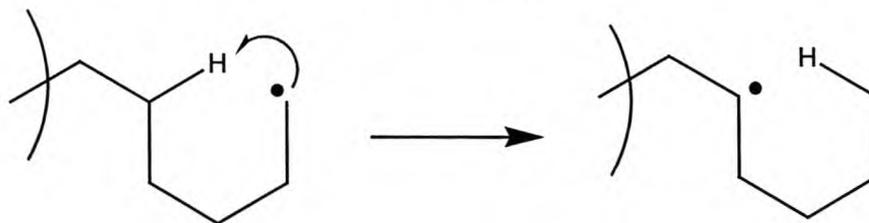
This equation, which will be used for the practical description of the homogeneous reaction rates in this dissertation, demonstrates the importance of the initiator concentration and its relation to the rate of the reaction. It should however be noted that this is a classical description and as average termination rates change during a reaction, and initiator decomposition is often quite dramatic, this description should be used with care.

2.1.4 Transfer

Chain transfer is the exchange of radical activity between molecules, or over a significant number of bonds within a molecule. Radicals are capable of undergoing change in type without undergoing radical loss events. Chain transfer is the second reaction, after propagation, which affects the reactivity of radical centres. Chain transfer can terminate chains and in that way affect the molecular weight distribution in a polymerization. In principle, transfer can occur to any species in the polymerization system, and for this reason it is very important to choose solvents with transfer properties that are suitable for the target system.

Chain transfer agents are commonly added to polymerizations to reduce the molecular weight of the polymeric product and to provide some sort of control over the

distribution of the chain lengths. Chain transfer can also occur to monomer and polymer in the system by a process of hydrogen abstraction. When chain transfer is an intramolecular event, it is referred to as backbiting.



Scheme 2.6 Transfer via backbiting

Typical examples of chain transfer agents include tetrabromomethane and a variety of mercaptans. These molecules transfer atoms readily via radical mechanisms in an irreversible fashion. Transfer is also a chain length dependent and viscosity dependent process.¹¹ The magnitude of transfer coefficients (C) with respect to different species is defined with a subscript and the most relevant is normally C_T , the transfer with respect to a chain transfer agent.

$$C_T = \frac{k_{trT}}{k_p} \quad (2.10)$$

In equation 2.10, k_{tr} is the overall rate coefficient for chain transfer. The k_{tr} values for tetrabromomethane and mercaptans, $2500 \text{ mol.L}^{-1}.\text{s}^{-1}$ and $1500\text{-}2500 \text{ mol.L}^{-1}.\text{s}^{-1}$ respectively (for styrene at $60 \text{ }^\circ\text{C}$)¹² are substantially lower than the values estimated for some dithioesters, which are estimated to be above $10\,000 \text{ mol.L}^{-1}.\text{s}^{-1}$.¹³

2.2 Heterogeneous or multiphase systems

A large part of modern chemistry is devoted to the development of heterogeneous processes. Heterophasic reactions can be carried out with a variety of different continuous and discrete phases. These processes have a number of commercial advantages when separation of products is considered, but they pose a number of problems for the chemist. Heterogeneous systems are invariably more complex than the comparable homogeneous systems. This is largely because chemical reactions are directly dependent on the ability of the reactants to interact physically. When the reactants are not in the same phase in a reaction, methods have to be developed to allow transfer of species between phases. Transfer between phases is often carried out using a phase transfer agent, which is typically a molecule that has partial solubility in

multiple phases. To be able to fully describe such a system, there are a significant number of extra variables. For this reason, the number of models available is very large, and the systems to which they are successfully applied is limited.

Polymer chemists have a number of different heterophase polymerization techniques at their disposal.¹⁴ These heterophase polymerizations produce colloids, which are materials in a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 μm , or that discontinuities of that order are found in the system. Applications of colloidal materials include inks, cement, rubbers and cosmetics. Emulsions, colloidal fluid systems in which liquid droplets, liquid crystalline droplets, or both, are dispersed in a liquid, are a common part of most people's lives. Milk is an excellent example of an oil-in-water emulsion. Polymerizations carried out in heterophase systems include emulsion, precipitation, suspension and dispersion polymerizations. In a heterophase polymerization, a number of terms are commonly used. A droplet is a discrete phase that contains monomer that has not been initiated, i.e. no polymer is present. A particle is a discrete phase that can contain both polymer and monomer. Some general properties of colloidal heterophase polymerization systems are given in Table 2.1.

Table 2.1: Heterogeneous polymerizations¹⁴

Type	Particle Size (typical)	Droplet size	Initiator (typical)	Continuous phase
Emulsion	50-300 nm	1 -10 μm	Water soluble	Water
Precipitation	50-300 nm	none	Water soluble	Water
Suspension	>1 μm	1 -10 μm	Oil soluble	Water
Dispersion	>1 μm	none	Oil soluble	Organic
Microemulsion	10-30 nm	10-30 nm	Water soluble	Water
Inverse emulsion	100 nm-1 μm	1 -10 μm	Oil or water soluble	Oil
Miniemulsion	30-100 nm	30-100nm	Oil or water soluble	Water

Heterophase polymerizations have a number of advantages. The decreased viscosity of the heterophase systems allows higher solids contents to be used in the reactions, while maintaining ease of processing. The most commercially relevant heterophase

techniques are those techniques that are water-based. These techniques include emulsion, miniemulsion, microemulsion and inverse emulsion systems.

It is important to note that when one liquid is dispersed in a second immiscible liquid, the mixture that is formed it is not generally stable; an example of this behaviour would be oil in water or oil in vinegar – two household examples of emulsified systems. The liquids will generally phase separate rapidly and form layers based on density differences.

To help stabilize emulsions, an entire branch of applied chemistry has developed – namely surfactant science. A surfactant is a surface-active molecule, i.e. it is typically found on the interface between two phases, and consists of parts that have affinity for both phases/liquids in the system (also known as amphiphiles, from the Greek, roughly translated as meaning “loving both”). Typical soaps that are used for cleaning processes function in precisely the same fashion as a surfactant in more complex emulsions, forming kinetically stable systems with multiple immiscible phases. These molecules then form an interface between the two phases and help to stabilize the system.

The reason for the industrial significance of aqueous heterogeneous polymerization techniques, especially emulsion polymerization, lies in the unique advantages that water provides to an industrial process. It is environmentally friendly, but at the same time has excellent heat capacity. An additional benefit that polymer chemists derive from the compartmentalization in a heterophase system is that the rate of polymerization is often higher than in a homogenous polymerization, as is the molecular weight of the polymer formed. This can be understood when comparisons are made between the rate of polymerization and degree of polymerization in bulk and emulsion in a radically polymerized system. Equation (2.8) is the rate expression in homogeneous media while equation 2.11 is the rate expression in an emulsion system.

$$-\frac{d[M]}{dt} = \frac{k_p \cdot [M] \cdot \bar{n} \cdot N_c}{N_A} \quad (2.11)$$

Where N_c is the number of latex particles per unit volume, \bar{n} is the average number of radicals per particle and N_A is Avogadro’s number.

When equation 2.11 is integrated, we obtain:

$$\ln\left(\frac{[M]_b}{[M]_i}\right) = \frac{k_p \cdot \bar{n} \cdot N_c}{N_A} \cdot t \quad (2.12)$$

Equation 2.12, which is only valid if \bar{n} is constant will be used to describe reaction rates in heterogeneous reactions in this dissertation. Equation 2.13 provides an expression for the average degree of polymerization in an emulsion:

$$\overline{DP} = \frac{k_p \cdot [M] \cdot \bar{n} \cdot N_c}{2f \cdot k_d \cdot [I]} \quad (2.13)$$

Equation 2.14 provides an expression for the average degree of polymerization (\overline{DP}) in a homogenous system.

$$\overline{DP} = k_p [M] \left(\frac{1}{f \cdot k_d \cdot k_t \cdot [I]} \right)^{0.5} \quad (2.14)$$

The equations show us that that it is possible to increase both the rate and the chain length of the polymer by simply increasing the number of particles, which is equivalent to decreasing the particle size, if the oil phase to aqueous phase ratio remains constant. This is relatively easy to accomplish in an emulsified system, as we will discuss in chapter four. However, an increase in initiator concentration, while increasing the rate of polymerization will simultaneously decrease the number average degree of polymerization. This is due to the termination dependence of the number average molecular weight, \overline{M}_n .

2.3 Emulsion polymerization

Polymerization in an emulsion medium can be carried out using a number of different mechanisms, including condensation and radical mechanisms. For the purpose of this dissertation, our discussion will be restricted to radical polymerization in emulsion.

2.3.1 Radical polymerization in emulsion

When the term emulsion polymerization was coined, it was widely presumed that polymerization took place in the droplets of a monomer dispersed in water. The process in which radicals generated in the aqueous phase or oil phase, enter droplets and propagate to form particles is known as droplet nucleation. Droplet

polymerization is however insignificant for most so-called emulsion polymerizations. The formation of a polymer latex is a complex process with numerous variables. This makes each specific system behave in its own unique fashion. The actual process of polymer formation generally occurs in particles that are formed in the aqueous phase. This can occur by one of two mechanisms, namely homogeneous nucleation or micellar nucleation.

2.3.1.1 Homogenous nucleation

For the homogenous nucleation of particles, oligomers growing in the aqueous phase begin to precipitate from solution as they exceed their solubility limit. The oligoradicals that reach their solubility limit in the aqueous phase are termed j -mers and have a critical length, j_{crit} , at which homogenous nucleation will occur. J_{crit} can be estimated from:¹⁵

$$j_{crit} = 1 - \frac{55 \text{ kJ mol}^{-1}}{RT \ln C_W^{SAT}} \quad (2.15)$$

Where C_W^{SAT} is the saturated aqueous-phase concentration of monomer in mol.dm^{-3} and the energy value is derived from the hydrophobic free energy of adsorption for n -alkyl sulfates, which provides values for styrene ~ 5 units. The oligoradicals then form precursor particles that are stabilized by adsorbed surfactant. These particles then grow by a process of coagulation up to the point at which their size allows them to absorb enough monomer for polymer formation in the particle to become the dominant growth process.

2.3.1.2 Micellar nucleation

Surfactant aggregation is a concentration dependent phenomenon that takes many forms. Sodium dodecyl sulfate has a phase diagram that encompasses a number of different aggregates, the simplest of which is spherical micelles.¹⁶ If sufficient surfactant is present in the system for surfactants to aggregate, i.e. the critical micelle concentration has been exceeded, then the hydrophobic tails of the aggregates will typically be swollen by monomer, giving what are commonly referred to as monomer-swollen micelles. These micelles can be entered by oligoradicals as the radicals become surface-active. These surface active oligoradicals are termed z -mers. The term

z indicates the number of monomer units in the oligomer. This process is known as *micellar nucleation*.

The value of z can be obtained from hydrophobic free energy consideration using equation 2.16.¹⁵

$$z \approx 1 + \frac{-23 \text{ kJ mol}^{-1}}{RT \ln C_w^{SAT}} \quad (2.16)$$

Equation 2.16 provides values for $z < 3$ units for styrene with a sulfate endgroup. It should be noted that the calculations for j_{crit} and z presented here are by no means definitive, and there are still methods being developed to calculate these values in specific systems.¹⁷ The importance of the z value can be seen when we examine the Hansen-Ugelstad-Fitch-Tsai (HUFT) theory, which provides the entry rate efficiency coefficient for radical entry into particles in the form:

$$f_{init} = \left(\frac{\sqrt{2fk_d[I]k_{t,aq}}}{k_{p,aq}C_w} + 1 \right)^{1-z} \quad (2.17)$$

Equation 2.17 plays an important role in the prediction of number average molecular weight in chapter five.

2.3.1.3 The mechanism of radical emulsion polymerization

The reason that monomer swollen particles and homogeneously nucleated particles are able to compete so efficiently for radical species is the large surface area differential that exists between the micelles or precursor particles and the droplets. The large number of small particles can explain this, with concomitant high surface area compared to the droplets, which have micron sizes and are relatively few in number, leading to a much lower relative surface area. Some general theories have been derived for the process of emulsion polymerization, based on work by Harkins,¹⁸ Smith and Ewart,¹⁹ among others. The classical description of an emulsion polymerization process, above the critical micelle concentration (CMC), for a monomer with low water solubility, begins with three intervals of polymerization.

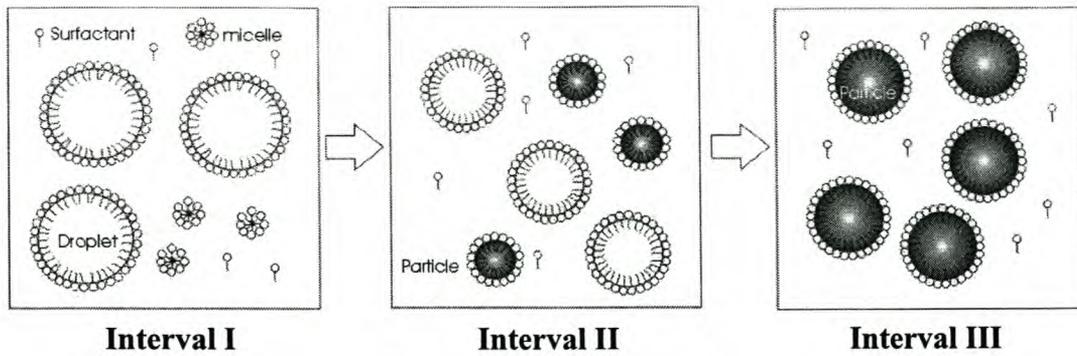


Figure 2.1 Emulsion intervals showing the presence of droplets, micelles, free surfactant, nucleated particles and final latex particles.

Interval I: Large monomer droplets are present in the reaction vessel with many small micelles. Surface-active radicals generated in the water phase enter the micelles and continue to polymerize, creating a monomer diffusion gradient from the aqueous phase, leading to a gradual depletion of the droplets as they replenish the aqueous phase. The key aspects of interval I are that there are micelles and droplets present, the particle number and particle size are increasing, and thus the rate of the reaction is increasing.

Interval II: Particle formation has ceased and micelles have disappeared either by becoming particles or by acting as monomer and surfactant reservoirs and being depleted by adsorption to the increasing surface area of the particles. The key aspects of interval II are that there are no longer micelles present, but monomer droplets are still present, although decreasing in size due to depletion by the aqueous phase, (which is being depleted by the particles). The particle number is constant, while the particle size is increasing, and the concentration of monomer within the droplet is constant. The fact that the monomer concentration and particle number remain relatively stable leads to the fact that the rate of polymerization during this interval is relatively constant.

Interval III: No more monomer droplets are present. The remaining monomer is in the particles and is consumed without any dependence on transport phenomena. The key aspects of interval III are that there are no micelles or droplets, the particle size and particle numbers remain constant while the concentration of monomer within the droplets is decreasing and thus the rate of the reaction is decreasing. It should be noted that in the case of a glassy system, the rate of termination would decrease as

diffusion decreases due to increased viscosity. It is potentially possible that an autoacceleration will occur due to an increase in the number of radicals in the particle.

This classical theory is typically true for monomers such as styrene where homogenous nucleation above the critical micelle concentration (CMC) is limited. In the case of relatively water-soluble monomers such as methyl methacrylate, homogeneously nucleated particles play an important role, even above the CMC.

2.3.1.4 Problems with emulsion systems

The water solubility of a monomer is very important for an emulsion polymerization process. Monomers with extremely low water solubility such as dodecyl methacrylate cannot be homopolymerized in emulsion without phase transfer agents,²⁰ but are often used as comonomers. The water solubility of all the components in a heterogeneous system is important, as the rate-determining steps in the reaction process may be substantially different in an emulsion when compared to the rate-determining steps in homogeneous media. The rate of a radical polymerization is a function of the radical concentration. Most radicals in an emulsion polymerization are derived from the first order decay of an initiator (see 2.1.1). This decay is solvent dependent and has been determined for a number of compounds in specific solvent systems. For the purposes of this dissertation, it is important to examine the role of initiating species as well as their ability to transport through the aqueous phase.

2.3.2 Initiators

The initiator used for radical polymerization in emulsion can be an oil- or water-soluble compound. The specific nature of the initiating radical creates a large variation in the formation mechanisms of radical oligomers. Much of the literature information on emulsion systems is based around the use of a single initiator system, namely persulfate salts. The persulfate radical generation occurs in the aqueous phase of the system, and allows surface-active oligoradicals to form which will, when they reach surface activity through monomer addition, allow surface anchoring after adsorption to particle surfaces.

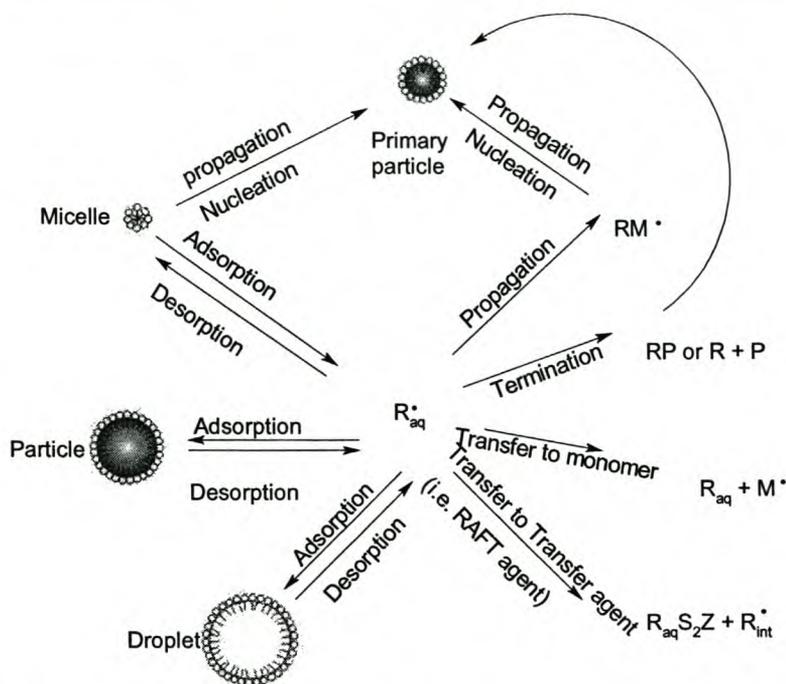


Figure 2.2 Emulsion particle nucleation steps showing the possible paths that may be taken by a radical species in a heterogeneous system above the critical micelle concentration. P indicates an existing polymeric species, while M indicates a monomeric species and R a new radical species

The use of oil-soluble initiators is a more involved route to latex preparation, but with a number of potential advantages; they are commonly non-ionic and impart varied endgroup functionalities. Disadvantages of persulfate initiators are that they affect pH, are pH-sensitive and play a significant role in particle morphology. Oil soluble initiators suffer from some interesting problems themselves. Geminate recombination is a problem that is still being investigated in the use of oil soluble initiators. If “zero-one” conditions hold, i.e. two radicals inside a particle results in instant termination (see 2.3.4), then radicals that are generated in the oil phase are instantaneously terminated. The problem of radicals reacting within the solvent cage to terminate one another instantaneously is dependent on particle size. If it is taken into account that the rate for the desorption of a radical from a particle is:

$$-\frac{d[M^{\bullet}]}{dt} = \frac{3D_w C_w}{r_s^2 C_p} [M^{\bullet}] \tag{2.18}$$

Where D_w is the diffusion coefficient of the radical in water, C_p is the concentration of monomer in the particles, r_s is the swollen particle radius, $[M^{\bullet}]$ is the radical concentration within the particles and the rate of termination in a particle is given by:

$$-\frac{d[M^*]}{dt} = \frac{3k_t}{2\pi N_A r^3} [M^*]^2 \quad (2.19)$$

We can observe that the relationship between termination and desorption is such that the probability of desorption will fall rapidly as particle size decreases, and the probability of termination will increase. According to Schork *et al.*,²¹ the number of radicals that form inside the oil phase and are able to contribute to polymerization successfully becomes negligible at particle sizes below 100nm. Their study also suggests that, as other authors have noted, the predominant source of radicals in an emulsion system initiated with an oil-soluble initiator is the fraction of radicals that are formed by aqueous phase initiator decomposition. Oil soluble initiators can also lead to systems failing to reach full conversion.²²

2.3.3 Particle size and particle number

Heterogeneous systems are very dependent on particle size. The size of the particles in an emulsion affects the rate of polymerization, due to compartmentalization effects.²³ Particle size also plays a role in latex stability with very large particles, i.e. micron size particles, often creating synthetic challenges. The importance of the particle size, and the advantages associated with small particles has led to considerable development of techniques to ensure small particles and the resulting rapid polymerizations. It is also possible to calculate the number of particles in the emulsion system if the size of the particles is known:

$$N_c = \frac{Mass_{polymer}}{\frac{4}{3}\pi(r_{unswollen})^3 d_p} \quad (2.20)$$

In equation 2.20 d_p is the density of the polymer, $r_{unswollen}$ is the radius of the unswollen particle and N_c is the number of particles in the system. The unswollen radius is the radius of the particles at the end of polymerization. This means that by simply determining particle size as well as the density and mass of polymer in a specific volume of latex, an estimation of the number of particles can be made. This of course assumes a narrow gaussian distribution in particle size. The particle size is dependent on a significant number of variables in an emulsion system. These include surfactant, stirring speed, pH as well the monomer being used. The particle size is

important for specific applications as well as the compartmentalization of the reaction loci.

2.3.4 Zero-one conditions

One of the most significant advantages of emulsion polymerization is the ability to compartmentalize radical species, minimizing termination and allowing long polymer chains to form. In an idealized system, a radical entering a particle in which there is already a radical present will instantly be terminated. Each particle contains either zero or one radicals and thus \bar{n} , the average number of radicals per particle is equal to or less than 0.5, which is referred to as “zero-one” conditions. “Zero-one” conditions are typically invalid at high conversions for most systems as the high viscosity in each particle leads to multiple radicals managing to survive due to the fact that termination is diffusion controlled. In the case of styrene homopolymerizations under “zero-one” conditions, transfer to monomer determines molecular weight.

2.3.5 Pseudo-bulk conditions

Pseudo-bulk behaviour refers to the behaviour of a system in much the way that would be expected for the corresponding bulk polymerization system. This means that multiple radicals are capable of coexisting in a particle and terminating one another at far higher rates than in the case of a zero-one system.

2.4 Miniemulsion

Miniemulsion polymerization is actually as much of a misnomer as emulsion polymerization. The miniemulsion polymerization process is in principle a true emulsion polymerization process in that droplet polymerization is seen as the predominant mechanism of particle formation. The means by which this is achieved is by removing the surface area differential between the droplets and swollen micelles in the system by homogeneously distributing the components and then stabilizing the droplets to prevent their growth or shrinkage.

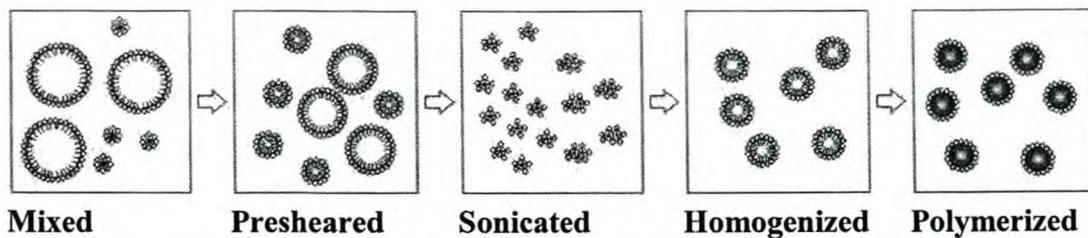


Figure 2.3 The five steps that occur during the formation of a miniemulsion latex.

The process of miniemulsion formation requires a mixing of all the components of the emulsion followed by a preshearing step in which the droplet size is mechanically reduced providing varied droplet sizes. At this point, ultrasonic homogenization is carried out via a fission-fusion process in such a manner that a homogeneous distribution is formed. After the application of the homogenization process, the system will relax to a homogenized state that is stabilized against particle growth, and at this point the system can be polymerized.

For a miniemulsion to be formed, a significant amount of energy is required to predisperse the system to a theoretical minimum particle size for each specific surfactant concentration. The precise time to reach the minimum particle size for each experimental setup needs to be determined, as machine differences as well as other environmental variables play a role. To experimentally determine the time required involves surface tension or turbidity measurements with time. When these values have reached a constant level, (in the case of turbidity this is beyond the maximum value for a stable emulsion, and in the case of surface tension this is simply a limit), the system has reached equilibrium, and homogenization can be halted.²⁴ At this point the particle stability is dependent on molecular diffusion degradation (Ostwald ripening, a process dependent on the individual particle) as well coalescence by collision (a process dependent on two particles).

2.4.1 Costabilizers

The biggest hurdle that must be overcome to obtain a miniemulsion is the fact that the droplets are not thermodynamically stable at the theoretical minimum particle size and would prefer to return to equilibrium conditions. The process by which particles grow is referred to as Ostwald ripening. To overcome this behaviour, the use of cosurfactants, such as hexadecanol, or ultrahydrophobes such as hexadecane are used. Cosurfactants, which were pioneered by El-Aasser *et al.*,²⁵⁻²⁷ are capable of packing in the surfactant layer and aiding stabilization, as the name implies. Ultrahydrophobes

(substances with a water solubility of less than 10^{-7} mol.cm⁻³)²⁴ or simply hydrophobes, have been investigated by Landfester *et al.* to confirm the role played by the ultrahydrophobe in a miniemulsions system.²⁸ It was determined that, unlike cosurfactants, the ultrahydrophobe is distributed homogeneously throughout the droplets and prevents Ostwald ripening by increasing osmotic pressure in the droplets. Ostwald ripening has been described by the Lifshitz-Slyozov-Wagner (LSW) theory.²⁹ The osmotic pressure buildup occurs via an inverse second order dependence on radius:

$$P_{osmotic} = \frac{3TM}{4\pi r^2} \quad (2.21)$$

Where r is the radius of the droplet, M is the number of moles in the oil phase and T the temperature at which the determination is occurring. The driving force for Ostwald ripening is the Laplace pressure in the particles, which is driven by a first order inverse dependence on radius:

$$\frac{3\gamma_{LL}}{r} = P_{Laplace} \quad (2.22)$$

Where γ_{LL} is the interface energy of the oil droplet and water interface. The point at which the particles are thermodynamically stabilized is then the point at which the opposing pressures balance each other although the effective pressure is non-zero. i.e. there is an energy minimum with a constraint of constant particle number. This is due to the fact that the Osmotic pressure climbs faster as the radius of the particles shrinks (r^{-2} versus r^{-1} dependence).

High molecular weight polystyrene has been reported to enhance droplet nucleation and can be compared to extreme examples of hydrophobes.²⁷ The sheer size is more important than the hydrophobicity in this case, as the solubility of the polymer will typically be very poor even if the monomer and shorter oligomers retain some water solubility. The enhancement is thought to be kinetic rather than thermodynamic in nature, but due to the rapid nucleation that occurs in miniemulsion polymerization, it can play a significant role. Enhanced droplet nucleation was reported in the presence of polymer in cases where cosurfactants were used, and it was concluded that the polymer helped preserve the droplet number.³⁰ This was found to be a less significant contributor than in the case of the more efficient ultrahydrophobes. The role of the ultrahydrophobes in particle nucleation could still however be observed.³¹

A more thorough approach was taken by Webster and Cates.³² They describe a miniemulsified system in terms of the chemical potentials in the bulk, continuous as well as discrete phases that may coexist in emulsion systems:

$$\mu_d = \mu_b + \frac{2\gamma v_1}{r} \quad (2.23)$$

while:

$$\mu_c = \mu_{c0} + k_b T \ln C \quad (2.24)$$

Where the interfacial tension (γ), molar volume (v_1), radius (r) and concentration in the continuous phase (C) are used to calculate the chemical potentials of the continuous (μ_c) and discrete (μ_d) phases using reference values in the bulk (μ_b) and continuous phases (μ_{c0}). Webster and Cates were then able to define a growth velocity (U) in terms of the droplet radius and the reduced supersaturation of the dispersed species (ε):

$$U(r, \varepsilon) = \frac{2\gamma v_1 \varepsilon}{r k_b T} - \left(\frac{2\gamma v_1}{r k_b T} \right)^2 + \frac{3\gamma \eta v_1^5}{2\pi k_b T r^4} \quad (2.25)$$

Where η is the number of moles of dispersed species per particle. If we model the equation in such a way as to determine the possibilities of stable systems, then the following results are obtained. If we set the number of moles of dispersed species to zero then we are able to see that for those values where the reduced supersaturation is greater than zero (which are those values which should occur in an unstabilized system), the growth velocity shows a single unstable intersection with the zero plane.

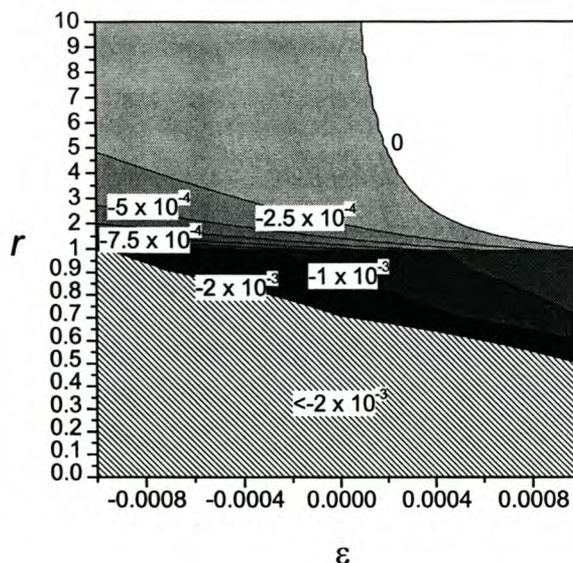


Figure 2.4 The growth velocity (U) of droplets in a system without a trapped species, as a function of reduced supersaturation (ϵ) and droplet radius (r).

When there is a trapped species included in the system, the growth velocity tends to increase as r tends to zero and shows only stable intersections with the zero plane indicating that Osmotic and Laplace pressures in the system will be able to create a kinetically stable system. This is shown in figure 2.5.

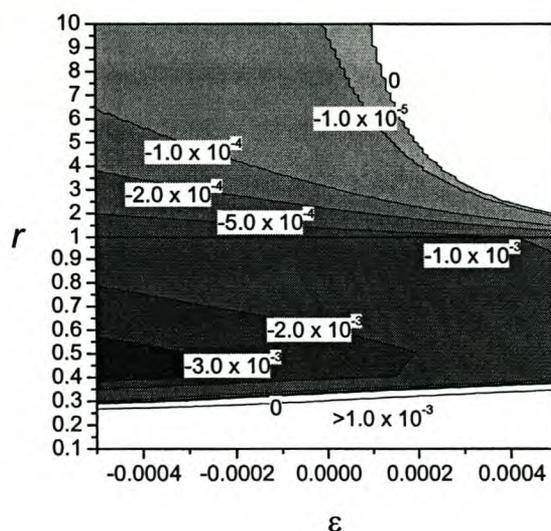


Figure 2.5 The growth velocity (U) of droplets in the presence of a trapped species as a function of reduced supersaturation (ϵ) and droplet radius (r).

Thermodynamically, the droplets with trapped species will not have a zero pressure difference between Ostwald and Laplace pressures. A state of equal effective pressure

in each droplet stabilizes the miniemulsions effectively against Ostwald ripening; what occurs is a minimum of free energy under the constraint of constant droplet number.²⁴ The particles are not thermodynamically stable but are kinetically stabilized.

2.4.2 Particle size

The size of a miniemulsion particle is controlled by a number of factors, but the most important variable in an optimally homogenized miniemulsion is the surfactant concentration. A number of authors^{24,33} have examined the effect of surfactant concentration and Paunov *et al.*³⁴ developed a model to help predict the particle size for a sodium dodecyl sulfate stabilized emulsion based on the work of Landfester *et al.*²⁴ Systematic studies on other surfactants have not yet been published, but the model can quite easily be adapted for other surfactant systems. Paunov *et al.* derived the following relationship for stabilized droplet diameter:

$$D_r = \Gamma_\infty \theta \frac{V_0}{N_s} \quad (2.26)$$

In equation 2.26, the ratio (V_0/N_s) of the volume of oil to the amount of surfactant is fixed by the experimental conditions and (Γ_∞) is the maximum possible adsorption of surfactant. The ratio V_0/N_s can be calculated from the reactant component ratios. θ is the degree of surface coverage with surfactant or surface saturation, which is $\cong \frac{\Gamma}{\Gamma_\infty}$.

This model can be successfully extended to different surfactants, but fails to take into account the fact that the degree of surface coverage is not a constant value, in fact low surface coverage is the norm for larger particle sizes. The second problem with the model is the fact that at high surfactant concentrations the concentration of aqueous surfactant begins to increase. The authors discuss the possibility of using an adsorption isotherm for the surfactant sodium dodecyl sulfate (SDS) to improve the model, although the fact that the particle size varies with surfactant concentration creates a number of difficulties in this regard, as the available surface area is not a constant. Erdem *et al.*³⁵ made use of a Gibbs adsorption isotherm during a study on droplet sizes in miniemulsions of styrene, hexadecane and SDS.

$$\Gamma_m = - \left(\frac{1}{4.606RT} \right) \left(\frac{d\gamma}{d \log C} \right)_T \quad (2.27)$$

Where Γ_m is the number of moles of surfactant adsorbed per square centimeter of the surface (mol/cm^2), R is the gas constant ($8.31 \times 10^7 \text{ J.K}^{-1}.\text{mol}^{-1}$), T is the temperature in Kelvin (K), and $\left(\frac{d\gamma}{d \log C}\right)_T$ is the slope of the surface tension versus log surfactant concentration plot approaching the cmc from below. From the surface excess concentration (Γ_∞), the area per molecule (a_s) at the interface can be calculated using the following equation (where N_A is Avogadro's number):

$$a_s = \frac{10^{16}}{N_A \Gamma_m} \quad (2.28)$$

Erdem *et al.* determined the a_s value as 0.44 nm^2 via soap titration providing a θ value of 0.476 at saturation, which is substantially larger than the value of 0.256 used by Paunov *et al.* The reason for this difference lies in the fact that Erdem determined the saturated area per headgroup of an unpolymerized droplet as being close to twice that of reported values for polymerized systems. Erdem *et al.* attributed this difference to the use of persulfate and reported that particle size and droplet size are very similar. The results suggest that the aqueous surfactant concentration decreases with time. A decrease in aqueous surfactant concentration with time occurs in a traditional emulsion polymerization where the surface area available for adsorption is a function of time, but the reason for this behaviour in a miniemulsion system is unclear. The most likely suggestion is increased surfactant interaction with high conversion latexes.

2.4.3 Differences from Emulsion

Polymerizable miniemulsions have been studied to determine the mechanisms that are important in maintaining stability in these systems. Differences between traditional emulsion systems have been observed by Schork *et al.*²¹ when using oil soluble initiators. It was observed that oil phase initiation was a significant contributor to polymerization in particles larger than 100 nm, while aqueous phase initiation was predominant in the case of traditional emulsions of comparable composition. The theory and application of miniemulsions systems have been reviewed by a number of authors and for further reading some of these reviews may prove useful.³⁶⁻³⁹

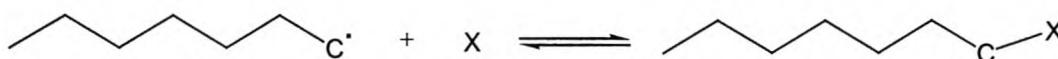
2.5 Living Radical Polymerization

Living radical polymerization is a branch of polymer chemistry with a split identity. There is significant debate⁴⁰ about when a polymerization process should be

considered a living process and when the process should be considered controlled, although it has been suggested that the term “living” be used for all processes that allow the formation of dormant species and that the term controlled be avoided. For the purpose of this discussion, the terms will often be used interchangeably, although correctly speaking it is possible to control a polymerization process without it being a living process, and it is possible to have a living process without having control of the molecular weight distribution. A living process requires that block polymers can be synthesized, i.e. chains are reversibly terminated. A controlled process on the other hand requires narrow polydispersity polymer of a molecular weight that can be controlled and tuned as desired as well as being predictable. The confusion arises from the fact that in many cases the agent that provides control of the reaction also allows reactivation of the chains to form block polymers.

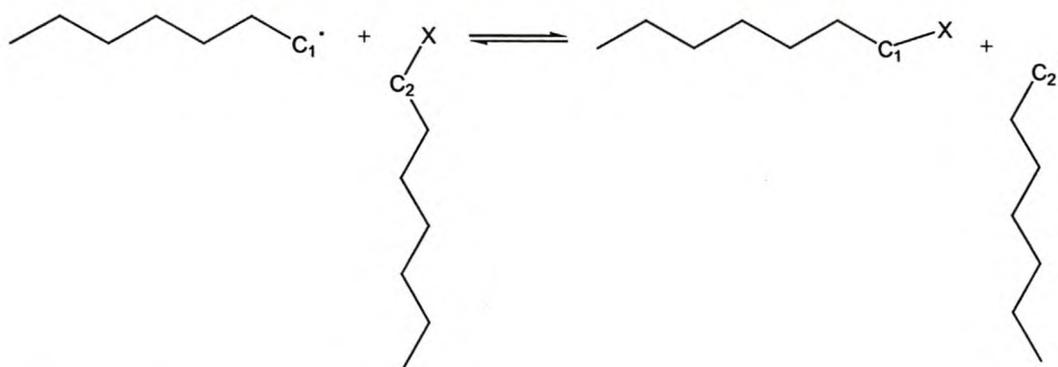
Two main classes of agents can be defined that provide living characteristics:

- 1) **Reversible end-capping species.** These are characterized by the fact that only a single polymer chain is interacting with the agent at any one time.



Scheme 2.7 Reversible end-capping

- 2) **Transfer species.** These are characterized by the fact that more than one polymer chain is required for a change from dormant to active species to occur.



Scheme 2.8 Transfer

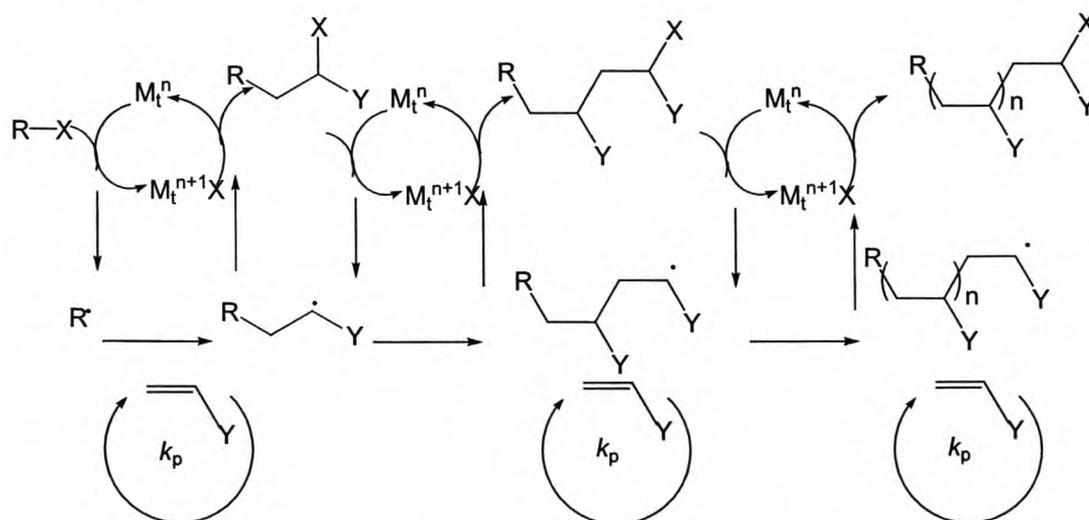
This is of course a generalized concept of the two classes, as each specific technique may include different species and additional steps in the process.

2.5.1 Reversible End Capping

The two dominant techniques that use reversible end capping are Atom Transfer Radical Polymerization (ATRP), and Nitroxide Mediated Polymerization, which is also referred to as Stable Free Radical Mediated Polymerization (NMP or SFRP).

2.5.1.1 ATRP

ATRP was discovered independently by Matyjaszewski and Sawamoto in 1995, although the terms ATRP and transition metal catalyzed radical polymerization were used respectively.^{41,42} In the case of ATRP, a metal species, typically copper but possibly ruthenium or iron among others, undergoes a redox reaction in which an atom is transferred to or from a chain. This atom is typically a halide or pseudo-halogen.



Scheme 2.9 The ATRP process

Atom transfer polymerization has a number of advantages in radical polymerizations. The initiating species is predetermined and the initiation step is very fast if the correct species is chosen.^{43,44} This means that there is no chain initiation throughout the reaction as is the case in a conventional free radical polymerization. By keeping a low radical flux in the system it is possible to produce very low polydispersity polymers.

There are however, a number of disadvantages associated with the technique. The most obvious problems relate to the catalyst. Firstly, the removal of the metal catalyst is typically an expensive, but necessary step. Secondly, the metal is sensitive to other redox processes and ATRP has a number of problems for this reason in aqueous or

acidic media. Investigations have been carried out to overcome these problems and some techniques have been developed that are successfully applied.⁴⁵

2.5.1.2 SFRP

Rizzardo *et al.* and Georges *et al.*^{46,47} laid the groundwork for SFRP. Georges *et al.* were the first authors to report living radical polymerization using the technique in 1993. Nitroxides are stable free radicals, the most common example of which is TEMPO, (2,2,6,6-tetramethyl-1-piperidinyloxy free radical), which is shown in figure 2.6.

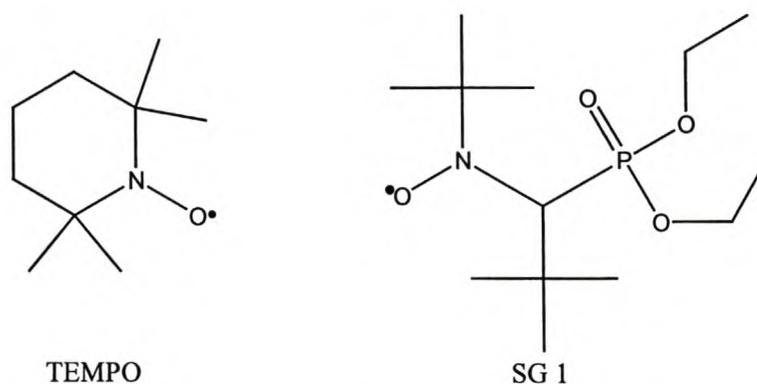
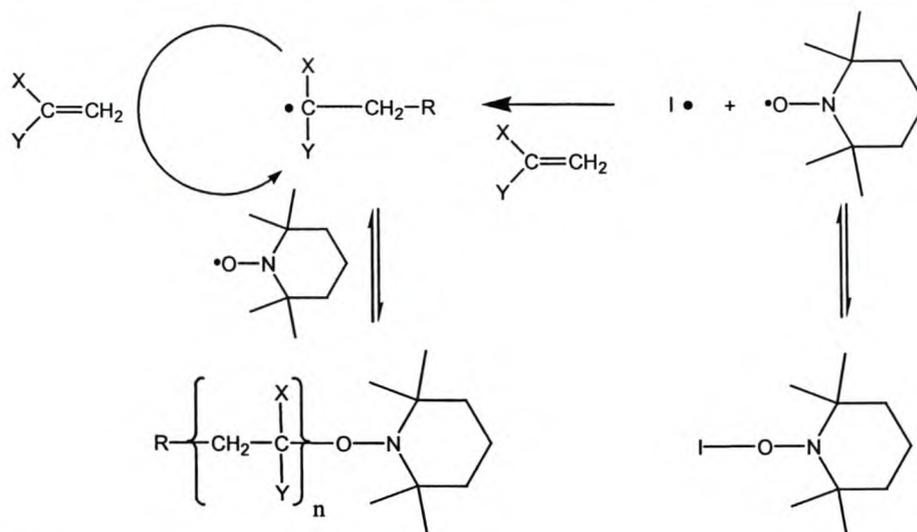


Figure 2.6 SFRP agents TEMPO and SG1 (*N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide*).

These species are capable of reversibly bonding to a chain via a radical process although they are not reactive enough to engage in a propagation step. The problem that was encountered with nitroxide end-capped species is that they are rather unreactive and were originally only suitable for high temperature reactions, typically well above 100 °C. This was due to the fact that the bonds that were formed were so stable that the rate of fragmentation of these bonds was not suitable at lower temperatures. More advanced nitroxide species such as SG1 (shown in figure 2.6) are now being applied well below 100 °C.⁴⁸



Scheme 2.10 Schematic representation of SFRP

A second problem encountered with these stable radicals was that the steric bulkiness of the nitroxide species made access to the oxygen-centered radical difficult for sterically hindered monomers such as those monomers with α -methyl substituents problematic. The progress in the use of nitroxide species for the mediation of radical polymerization has been reviewed by Hawker *et al.*⁴⁹

2.5.2 Transfer

The RAFT or reversible addition-fragmentation chain transfer process currently dominates the second class of living radical polymerization techniques, i.e. the transfer reactions. These transfer reactions are commonly considered to be degenerate processes, as the total number of radicals remains unchanged and the total energy of the species is maintained. This is not strictly correct for the RAFT process, but for the purpose of the definition of techniques, the approach will serve. The RAFT process will be discussed in detail in 2.6. Other transfer processes include degenerative transfer using alkyl iodides and catalytic chain transfer (CCT).

2.5.2.1 Catalytic chain transfer

Catalytic chain transfer is a useful method for the preparation of polymers with a C=C end group which can be used as macromonomers. Low-spin cobalt (II) catalysts are used for this method, and the most likely mechanism for the process is a reversible beta hydrogen abstraction.⁵⁰ This provides molecular weight control and is especially applicable to alpha methyl vinyl monomers. It should be noted that catalytic chain

transfer is exactly that – a catalytic process that does not require the interaction of two chains for a successful transfer.

2.5.2.2 Degenerative transfer

The use of alkyl iodides to carry out a living polymerization was first reported by Matyjaszewski *et al.* in 1995.⁵¹ Despite some improvement in the agents that are used for this process, it remains reasonably inefficient, although capable of producing living characteristics. It has however been reasonably successfully applied in heterogeneous media.^{52,53}

2.6 RAFT

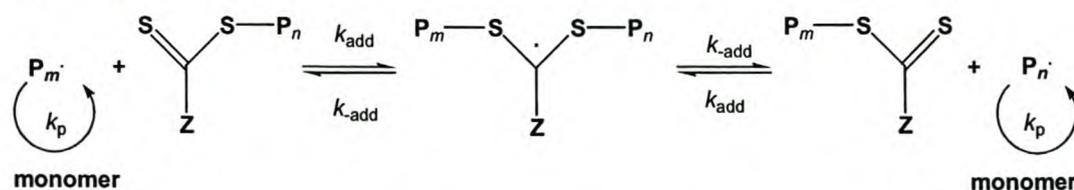
Le *et al.*⁵⁴ patented the RAFT process in 1998, leading to a major shift in the field of living radical polymerization. They had pioneered addition-fragmentation mediated polymerization through the use of methacrylate macromonomers,⁵⁵ which were readily available from catalytic chain transfer,⁵⁶ but were not highly efficient. The shift to efficient addition-fragmentation agents in the form of dithioesters provided what is probably the most versatile technique available for living radical polymerization.

As with every chemical process, it is important to understand the mechanism of the RAFT process as well as the kinetic processes that govern it. Understanding of the mechanism allows us to explain and predict the products of the process. The ability to predict products is essential if the method is to be applied to industrial processes. Producing the correct product with minimum energy consumption and time is immediately reflected in profits.

2.6.1 Mechanism and Kinetics

The exact mechanism of the RAFT process is still very much under discussion, but the general process is reasonably well understood. Certain dithioester compounds are subject to radical addition. Coote *et al.*⁵⁷ have examined the reasons for this from basic principles using a variety of high-level *ab initio* molecular orbital procedures. They found evidence for contra-thermodynamic radical addition to the sulfur of a thiocarbonyl and preference for the thermodynamically less stable carbon-centered

radical to form as a product. In Scheme 2.11, the elementary reactions for the central exchange process of the RAFT mechanism are depicted.



Scheme 2.11 The elementary RAFT process as commonly accepted in the literature.⁵⁴

This means that in the RAFT process a growing polymer chain is able to add to a dithioester with extremely high specificity for the sulfur atoms. This creates an unstable intermediate predominantly carbon centered radical which has been detected by electron spin resonance spectroscopy (ESR).⁵⁸⁻⁶⁰ The relatively stable intermediate macroradical that is formed by the addition process can fragment to release one of two radical species. Namely, the original incoming radical species (P_m^\bullet , a propagating radical of degree of polymerization m) and the original dithioester compound, or the homolytic leaving group (P_n^\bullet) that was previously a part of the RAFT agent and a new dithioester.

Certain terminology has sprung up around the RAFT process and it has become common to refer to the dormant radical fragment of the dithioester species as an R group and the group attached to the carbon centre of the dithioester as the Z group.^{61,62}

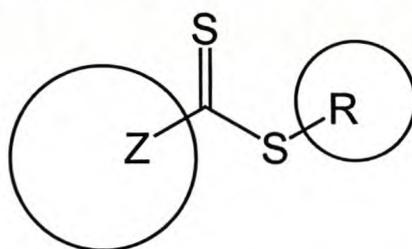


Figure 2.7 A generic structure of a RAFT agent showing the Z or radical supporting group, as well as the R or radical leaving group.

The number of Z and R groups that have been used in the literature are quite substantial at this time, but among the most common Z groups are xanthates (O-functional Z groups),⁶³⁻⁶⁹ dithiocarbamates (N-functional Z groups),^{70,71} trithiocarbonates (S-functional Z groups)^{72,73} and dithioesters (C-functional Z groups).^{74,75} R groups are commonly related to the monomer being used⁷⁶ or to initiators that have proven successful in conventional free radical polymerizations.^{64,77}

Specific R and Z groups are suitable for specific types of monomers and at this time there is no completely universal agent.

The RAFT process constitutes a living polymerization because when a suitable dithioester is used, the rate of “transfer” is significantly faster than that of propagation. This means that less than one monomer unit is inserted per activation deactivation cycle in an efficient process. The radical activity is also able to transfer through a large number of addition-fragmentation cycles before it is terminated through a normal radical termination mechanism, as the frequency of transfer is substantially higher than the frequency of termination.

Instead of a single chain undergoing multiple monomer additions prior to radical termination, in the RAFT process multiple chains undergo a single monomer addition prior to radical termination. This implies that the RAFT process has a built in tailing factor on the chain length distribution, as every time termination occurs a new dead chain is formed. The number of RAFT agents does not decrease (substantially), but there is a constant generation and termination of propagating chains. As termination is diffusion controlled, the probability of a short chain terminating is substantially higher than that of longer chains. New chains, which are constantly being formed by initiator decomposition, thus have a higher probability of termination, which exacerbates the tailing factor even if the termination is between short and long chain radicals, although the effect will be more striking in the case of two short chain radicals terminating. Short-long termination will reflect the instantaneous distribution of the polymer.

To fully understand the RAFT process it is important to examine the nature of the radical species that are present in each reaction. Radical reactivities for addition and radical leaving group stabilities are very important factors that, together with reactant concentrations, determine the rates of polymerization in a RAFT-mediated polymerization. Moad and Solomon’s review provides a deeper examination of the general factors that affect radical stabilities and reactivities.⁷⁸ It is instructive to consider that, within a series, tertiary radicals are typically more stable and less reactive than secondary radicals and, by the same token, secondary radicals are more stable and less reactive than primary radicals. Within the three classes of radicals, the substituents play a crucial role in determining radical behavior. Both steric and

electronic effects are important to determine rates of reactions with specific molecules.^{79,80}

When an intermediate radical is formed by the addition of two different leaving groups, it will have preference to fragment in a direction based on the leaving group potential of the two radicals. This provides us with a preferred monomer addition sequence for the production of block copolymers. It has been shown that the preference for block sequence is methacrylates > styrenic > acrylate monomers.⁷⁴

The most significant anomalies in RAFT systems are the inhibition and retardation phenomena that occur in many polymerizations.^{60,81-83} If we examine equation 2.8 it is clear that the rate of polymerization should be a function of the initiator concentration and the monomer concentration in a reaction. A transfer step, which results in no net change in radical concentration, should not lead to rate retardation. The formation of intermediate radicals should not lead to retardation, as equilibrium concentrations of intermediate radicals should rapidly be established. Inhibition and retardation have been investigated by a number of authors and most investigations have focused on the fate of the intermediate radical species that is formed in the RAFT process and its effects on polymerization kinetics.^{81,84-87} ESR data provides us with the intermediate radical concentration in a RAFT polymerization, and the value is approximately constant for long chains.^{60,88} This implies an equilibrium condition and means that the propagating radical concentration in the systems, which is a function of the rate of radical generation and radical loss, should be the same in a RAFT-mediated process as in a conventional free radical process, however this is not the case. This means that the central exchange process cannot be all that controls the RAFT-mediated polymerization reaction (see 2.6.3). This dissertation is predominantly concerned with the problems that have been encountered when using the RAFT process in aqueous heterogeneous media. The most important stage in the formation of a particle in an emulsion process is the nucleation of that particle, i.e. the growth of polymer to the point at which the particle is stabilized. Inhibition and retardation are significant issues in heterogeneous media where particle nucleation is critical. To be able to understand these phenomena in heterogeneous media it is important to first investigate reasons for inhibition and retardation in homogenous media, to identify those phenomena that are dependent on the process itself and those phenomena that are dependent on the medium of polymerization. This issue will be addressed further in chapter four.

2.6.2 Heterogeneous Systems

Studies of reversible addition fragmentation transfer in heterogeneous media have been among the most complicated that have been carried out in the further investigation of this living polymerization process. As a transfer technique RAFT polymerization appears to be the best choice for control in water borne systems, as it does not require significantly more stringent reaction conditions than ordinary free radical polymerization. The Le *et al.*⁵⁴ patent of the RAFT process includes a number of examples of RAFT in heterogeneous media. The reactions were only studied at low conversions and when other authors began to expand the work, a number of problems were encountered.

Monteiro *et al.*⁸⁹ and Uzulina *et al.*⁹⁰ were the first authors to examine *ab initio* emulsion using the RAFT process. Neither group was able to prepare stable controlled emulsions, although Monteiro *et al.*^{65,66,91} were able to prepare complex latex particles using xanthate agents, which operate via an inefficient RAFT mechanism. The control that is sought has however remained elusive unless special techniques are used, *e.g.* controlled-feed,⁵⁴ or the use of phase transfer agents.⁹² A problem that was observed with RAFT, unlike other degenerative controlled polymerization techniques in organic dispersions in aqueous media, was that phase separation occurred at the beginning of the polymerization in both emulsion and miniemulsion systems.^{89,93}

Although previous studies^{94,95} have shown that predispersed emulsified RAFT systems can be polymerized successfully and similar results have been shown in the original patent,⁵⁴ there appear to be drawbacks to most of the systems for which results have been published. The control is typically worse than that in a solution system (often with polydispersity indices (PDIs) above the theoretical minimum of 1.5 for conventional free radical polymerizations) or polymeric surfactants have been required.⁹⁶

There are significant reasons for the fact that xanthates are capable of being used directly in emulsion systems. The most important is the fact that long chains are formed quite rapidly in the polymerization and particle nucleation is consequently substantially more efficient. Monteiro *et al.* further extended the investigation of efficient RAFT agents to include the use of predispersed systems, although initially with some difficulty.^{93,97} The investigations into predispersed systems culminated

with the use of polymeric stabilizers and allowed the formation of block copolymers in heterogeneous media via an efficient RAFT process.⁹⁶ Here the concept of two polymerization mechanisms competing in one RAFT reaction was introduced. The nature of the RAFT process meant that it was possible for particles containing dithioester end-capped polymers to be polymerized in the presence of particles that followed a conventional free radical process. This provided latexes that contained two different distributions of particles and polymer. The obstacles that were encountered by Monteiro *et al.* when using ionic surfactants were further explored by Butté *et al.* and Lansalot *et al.* but with mixed success.^{94,95} Specific agents were found to be suitable for the preparation of stable latexes, but best results were obtained when using a polymeric RAFT agent, which suggested that the instability problems were related to the exit characteristics of the leaving group radical species as well as the RAFT agents themselves.

Conventional emulsion polymerizations often exhibit inhibition periods in which very little monomer is consumed. Inhibition is a common artifact in aqueous based systems due to dissolved oxygen, which acts as an inhibitor.⁹⁸ Once the period is complete however, the formation of particles is no different from an emulsion system that does not have an inhibition period. RAFT-mediated emulsion polymerization has more significant inhibition than conventional emulsion polymerization. The effect of this RAFT related inhibition on emulsion polymerizations is discussed in chapter five.

2.6.3 Six orders of magnitude?

To discuss the RAFT process it is important to examine all of the radical and nonradical species that play a role in the RAFT mechanism. The rate of polymerization in a radical polymerization is a function of the concentrations and type of radicals available for propagation as well as being a function of all radical generation and loss mechanisms. If the central equilibrium is not the only factor controlling the polymerization process (see 2.6.1), then there is at least one other process that is significant.

A number of authors have addressed the possible processes that could be involved in retardation and inhibition, which are reported as being RAFT agent dependent, and two main schools of thought have developed. The possibility of termination of the intermediate radicals has been investigated by Monteiro *et al.*,⁸¹ who showed that an intermediate radical was capable of undergoing reactions and that an intermediate

radical termination process could account for the decreased propagating radical concentration. This was supported by the results of Kwak *et al.*,⁶⁰ who showed that these products could be generated without the requirement of UV degradation. Barner-Kowollik *et al.*⁸² approached the problem by discounting the possibility of intermediate radical termination and suggesting that the retardation that is observed in some particular RAFT polymerizations could be explained (from modeling results) by the concept of slow fragmentation, which required long intermediate radical lifetimes, of the order of 0.03 s. The model was however incompatible with the ESR data which had been determined independently by three different groups.⁵⁸⁻⁶⁰ Most recently Barner-Kowollik *et al.*⁸⁴ proposed a reduced irreversible termination and a potential reversible termination of the intermediate radical.

The models provided by these studies do not fully explain all of the phenomena that have been observed or have not been experimentally validated. The slow fragmentation approach is contradictory⁹⁹ to published ESR experimental data⁵⁸ and the products of the termination of the intermediate radical have only very recently been shown to form during the course of a polymerization.¹⁰⁰

An extended inhibition period, when compared to conventional polymerizations, in some systems is peculiar to RAFT polymerizations, using specific RAFT agents. In RAFT-mediated polymerizations, reports of inhibition are found in homogenous as well as heterogeneous systems, and these inhibition periods can often be relatively long in relation to polymerization time. This issue will be addressed in detail in the chapter concerning homogeneous studies, chapter four.

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Chapter 3: RAFT agent synthesis

Abstract

This chapter discusses the synthetic pathways that were investigated for the preparation of dithioesters and trithiocarbonates. The focus is largely on the use of Grignard agents although other routes are also addressed.

“.....he who knows and understands Grignard reactions has a fair grasp of organic chemistry.....”¹

“Why won't this thing start?” – a frequent question in our synthetic laboratories

3.1 Introduction

RAFT agent synthesis has developed in a largely unsystematic manner due to the vast number of variables in the system (see figure 3.1).² If Otsu^{3,4} had been aware that the dithiocarbamates that he used as iniferters could be far more effective chain transfer agents if the nitrogen atom were included in an aromatic ring, then RAFT might have been an important process a decade or two earlier. That is unfortunately the problem with research – eagle eye hindsight does not allow us to speed up the rate of progress!

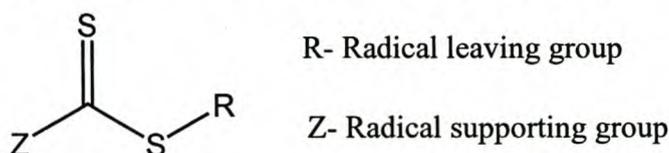


Figure 3.1 General RAFT agent structure R, Z being any suitable functionality for the preferred monomer.

The original compounds patented as reversible addition fragmentation transfer agents were largely prepared by the Grignard reaction of a bromobenzene derivative and carbon disulfide. A number of other syntheses feature in the patent of Le *et al.*,² but none of them were extended in the academic literature. These processes and other potential routes have been amply discussed in the literature and investigation in depth would not serve much purpose when this has been carried out before.⁵ For this reason the depth of the discussion will be minimized and the focus will be on the procedures carried out.

If we are to discuss the Grignard reaction with carbon disulfide it is important to note the disadvantages. The Grignard process was and is unpleasant due to odour, and the products often require rigorous purification prior to use. The purification proved to be a major stumbling block in the early expansion of the process, especially due to the sensitivity of the agents.

The discovery that a stable disulfide of dithiobenzoic acid could be prepared by oxidative coupling with catalytic iodine and crystallized to purity from ethanol simplified procedures substantially.⁶ The further conversion of bis(thiobenzoyl) disulfide into effective RAFT compounds was a relatively effortless process and allowed proliferation of the use of dithiobenzoate agents. In this chapter we will address the use of Grignard reactions as well as some more recent developments in RAFT agent synthesis.

3.2 Literature techniques

A number of techniques are currently commonly used for the synthesis of RAFT agents in the literature. We will give a brief background to the most important of these and then discuss the syntheses that were significant to this study in detail.

3.2.1 Grignard

The Grignard process is one of the most versatile methods for introducing new structural units to an organic compound. The use of organometallic compounds to assist in the formation of carbon-carbon bonds is a much-studied field in organic chemistry.⁷ The most traditional use of the Grignard reaction is the addition of organomagnesium compounds (Grignard reagents) to carbonyl compounds to generate alcohols, although reactions with acid chlorides to form ketones are also possible.⁸ A more modern interpretation extends the scope of the reaction to include the addition of Grignard reagents to a wide variety of electrophilic substrates. The Grignard reagent is capable of acting as a nucleophile, but because of the vast application of Grignard agents as well as the common reduction of these materials to disulfides, the use of the Grignard agent as a nucleophile is addressed separately later in this chapter. Grignard agents are structurally dependent on the Schlenk equilibrium, which is in turn dependent predominantly on the solvent in the system. THF produces monomeric predominantly covalently bonded organomagnesium compounds and was chosen as the solvent for this dissertation.⁹ The Grignard reaction with carbon disulfide occurs via a similar pathway to the reactions with ketones and will be the predominant route of synthesis for dithioesters in this dissertation.¹⁰

3.2.2 Transesterification

The transesterification of commercial dithioesters to form RAFT agents has proved useful to a number of research groups.¹¹ This facile procedure is reported to produce quantitative yields. It is however limited by the number of starting materials that are available and for that reason has not been used during this study. To efficiently apply this process it is necessary to have a method to remove the poor leaving group mercaptan from the reaction mixture. In the case of S-(thiobenzoyl)thioglycolic acid (a commercially available starting material), the reaction is heterophasic, which is a

considerable advantage as the product is continuously removed by separation as an oil phase.¹¹

3.2.3 Nucleophilic addition

The generation of a nucleophile, particularly from a thiol, amine or alcohol is a facile route to a reactive species that is capable of adding to carbon disulfide. This approach has been used to generate a vast variety of Z groups for RAFT agents including xanthates,¹² dithiocarbamates¹³ and trithiocarbonates.¹⁴ The problem with this synthetic route, like many others, is the insertion of a suitable leaving group. The simplest manner in which this is achieved is by the substitution of a good ionic leaving group such as a halogen. However halogen leaving group compounds are not accessible on a large enough scale to provide a great deal of variety in the R groups that are added to these compounds. In addition, tertiary halogens are less reactive, while tertiary leaving groups are the most efficient RAFT leaving groups. The use of sulfonyl chlorides as potential leaving groups was found to be problematic from a stability viewpoint in this thesis due to the anhydride that is formed, which shows rapid hydrolysis. The supposed structure is given in figure 3.2.

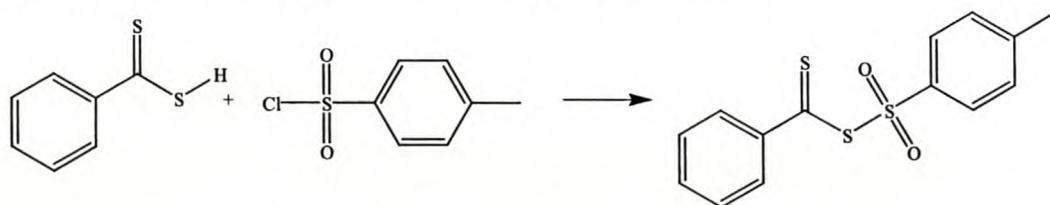


Figure 3.2 Sulfonyl dithiobenzoate anhydride

It should be pointed out that the number of potential RAFT leaving groups is far smaller than the number of potential ATRP initiators, which are commonly halogenated compounds that are used directly. This is due to the transfer requirements of the RAFT process.¹⁵

We will discuss alternative routes to substitution of thiocarbonyl thio compounds later in the chapter.

3.3 Experimental

3.3.1 Materials

Azo bis(cyanovaleric acid) [2638-94-0] 75%(Sigma-Aldrich), 2,2' azo bis(isobutyro nitrile) [78-67-1]. Aliquot 336 [5137-55-3] (Fluka), n-dodecyl mercaptan [112-55-0] 98%+ (Aldrich), diethyl ether [60-29-7] 99.5% (Merck), chloroform [67-66-3] 99% (Labchem) sodium hydroxide [1310-73-2] 50% solution (Aldrich), HCl [7647-010] 32% (ACE), phenyl magnesium chloride [6921-34-2] 1.0 M in ether (Aldrich), bromobenzene [108-86-1] 99% (Aldrich), carbon disulfide (CS₂) [75-15-0] 99.9% (Aldrich), acetone [67-64-1] 99.5% (SAARChem), p-toluene sulfonic acid [98-59-9] 98.5%, (Sigma-Aldrich), carbon tetrachloride [56-23-5] (CCl₄) 99.9% (Aldrich), ethyl acetate [141-78-6] CP, isopropanol [67-63-0] CP, pentane [109-66-0] CP, heptane [142-82-5] CP (ACE), (1-bromoethyl)benzene [103-63-9] 97% (Aldrich), sodium hydroxide CP (SAARchem), THF [109-99-9] was distilled from LiAlH₄ [16853-85-3], 2-bromopropionic acid [598-72-1] 99% (Aldrich), iodine [7553-56-2] 99%(Aldrich), magnesium 98% [7439-95-4] (Aldrich). sodium sulfide nonahydrate [1313-84-4] (Aldrich) 98+%.

Unless otherwise stated, all syntheses were carried out under an anhydrous nitrogen atmosphere. CAS numbers for all chemicals used are given in parentheses.

3.4 Grignard synthesis

3.4.1 Dithiobenzoic Acid

There are a number of literature procedures that are commonly used to prepare dithiobenzoic acid.^{2,10,16} The one that provides the highest purity product is however the Grignard preparation from bromobenzene.⁵ The general preparation of this Grignard agent is discussed in the experimental section below. Some overriding points that should be noted are that chloride-derived starting materials are better suited for this type of synthesis and THF is a preferred solvent. Iodine is used as a catalyst for the *in situ* activation of the magnesium substrate.⁷ A large number of synthetic approaches which include the use of catalysts such as copper (I) bromide¹⁷ are available and have been discussed in more detail by other authors.⁵ It is also

possible to convert the Grignard agent into stable ammonium salts which can be stored.¹⁸

3.4.1.1 Experimental procedure

Magnesium turnings were weighed and placed in the reaction vessel with a crystal of iodine in a little dry THF (distilled from LiAlH_4) and a stirrer bar. Bromobenzene and the remaining THF were placed in two separate addition funnels. Approximately 10% of the THF and the bromobenzene were added to the magnesium turnings and heat was applied using a heat gun until the reaction began (indicated by the colour change from the brown of the iodine in solution to clear). The temperature of the reaction system was maintained below 40 °C using an ice bath. The remaining solvent and bromobenzene were added dropwise. After completion, the reaction vessel was allowed to cool. The reaction mixture was metallic in colour (green to brown).

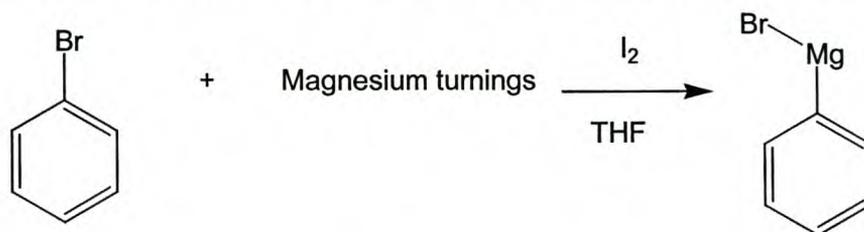


Figure 3.3 Grignard reagent formation

The carbon disulfide was slowly dripped into the Grignard mixture. The reaction temperature was carefully maintained at this point, as the reaction is very exothermic. The reaction turned brown / red during addition. After the addition was complete and the vessel had cooled, the product was poured into ice-cold water, in a large separating funnel, terminating the reaction.

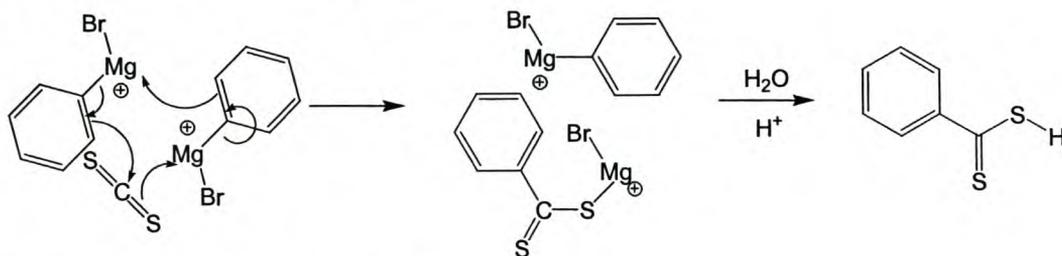


Figure 3.4 Dithiobenzoic acid formation.

The reaction scheme in figure 3.4 shows ionic intermediates although the mechanism by which this type of reaction occurs is typically complex and requires individual detailed study.⁹ Radicals are known to be present in some Grignard reactions and

Chemically Induced Dynamic Nuclear Polarization (CIDNP) has been shown to be present during Grignard formation.¹⁹

The aqueous salt was acidified using 33% fuming HCl. The colour change was quite clear becoming pink/purple. The organic layer was washed with water and dried over anhydrous magnesium sulfate. The product was recovered by concentration of the organic layer. Dithiobenzoic acid is an unstable compound and was reacted immediately to prevent extensive product loss. Depending on the further reactions that were carried out using the acid product, extraction of organics prior to acidification was carried out, as well as filtration to remove unreacted magnesium from the system. For the preparation of disulfides these steps are normally skipped as the acids are unstable and require conversion to a stable product as rapidly as possible. As disulfides are easily purified by crystallization, the removal of contaminants is rarely a problem.

3.4.1.2 Cumyl dithiobenzoate

The synthesis of cumyl dithiobenzoate was carried out according to the method of Le *et al.*² Dithiobenzoic acid and alpha methyl styrene (1.3 equivalent) were mixed. The reaction was carried out at 70 °C in carbon tetrachloride (~30% v/v reactants) and catalyzed by para toluene sulfonic acid. The reaction was allowed to continue for 6 hours. The product was purified by successive liquid chromatography on silica and alumina using hexane as an eluent system. The purified product was crystallized after vacuum removal of solvent and storage below -10 °C. The purity was estimated by ¹H NMR to be > 95%.

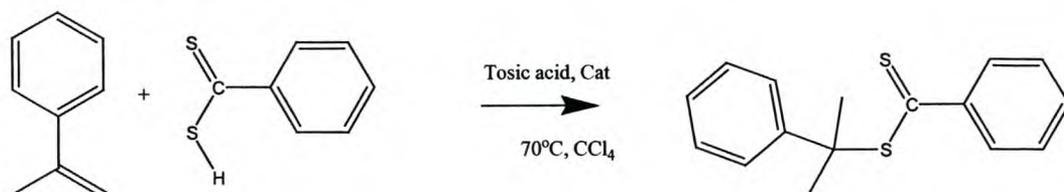


Figure 3.5 Cumyl dithiobenzoate formation

A typical example of reaction volumes and yields is 10 g (0.065 mol) dithiobenzoic acid was reacted with 10 g (0.084 mol) alpha methyl styrene to provide a final yield of 5.30 g (0.019 mol) cumyl dithiobenzoate (30%).

¹H NMR (C₆D₆) δ: 1.86, s, 6H, H_{methyl}; 7.4-7.8, m, 6H, H_{aromatic}; 7.9, dd, 2H, O_{cumyl ring}; 8.10, dd, 2H, O_{Dithiobenzoate ring}.

3.4.1.3 Bis(thiobenzoyl) disulfide

Bis(thiocarbonyl)disulfide was prepared according to Le *et al.*² Catalytic iodine and a double molar ratio of dimethyl sulfoxide were added to dithiobenzoic acid in a medium of absolute ethanol. The reaction proceeded at room temperature. The product crystallized out of the solvent and was filtered and washed with cold ethanol.

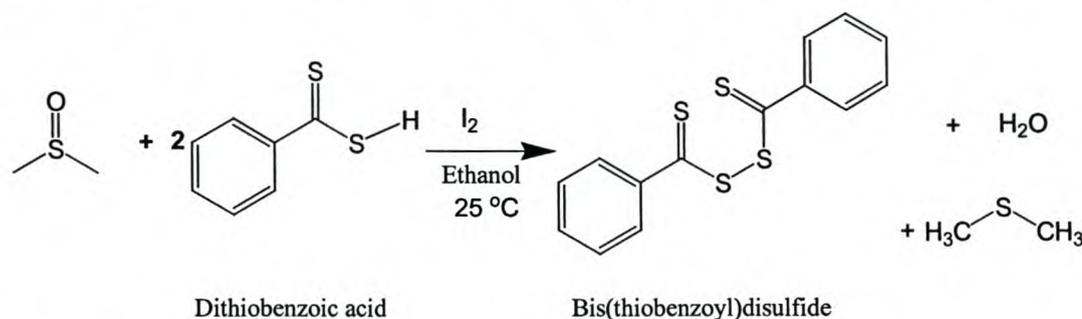


Figure 3.6 **Bis(thiobenzoyl)disulfide formation**

The reaction provides yields often over 85%. An example of typical reaction volumes and yields is 15.0g (0.098 mol) dithiobenzoic acid was reacted with 15.0 g dimethyl sulfoxide (0.192 mol) in a medium of absolute ethanol (100 ml) with catalytic iodine. Dimethyl sulfide (bp 38 °C) evolved during the reaction, bubbled out of the sealed system via the bubbler. The crystalline product formed within 20 minutes, and the reaction vessel was placed in the fridge overnight to aid crystallization, prior to filtration and drying to yield 13.72 g of the product (91%). The purity of the compound was examined by ¹H NMR in CDCl₃ and found to be greater than 98%, although the contamination by minor amounts of the acid is difficult to eliminate.

¹H NMR (CDCl₃) δ: 7.5, m, 4H, H_{meta}; 7.6, dd, 2H, H_{para}; 8.21, dd, 4H, H_{ortho}.

3.4.1.4 Bis(thioanisoyl) disulfide

The synthesis of bis(thioanisoyl) disulfide proceeds in a similar fashion to that of bis(thiobenzoyl) disulfide. The Grignard preparation of dithioanisic acid is analogous to that of dithiobenzoic acid. The colour of the acid and the final crystalline product are however more red in nature. The final crystalline product is a fine powder with a distinct but not unpleasant odour.

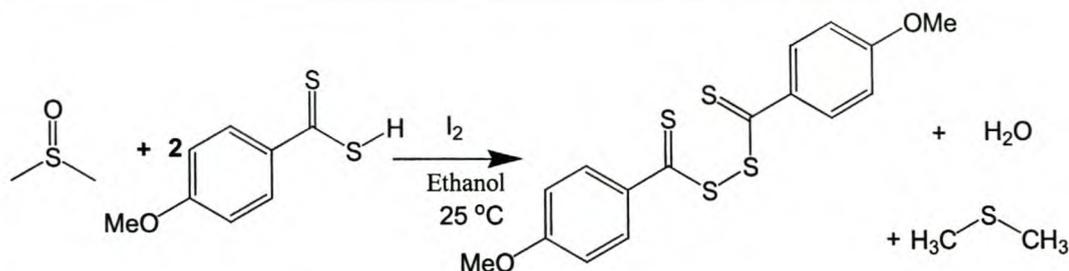


Figure 3.7 Bis (thioanisoyl)disulfide formation

A typical example of reaction volumes and yields is 15.0g (0.082 mol) dithioanisoic acid was reacted with 13.0 g dimethyl sulfoxide (0.167 mol) in a medium of absolute ethanol (100 ml) with catalytic iodine to provide 22g (0.060 mol) bis(thioanisoyl) disulfide (73%). $^1\text{H NMR}$ (C_6D_6) δ : 3.8, s, 3H, H_{methyl} ; 7.0, dd, 4H, H_{meta} ; 7.6, dd, 4H, H_{ortho} .

3.4.1.5 Cyanoisopropyl dithiobenzoate (CIPD/AD)

The further reaction of the disulfides of dithioesters with radical species allows generation of the final RAFT agents.²⁰ To compensate for irreversible geminate recombination reactions an excess of the radical generating species is normally added. This is typically in the region of a 30% molar excess. The reaction is carried out under an inert atmosphere (UHP nitrogen) and allowed to continue for ~ 5-6 half lives of the chosen initiator at the reaction temperature. It must be kept in mind that the initiator decomposition rate is a first order exponential decay and that the length of time required to reach a higher conversion thus increases exponentially. For the reaction in question, the temperature used was typically 85 °C, the solvent was ethyl acetate and the reaction time was around 6 hours. This is substantially shorter than some reaction times reported for this procedure but the sensitivity of these compounds means that there is reason to be careful about extending reaction times unnecessarily.

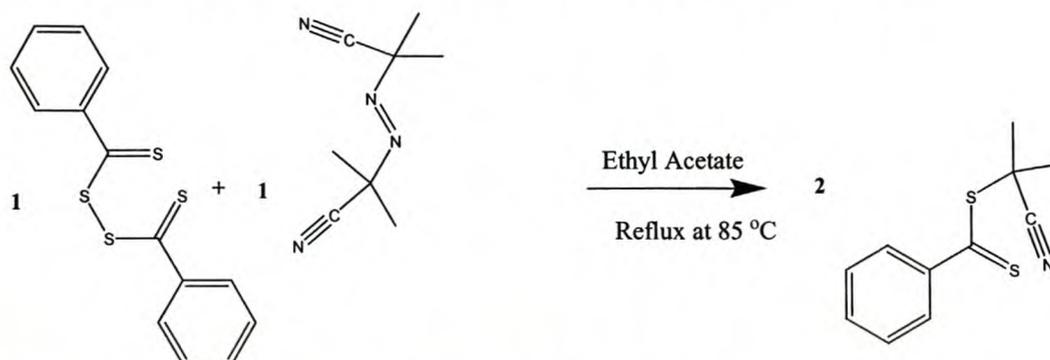


Figure 3.8 Cyanoisopropyl dithiobenzoate formation

The reaction mixture is then concentrated and purified by column chromatography on silica using volume ratios of 1:1:0.15 pentane:heptane:diethyl ether. The yield is typically ~60% after purification, and purity is normally ~97% with the largest impurity being tetramethyl succinonitrile (TMSN), the geminate recombination product of cyanoisopropyl radicals. This product sublimes out under extended vacuum purification.

The proposed reaction mechanism involves the reaction of cyano isopropyl radicals with the sulfur of a C=S double bond, followed by the breaking of the disulfide and the formation of a sulfur centered radical that then proceeds to react either with a second sulfur centered radical or the carbon centered radical of the cyano isopropyl radical.

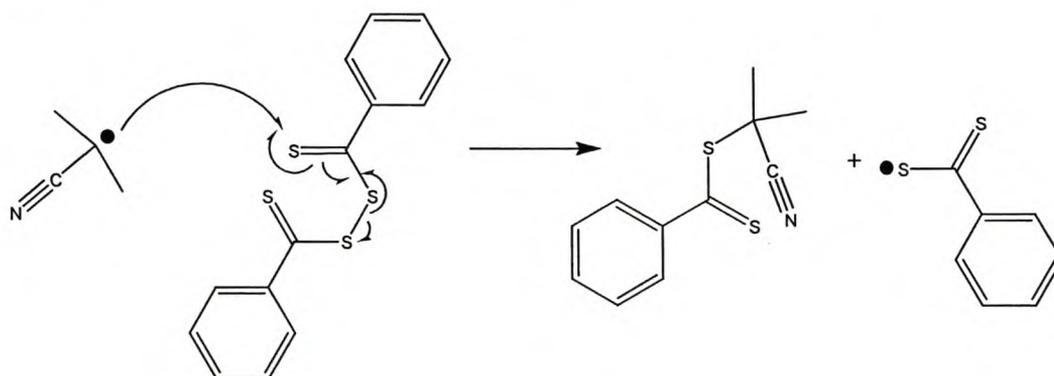


Figure 3.9 Mechanism of radical attack on disulfide

This reaction has been followed by ^1H NMR, and as expected, the rate determining step is the decomposition of the azo compound. The reaction was carried out at 80 °C, in deuterated benzene.

3-D NMR experiment

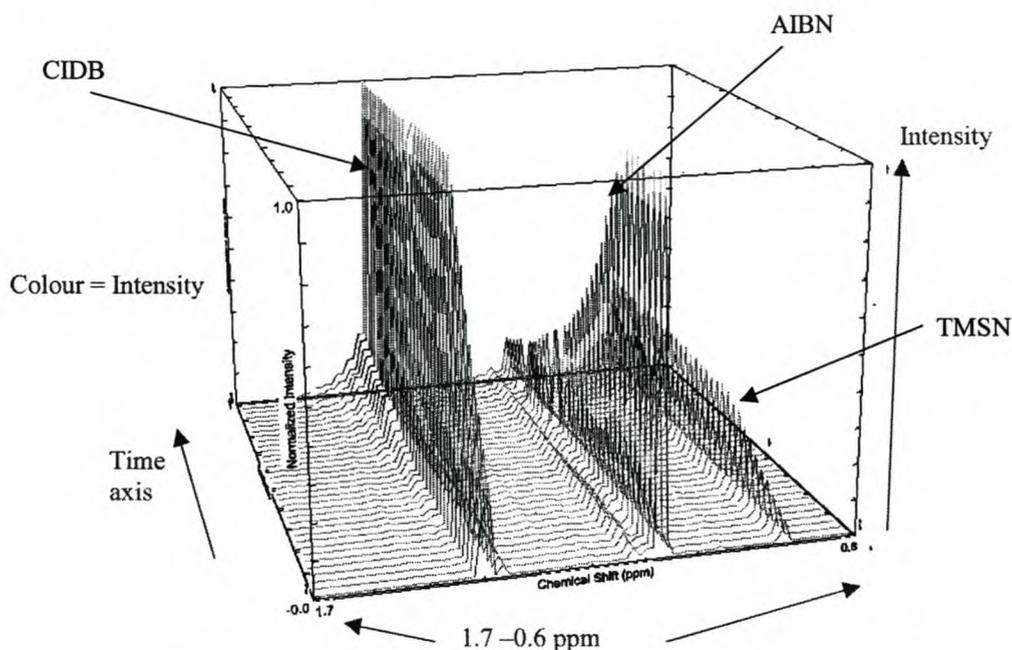


Figure 3.10 3-D array of NMR experimental data for cyanoisopropyl dithiobenzoate formation.

A typical example of reaction volumes and yields is 10.0g (0.032 mol) bis(thiobenzoyl)disulfide reacted with 7.0 g AIBN (0.042 mol) to provide 7.95 g (0.036mol) cyanoisopropyl dithiobenzoate (56%). ^1H NMR (C_6D_6) d: 1.45, s, 6H, H_{methyl} ; 7.5, m, 2H, H_{meta} ; 7.6, dd, 1H, H_{para} ; 7.71, dd, 2H, H_{ortho} .

3.4.1.6 Cyanovaleric acid dithiobenzoate

(4-cyano-4-((thiobenzoyl)sulfonyl) pentanoic acid/CVADTB)

The synthesis of 4-cyano-4-((thiobenzoyl)sulfonyl)pentanoic acid was carried out according to the method of Le *et al.*^{2,6} Bis(thiobenzoyl)disulfide and 4,4'-azo-bis(4-cyanovaleric acid) were allowed to react in a medium of refluxing ethyl acetate at 85 °C for 24 hours. The ethyl acetate was then removed by rotary evaporation. The product was purified by column chromatography on silica. A mixture of a 3:3:4 pentane:heptane:ethyl acetate was used as an eluent system.

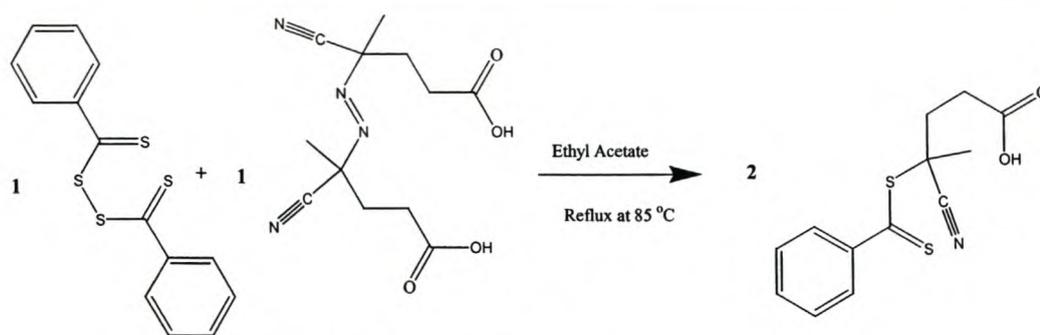


Figure 3.11 Formation of cyanovaleric acid dithiobenzoate

The product was crystallized with the help of a drop of chloroform, and dried under vacuum.

A typical example of reaction volumes and yields is 10g (0.032) mol Bis(thiobenzoyl)disulfide reacted with 12 g Azobis (cyanovaleric acid) (25% H₂O) (0.032 mol) to provide 11.54 g (0.041 mol) of cyanovaleric acid dithiobenzoate 64%, estimated purity >98%; impurities include trace water. ¹H NMR (CDCl₃) δ: 2.00, s, 3H, H_{methyl}; 2.4-2.8, m, 4H, H_{methylene}; 7.5, m, 2H, H_{meta}; 7.6, dd, 1H, H_{para}; 7.95, dd, 2H, H_{ortho}.

3.4.1.7 Cyanoisopropyl para methoxy dithiobenzoate

Bis(thioanisoyl)disulfide and azobis(isobutyronitrile) were mixed in a medium of ethyl acetate:toluene 70/30 and allowed to react for 6 hours at 85°C. The bis (thioanisoyl)disulfide is characterized by poor solubility in many of the solvents commonly used in laboratories; but it was found that even if some heterogeneity is present, this rapidly decreases as the reaction progresses.

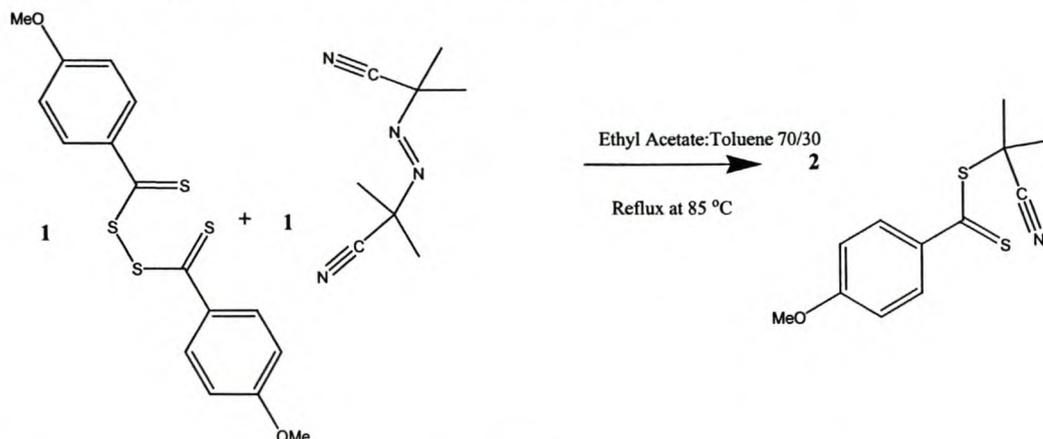


Figure 3.12 Formation of cyanoisopropyl para-methoxy dithiobenzoate

Purification was carried out by column chromatography on silica using volume ratios of 1:1:0.15 pentane:heptane:diethyl ether. A typical example of reaction volumes and yields is 10.0g (0.027 mol) bis(thioanizoyl)disulfide reacted with 7.0 g AIBN (0.042 mol) to provide 7.95 g (0.036mol) cyanoisopropyl para-methoxy dithiobenzoate (56%). ^1H NMR (C_6D_6) δ : 1.45, s, 6H, H_{methyl} ; 3.8, s, 3H, $\text{H}_{\text{methoxy}}$; 7.0, m, 2H, H_{meta} ; 7.71, dd, 2H, H_{ortho} .

3.4.2 Phenyl dithioacetic acid

Phenyl dithioacetic acid was prepared according to the method of Quinn *et al*²¹ with the following modifications. Benzyl magnesium chloride (3.0 molar in diethyl ether) was used as reagent. The Grignard agent was added to CS_2 , in a molar ratio, in a dropwise fashion under nitrogen while the reaction temperature was maintained below 20 °C by using an ice bath. After the CS_2 addition was completed, pouring the reactor contents into ice water terminated the reaction. The organic byproducts were extracted using diethyl ether. The aqueous layer was then acidified with 33% HCl and extracted with diethyl ether. This organic layer was concentrated to provide the title compound, which immediately reacted further. This product is highly unstable and extreme care should be taken to ensure maximum yields.

3.4.2.1 Cumyl phenyl dithioacetate

A molar equivalent of α -methyl styrene was added to the phenyl dithioacetic acid. *p*-Toluene sulfonic acid was added in catalytic quantities, and the mixture was allowed to reflux in CCl_4 overnight. The product was then concentrated and crystallized from cold methanol. ^1H NMR purity was estimated at 99%.

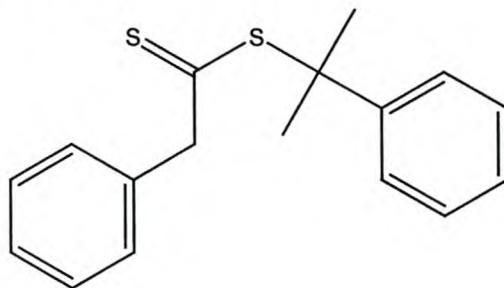


Figure 3.13 Cumyl Phenyl Dithioacetate.

A typical example of reaction volumes and yields is 10.0 g (0.059 mol) phenyl dithioacetic acid reacted with 10.2 g (0.086 mol) alpha methyl styrene to produce 6.18

g (0.021 mol) cumyl phenyl dithioacetate (36%). $^1\text{H NMR}$ (CDCl_3) δ : 2.00, s, 6H, H_{methyl} ; 4.2, s, 2H, $\text{H}_{\text{methylene}}$; 7.2-7.4, m, 8H, $\text{H}_{\text{aromatic}}$; 7.6, dd, 2H, H_{phenyl} .

3.5 Other nucleophile generation techniques

The addition of carbon disulfide to a strong base is possible by a number of routes. One of the more common and more flexible routes is the use of a hydroxide base in aqueous media to generate a sulfur anion.²² Sulfur anions show high selectivity for carbon disulfide addition and also allow the generation of trithiocarbonate species with two good leaving groups attached to the trithiocarbonate moiety.²³

3.5.1 S-Dodecyl S'-(isobutyric acid) trithiocarbonates (DIBTC).

Phase transfer and interfacial methodologies are quite common in organic syntheses.²⁴ In the case of phase transfer reactions, ionic species are carried into the organic phase of an aqueous/organic biphasic system. This is possible due to the nature of the substituents on the phase transfer catalyst, which is normally a quaternary ammonium or phosphonium salt. The substituents are normally alkyl in nature and thus allow significant organic phase solubility. To maintain the electrical neutrality of each phase, the ionic phase transfer catalyst must cross to the organic phase in the presence of a counterion from the aqueous solution. In this dissertation, a quaternary ammonium salt was used as catalyst.

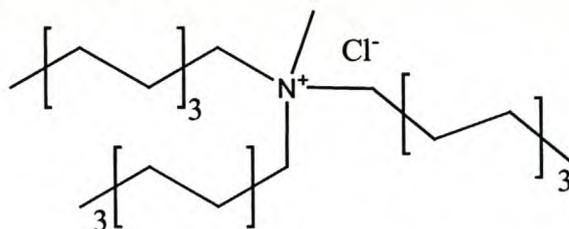


Figure 3.14 Aliquot 336 Tricapryl methyl ammonium chloride

It is also possible that interfacial transfer takes place in which ion exchange occurs directly at the interface between the organic and aqueous layer, however this is a less efficient process.²⁵ Using phase transfer methodology S-1-dodecyl-S'-(isobutyric acid) trithiocarbonate was prepared according to the method of Lai et al.¹⁴ 1-Dodecanethiol (80.0 g, 0.40 mol), acetone (~ 6x molar excess), and Aliquot 336 (tricapryl methyl ammonium chloride, 6.5 g, 0.016 mol) (a phase transfer catalyst)

were mixed in a reactor cooled by ice under a nitrogen atmosphere. Sodium hydroxide solution (50%) (35 g, 0.43 mol) was added over 20 min.

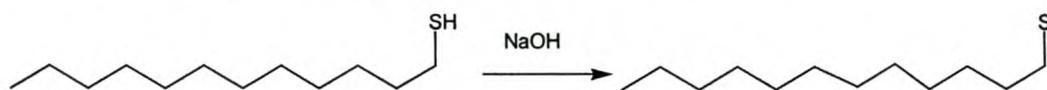


Figure 3.15 Sulfide anion formation.

The reaction was stirred for an additional 15 min before carbon disulfide (31 g, 0.41 mol) in acetone (40.0 g, 0.69 mol) was added over 20 min, during which time the color turned yellow.



Figure 3.16 Carbon disulfide addition.

Ten minutes later, chloroform (70.0 g, 0.60 mol) was added in one portion, followed by dropwise addition of 50% sodium hydroxide solution (160 g, 2 mol) over 30 minutes. The reaction was allowed to stir overnight. The use of dodecyl mercaptan creates significant mixing problems in this reaction and for that reason it is imperative to have a large vessel available that can be manually shaken.

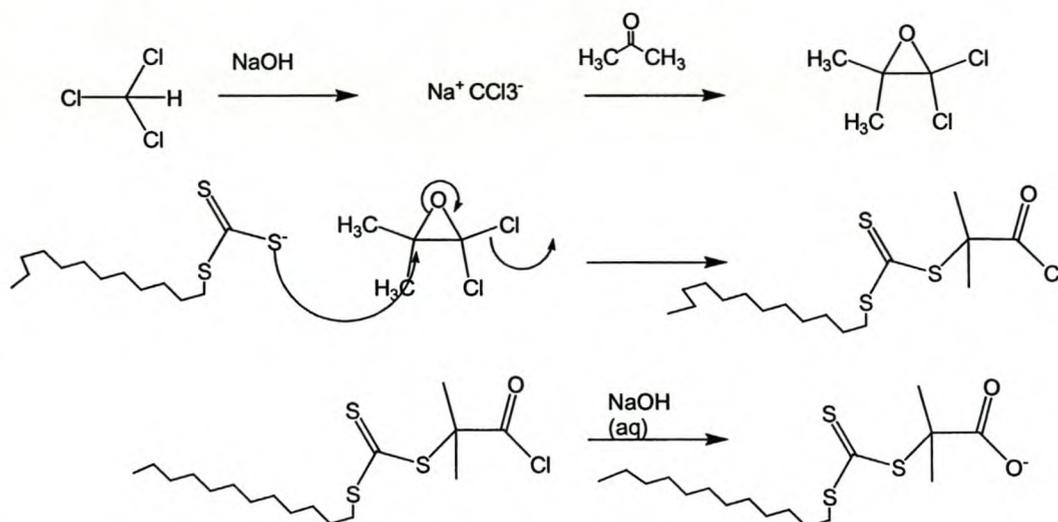


Figure 3.17 Isobutyric acid leaving group formation.

After stirring overnight, the reaction mixture was poured into a 5L beaker and stirred at high revolutions. ~ 600 mL of water was added to the reaction mixture, then hydrochloric acid was added until the mixture was neutralized (100 mL of 33%

concentrated HCl was added). The reaction mixture was then stirred until the acetone evaporated and the product had congealed. The solids were then filtered and stirred in excess isopropanol. After half an hour the solids were removed by filtration and discarded as insoluble S,S'-bis(1-dodecyl) trithiocarbonate.

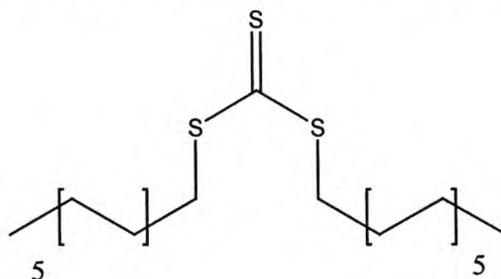


Figure 3.18 S,S' bis(dodecyl) trithiocarbonate.

The isopropanol solution was concentrated and poured into cooled hexane. The product was separated after crystallization to provide 84g (0.23 mol) of the desired product (50% yield based on carbon disulfide). Purity was estimated 99% by ^1H NMR. ^1H NMR (CDCl_3) d: 0.99, t, 3H, $\text{H}_{\text{terminalmethyl}}$; 1.37-1.47, m, 20H, H_{alkyl} ; 1.75, s, 6H, H_{methyl} ; 3.42, t, 2H, $\text{H}_{\text{methylene}}$; 13.05, s, 1H, H_{acid} .

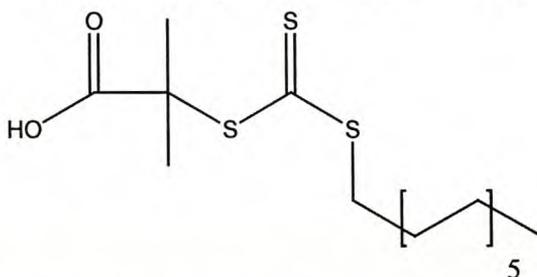


Figure 3.19 S-Dodecyl S'-(isobutyric acid) trithiocarbonate.

3.5.2 S-Dodecyl S'-(propanoic acid) trithiocarbonates (DPATC)

When bromo-compounds are used that have an existing acid functionality, reactions are substantially more successful when a minimum of water is present. The formation of a secondary leaving group radical with a dodecyl companion substituent was carried out as follows. Dodecyl mercaptan and sodium hydroxide are mixed in molar ratios in acetone in a cooled reactor. It is important to use a fine sodium hydroxide crystal for this purpose, as the solubility of the salt in acetone is poor. It is critical that this reaction is carried out in an anhydrous fashion. After ~ 20 minutes, a molar ratio of carbon disulfide was added and the reaction was allowed to continue stirring for ~ 30 minutes. At this point 2-bromopropionic acid was added dropwise to the reactor.

The viscosity of the reaction increased substantially. After stirring overnight, the reaction mixture was acidified using aqueous hydrochloric acid and the acetone was allowed to evaporate. The product was filtered and dissolved in isopropanol. It was then precipitated using hexane and allowed to crystallize overnight. This process was not as efficient as in the case of DIBTC, but a second crystallization after concentration allowed an excellent yield of the title compound.

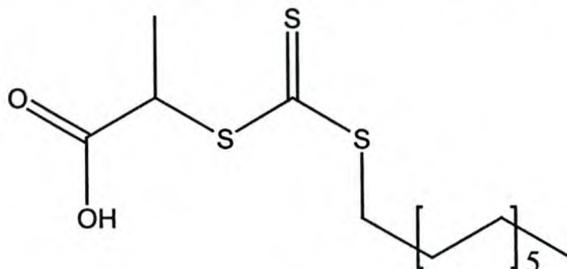


Figure 3.20 S-Dodecyl S'-(propionic acid) trithiocarbonate

A typical example of reaction volumes and concentrations is 20g dodecyl mercaptan (0.099 ml) reacted with 7.6g carbon disulfide (0.1 mol) in the presence of 2.0 grams Aliquot 336 after neutralization with sodium hydroxide 4.0g (~0.1 mol), (fine pellets) in acetone. In the second step 13.8 g (0.099mol) 2-bromopropionic acid was added. The reaction yielded 24 g of pale yellow crystals (71% yield). $^1\text{H NMR}$ (CDCl_3) δ : 0.99, t, 3H, $\text{H}_{\text{terminal methyl}}$; 1.37-1.47, m, 20 H, H_{alkyl} ; 1.65, d, 3H, H_{methyl} ; 2.5, q, 1H, $\text{H}_{\text{methine}}$; 3.42, t, 2H, $\text{H}_{\text{methylene}}$; 13.05, s, 1H, H_{acid} .

3.5.3 S,S'-Di(isobutyric acid) trithiocarbonates (DIIBTC)

The preparation of a trithiocarbonate salt can be carried out via one of two mechanisms. The first is the use of sodium sulfide as a nucleophile followed by the addition of carbon disulfide; the second is the *in situ* generation of sodium trithiocarbonate from carbon disulfide and sodium hydroxide. The latter is certainly the most accessible if carbon disulfide can be readily obtained. The former method is complicated by the presence of substantial water of crystallization in most of the commercial sodium sulfide. As some of the trithiocarbonates require anhydrous conditions, the water of crystallization is potentially problematic. The synthesis of S,S'-di(isobutyric acid) trithiocarbonate was accomplished via the method of Lai *et al.*^{14,26} Their development of the acid functionality via an acid chloride intermediate allows facile generation of a compound that would normally be difficult to synthesize in basic media without the complication of side products. Carbon disulfide, acetone

and chloroform and aliquot 336 were mixed in the presence of hexane. The reaction was cooled with an ice bath while aqueous sodium hydroxide was added dropwise. The reaction was allowed to stir overnight after which it was diluted in water and acidified using 33% HCl. The organic layer was collected and concentrated to dryness. The product was recrystallized from isopropanol to yield the clean S,S'di(isobutyric acid)trithiocarbonate.

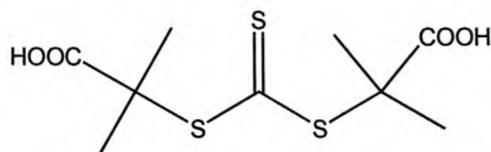


Figure 3.21 S,S'di(isobutyric acid)trithiocarbonate.

A typical example of reaction volumes and yields is: carbon disulfide (27.4 g, 0.36 mol) chloroform (107.5 g, 0.9 mol), acetone (52.3 g, 0.9 mole), and aliquot 336 (2 g) were mixed with 120 mL of hexane in a reactor cooled with an icebath. Aqueous sodium hydroxide (50%mass/mass) (201.6 g, 2.52 mol) was added dropwise over 90 min in order to keep the temperature below 25 °C. The reaction was stirred overnight. 900 mL of water was then added to dissolve the solid, followed by 120 mL of concentrated HCl. The product was washed with water, and 35 g of yellow crystalline product was obtained by crystallization from isopropanol (40 % yield). ^1H NMR (CDCl_3) δ : 1.6, s, 12H, H_{methyl} .

3.5.4 S,S'-Di(ethylbenzene) trithiocarbonate

The use of sodium sulfide as a nucleophile allowed the facile generation of the diethyl benzyl trithiocarbonate via direct bromide elimination from phenethyl bromide. Sodium sulfide nanohydrate is dissolved in excess water in the presence of a phase transfer catalyst and hexane as the oil phase. Carbon disulfide is added dropwise to the reaction over a period of 15 minutes at which time the red colour of sodium trithiocarbonate is clearly visible.

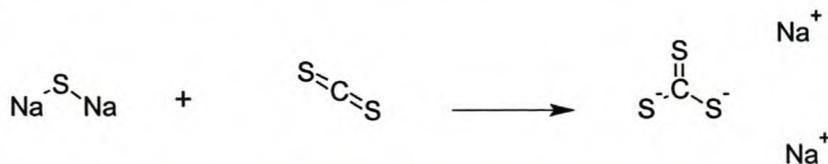


Figure 3.22 The formation of sodium trithiocarbonate.

At this point phenethyl bromide is added dropwise resulting in an immediate colour change from red to yellow and the movement of the product from the aqueous phase to the oil phase of the reaction mixture. After stirring overnight, the organic phase was separated, the aqueous phase was extracted, the organic phases were combined and washed with water. The organic phase was dried over anhydrous magnesium sulfate. The solvent was removed, and the product was purified by column chromatography over silica using hexane as an eluent.

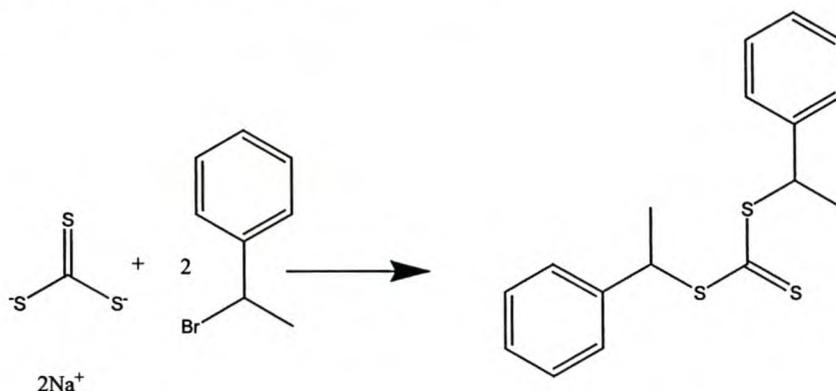


Figure 3.23 Formation of S,S'-di(ethylbenzene) trithiocarbonate.

A typical example of the synthetic approach is sodium sulfide (nonahydrate) 28 g (0.097 mol) was reacted with 7.6 g carbon disulfide (0.099 mol) in hexane and water (50:50 v/v) with 2g of Aliquot 336 as phase transfer catalyst. 1-Bromoethylbenzene 36g (0.194 mol) was then added to provide, after purification by column chromatography over silica with hexane, the product (65 % yield). ¹H NMR (CDCl₃) d: 1.6, dd, 6H, H_{methyl}; 5.2, q, 2H, H_{methine}; 7.1, m, 10 H, H_{aromatic}.

3.6 Conclusion

A number of RAFT agents were synthesized, each of which had different synthetic aspects that had to be addressed. The approaches to the syntheses presented here are by no means exclusive, but the preparations used are robust and repeatable. Generally speaking trithiocarbonate preparations are very easily followed and scaled. Dithioesters prepared via Grignard routes are limited in scale due to exotherms, and care must be taken to avoid product loss. The unstable intermediates that are formed also require considerably more care for successful agent preparation to be accomplished.

3.7 References

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Chapter 4: Homogeneous studies

Parts of this chapter are taken from publications that have been submitted to the journal Macromolecules

Abstract

In situ ^1H nuclear magnetic resonance (NMR) spectroscopy has been used to directly investigate the processes that occur during the early stages (typically the first few monomer addition steps) of AIBN-initiated reversible addition fragmentation chain transfer polymerization. The change in concentration of important dithiobenzoate species as a function of time has been investigated. The inhibition effect in the presence of RAFT agents in homogeneous media is addressed and explained in reference to the RAFT mechanism. A number of conclusions regarding the types of growing chains have been made, allowing further insight into the mechanism of the polymerization and possible implications for emulsified polymerizations.

4.1 Introduction

To understand the heterogeneous RAFT polymerization process it is important to first understand the process in homogenous media. Homogenous media have been the most studied environment of radical polymerization for a number of very important reasons. The most significant reason is that homogenous media are less complex than heterogeneous media. Homogeneous media allow us to study the effects of different components, i.e. monomer, solvent and initiator or chain transfer agent, without the problems associated with a multiphase process. To study any living radical polymerization technique, including the RAFT process, in any medium, it is important to examine a number of processes including the nature or the products formed, possible side reactions in the system, reaction rates, and the loss or preservation of important components. There are however two extra elements that may be dependent on the abovementioned characteristics, but should be examined in their own right, viz. controlled and living character.

4.2 Controlled character

To obtain control of the development of the molecular weight distribution of polymer being formed in a RAFT mediated polymerization, it is necessary that the exchange process between growing and dormant chains be highly efficient. In fact, if we wish to have complete control it is preferred that only a single monomer addition occurs prior to transfer. De Brouwer described the probability of multiple additions as (using two propagation steps as a minimum requirement):¹

$$P(\text{multiple}) = P(\text{propagation})^2 = \left(\frac{[M]}{[M] + C_T \cdot [RAFT]} \right)^2 \quad (4.1)$$

This suggested that the probability of adding multiple units becomes negligible for most conditions with:

$$C_T \gg \frac{[M]}{[RAFT]} \quad (4.2)$$

Typical ratios of monomer to RAFT agent are such that they will rarely exceed 1000, and thus for C_T greater than 1000, the probability of two or more propagation steps will decrease substantially. Predictions of polydispersities in RAFT-mediated systems

have been carried out using the equations developed by Müller *et al.*^{2,3} with the assumptions made by Smulders⁴ for demonstration purposes of the effect of C_T :

$$\overline{M}_n = \frac{\gamma x}{1 - (1-x)^{C_T}} M_0 \quad (4.3)$$

$$\overline{M}_w = \gamma \left(2 + \frac{(2-x)(1-C_T)}{C_T} \right) M_0 \quad (4.4)$$

In the equations the fractional conversion is represented by x while γ represents the initial monomer to RAFT ratio. M_0 is the molar mass of the monomer. C_T represents the chain transfer constant for the RAFT moiety in the system. \overline{M}_n and \overline{M}_w are the number and weight average molecular weights, respectively. As will be discussed later, this is a reasonably poor way of representing the transfer process in a RAFT polymerization, as the value of the transfer efficiency will vary during polymerizations. These equations predict a more rapid decrease in the polydispersity of polymer ($\overline{M}_w/\overline{M}_n$) produced with time via the RAFT process with increasing transfer efficiency. To illustrate this, figure 4.1 shows the effect of a monomer to RAFT ratio of 100:1 while varying the C_T value from 0.01 to 1000.

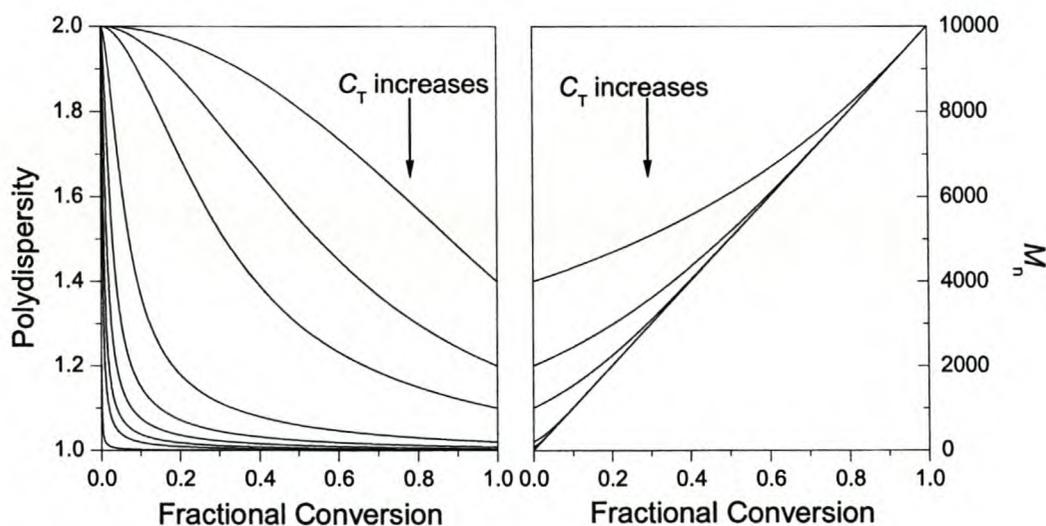


Figure 4.1 Predicted behaviour of number average molecular weight and polydispersities in a RAFT mediated polymerization where the efficiency of the transfer process, monomer to RAFT ratio of 100:1 while varying the C_T value from 0.01 to 1000.

The decreasing polydispersity with conversion has been reported by numerous authors in RAFT literature,^{5,6} (although competing processes, such as termination, can and do prevent this decrease from taking place under all conditions), and it appears that the equations provide at least qualitative behavioral prediction. It should be noted that in

Müller's original full equations,^{2,3} the polydispersity shows a sharp rise at very low conversions prior to the slow decrease. For reasons which will become clear later in this chapter, this seems more realistic for the RAFT process.² This result is similar to results produced for systems using persistent radicals to model living radical polymerization.⁷

4.2.1 Example

The kinetic studies in this chapter carried out followed the controlled character of the polymerizations. This is based on the linear increase of \bar{M}_n and conversion with time as well as the narrow polydispersity that is preferred.

The data in figure 4.2 for bulk styrene polymerization in the presence of hexadecane, (at miniemulsion loading levels of 52:1 by molar ratio (for direct comparison with miniemulsion experiments in chapter five)), demonstrated the linear increase of \bar{M}_n with conversion, and that the PDI of the polymer remained below the benchmark of 1.5. This showed that control in these systems could effectively be achieved. The fact that the polydispersity does not markedly decrease with conversion and appears to show a slight increase with time is largely due to experimental variables, including the amount (and type) of termination in the system.

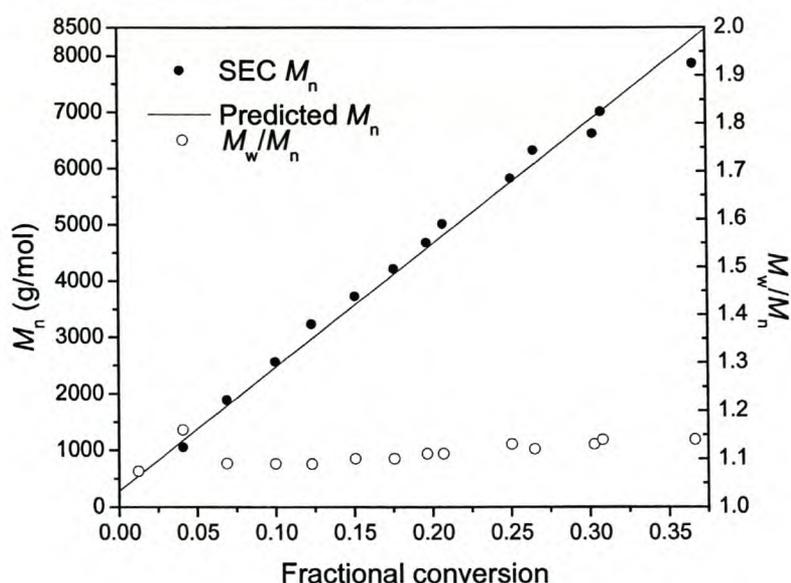


Figure 4.2 Evolution of \bar{M}_n and PDI for the RAFT polymerization of styrene (0.193 mol) in the presence of hexadecane (3.96×10^{-3} mol), at a molar ratio of 52:1 to styrene, and RAFT agent (1) (9.14×10^{-4} mol) using AIBN (8.35×10^{-5} mol) as initiator at a mol ratio of 1:14 to RAFT at 75 °C. The predicted line was generated using equation 4.5 (pg 77).

4.3 Living Character

Living character is best examined experimentally by determining the extent to which block polymers can be produced from a specific polymer sample. The possibility of block formation is limited by cross transfer, i.e. the incoming radicals ability to displace existing leaving groups, and for this reason it is important that the second monomer (if a different monomer is going to be used) be chosen with care. The block formation ability indicates the degree of “livingness” of the sample. Indications of living capabilities can also be derived from end-group analysis as polymer living characteristics are normally derived from living end-groups that are dormant due to specific functional groups. Most determinations are carried out by chromatographic means in this thesis.

4.3.1 Examples

Polymeric RAFT agents were prepared by solution polymerizations of 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid (**1**) with monomer (see Table 4.1) at 80 °C under nitrogen atmosphere in ethyl acetate, to produce RAFT end-capped polymer chains. To determine the efficiency of the end-capping, block polymers were synthesized from these RAFT end-capped homopolymers under the same conditions, by addition of a second batch of monomer and initiator to reinitiate the initial blocks. Initiator concentrations were below a 1:3 molar ratio with respect to the RAFT agent. As will be discussed later, this method of indicating the initiator in the system, although very common in the literature, is not very meaningful. However, for comparison purposes it is mentioned here.

To determine the efficacy of the RAFT agent, polymerization tests were carried out using 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid in ethyl acetate solvent or cumyl dithiobenzoate (**2**) in bulk (see Table 4.1). Reactions were not taken to completion, but were terminated by cooling and precipitating the polymeric product after a specific time period, typically 18 – 24 hours.

Table 4.1: Final polymers produced by homogenous polymerizations. Solution polymerizations were conducted in ethyl acetate at 20 percent solids. *MMA solution polymerizations were precipitated using pentane. In the case of BMA and BA the polymer was concentrated by evaporation. The initiator used was AIBN and the reactions were carried out at 80 °C for solution polymerizations and 90 °C for bulk systems.

<i>Reaction</i>	<i>RAFT agent</i>	<i>Monomer</i>	\bar{M}_n	\bar{M}_w/\bar{M}_n
Sol_1	(1)	BA	7800	1.08
Sol_2	(1)	BMA	6600	1.07
Sol_3	(1)	MMA	7200	1.07
Sol_4	Sol_3*	MMA-b-BA	38700	1.34
Sol_5	Sol_2*	BMA-b-MMA	14200	1.18
Bulk	(2)	STY	4800	1.39

It can quite clearly be shown that the RAFT process provides block copolymers that are living as well as controlled in nature. The term living will be used, as is convention, to describe the RAFT technique for the remainder of the dissertation, but the fact that there is controlled behaviour as well should be kept in mind. Figure 4.3 demonstrates a chromatographic determination of block polymer formation.

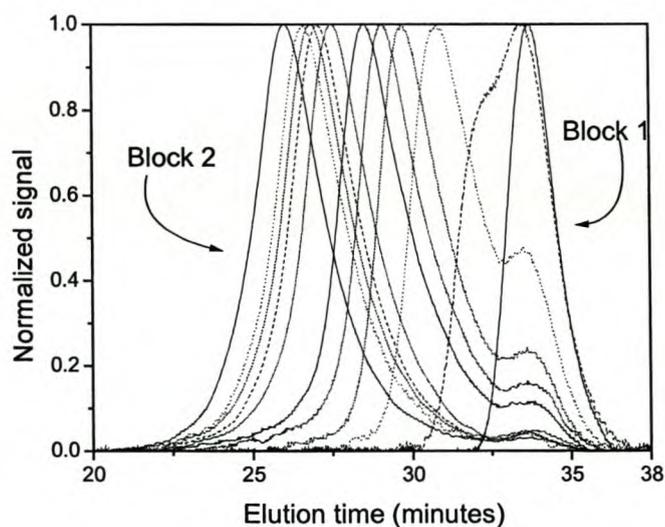


Figure 4.3 Examining block formation through chromatographic means, clearly illustrating the formation of block polymer as well as the presence of dead chains in the system.

Block purity, i.e. the number of chains that have been permanently terminated is determined by the use of hyphenated chromatographic techniques as will be seen in chapter 5.

4.4 Issues specific to RAFT

The RAFT process has a number of quirks that makes it quite unusual and therefore more complicated for study. These include:

The use of a conventional free radical initiator, which leads to a constant generation of new chains throughout the polymerization as well as termination, shorter chain life times and the concomitant tailing in the distribution. To combat the tailing in distributions, and to minimize termination, a low radical flux is quite common in RAFT literature, which has a number of disadvantages, including low polymerization rates.

The leaving group efficiency. The interaction of chains at the transfer species is dependent on the relative abilities of the radicals to leave, i.e. which C-S bond is weakest in the intermediate radical species. This means that there is a specific preferred monomer sequence for the formation of block polymers. It also means that monomers which form tertiary radicals, such as methacrylates, are invariably preferred for the first block and require very good leaving (R) groups in the starting RAFT agents to obtain an efficient RAFT process.

The fact that interactions between long chain species are required at high conversion (high \bar{M}_n) in normally high viscosity systems, creates a number of potential pitfalls in creating high solids, high conversion polymer systems and maintaining control. Diffusion of radicals⁸ can potentially be inhibited and transfer can then potentially become inefficient. The potential loss of efficiency of a RAFT system at high viscosity is dependent on the relative rates of addition, fragmentation and diffusion in the system.

4.5 Conventional free radical initiators

When we examine the use of traditional free radical initiators, we are bound by a number of inherent limitations. The steady state assumption is one of the most significant limitations that we need to consider. The steady state assumption states that the rate of radical generation and the rate of radical loss are equivalent during the course of a reaction. Conventional free radical initiators follow a first order decay and during the early part of the decay process this decay can be approximately linear. This corresponds to the first term in the Taylor series for equation 2.1.

In figure 4.4, the decay behaviour of AIBN is plotted as a function of time and temperature. It can clearly be seen in the figure that reactions using AIBN as an initiator only have radical generation events for short time spans at higher temperatures. In conventional free radical polymerizations, this does not usually pose a problem, as the rates of polymerization are often high enough that reactions exceeding a few of hours are quite uncommon.

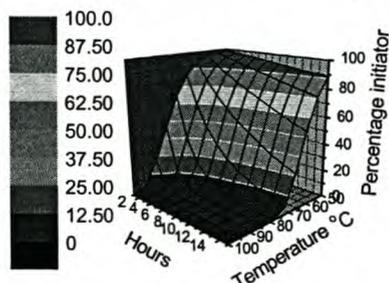


Figure 4.4 Thermal decay behaviour of AIBN.

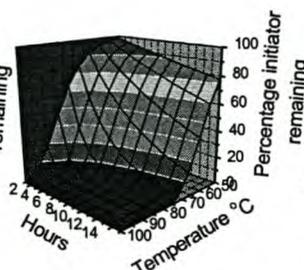


Figure 4.5 Thermal decay behaviour of Azobis(cyanopentanoic acid).

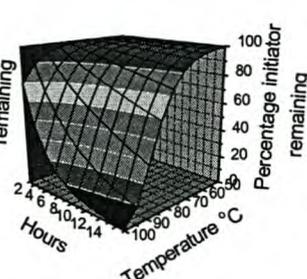


Figure 4.6 Thermal decay behaviour of Azobis(cyclohexylcarbonitrile).

The use of Azobis(cyanopentanoic acid) as an initiator is common where the corresponding R group RAFT agent is used to provide the transfer agent. The half-life of this initiator is however such that high temperature work should be avoided if a steady state radical flux is sought for a part of the reaction (see figure 4.5). In the RAFT process there are significant complications due to the rate retardation that has been observed by numerous authors.^{9,10} The rate retardation will often cause the polymerization to be retarded beyond the point at which there is significant radical generation in the reaction. This has meant that the specific initiators that are used to supply radicals to RAFT-mediated systems are often different to those that would be used for comparable conventional systems. This is significant in that the radical flux must be considered more carefully in a RAFT-mediated system than in a conventional polymerization.

Azobis(cyclohexylcarbonitrile) (see figure 4.6) is a typical example of an initiator that is more suitable for a RAFT polymerization when a constant radical flux is desired. Other options include an initiator feed into the system. This can however complicate data analysis substantially. To help reduce the relative amount of termination events, the initiator concentration is usually kept substantially lower than in conventional systems; some authors recommend using a lower concentration to help minimize the effect of generation of short chains throughout the reaction and in

that way help reduce the polydispersity of the produced polymer.¹¹ Another complicating factor is that short chains are more likely to terminate,¹² even if the termination is between short chains and long chains.¹³⁻¹⁵ One of the problems that are often faced in RAFT systems is that of terminal conversion, i.e. reactions do not reach conversions greater than 90%, which although largely undocumented in the published RAFT literature, can often be a factor in RAFT-mediated polymerizations. It should however be kept in mind that rates of conversion will be significantly reduced in systems in which there are no longer initiator-derived radical generation events.

4.5.1 Initiator efficiency

The second problem that is encountered when using a conventional free radical generator is the efficiency of the radical generation process. The typical loss process that is observed in radical generation is described as the cage effect.¹⁶⁻¹⁸ This description has created some controversy.^{19,20} The cage effect implies that radicals terminate each other before they are able to escape the solvent cage in which the original initiator decomposed. The principle of this description is that the volume of the sphere in which the two radicals find themselves is so small that termination is very likely. When initiators are used that decompose with release of molecules as seen in chapter two, e.g. azo initiators, the distance between the radicals is often as large as a solvent molecule, which in principle implies that the radicals have “escaped” the solvent cage. To avoid the controversy about the efficiency of the cage effect, the term geminate recombination will be used in this dissertation. The efficiency by which the radicals escape the solvent cage is usually termed initiator efficiency and is a function of conversion. In high conversion polymerization reactions, the initiator efficiency will tend to zero as the viscosity of the system will limit diffusion, and the lifetime of the cage will become very large. AIBN initiator efficiency is commonly taken as around 0.7 in RAFT systems.²¹ This is however a system dependent variable, and for complete accuracy should be determined as a function of conversion.

In a RAFT system, the initiator efficiency is very significant as the predicted number average molecular weight of the polymer produced is affected by the number of chains that avoid geminate recombination. To illustrate the effect on the predicted values, two distinct cases are considered. These are the two extreme termination mechanisms in the system. The dominant mode of termination for a specific monomer, i.e. disproportionation versus combination, plays a very significant role

when predictions of number average molar mass are carried out. This is because the number of dead chains produced by the two mechanisms differs. In figure 4.7, complete disproportionation is considered, and in figure 4.8, complete combination is considered. The fact that double the number of chains is produced in the case of disproportionation implies that the number of shorter chains will be greater and the effect of initiator efficiency will be more pronounced.

The number average molecular weight of polymer prepared via a RAFT process may be predicted using the following equation:

$$\bar{M}_n = M_{\text{RAFT}} + \frac{x[M]_0 M_M}{[\text{RAFT}]_0 + Cf[I]_0(1 - e^{-k_d t})} \quad (4.5)$$

Where \bar{M}_n is the predicted number average molar mass; M_M is the monomer molar mass; M_{RAFT} the molar mass of the RAFT agent; $[M]_0$, $[\text{RAFT}]_0$, $[I]_0$ are the initial concentrations of the monomer, RAFT agent and initiator respectively; k_d is the initiator dissociation constant; f is the initiator efficiency; and x is the fractional conversion at time t .

$$C = \frac{k_{tc} + 2k_{td}}{k_t} \quad (4.6)$$

C , a constant that describes the average number of chains per termination event, has a value of that varies between 1 and 2, and is dependent on whether termination is predominantly via combination or disproportionation. The termination rate constants k_{tc} , k_{td} and k_t are for combination, disproportionation and total, respectively.

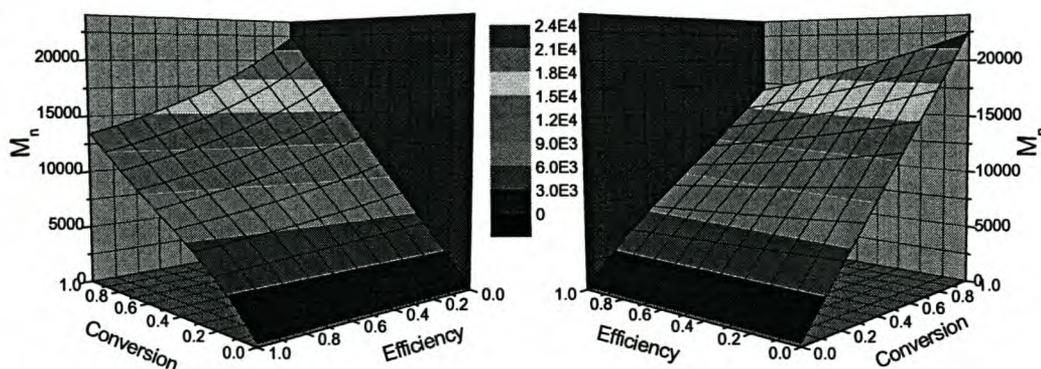


Figure 4.7 Predicted \bar{M}_n vs. varying initiator efficiency in the case of disproportionation; conditions chosen such that initiator decomposition is complete at 90% conversion.

Figure 4.8 Predicted \bar{M}_n vs. varying initiator efficiency in the case of combination; conditions chosen such that initiator decomposition is complete by 90% conversion.

In figures 4.7 and 4.8, experimental conditions are chosen such that the RAFT to initiator ratio is 3:1 and the efficiency factor (f) is varied from 0 to 1 to determine the theoretically predicted effect of AIBN efficiency on the predicted number average molecular weight of a polystyrene polymer. The variation in initiator efficiency has a very significant effect on the system as can be seen by the variation of molar mass between ~12000 and ~20000 Da. The specific number that is used for initiator efficiency plays a significant role in the prediction of number average molar mass. From figure 4.8 it can be seen that the variation of f between 1 and 0 for a system in which termination is predominantly via combination, results in a smaller effect on the molecular weight of the formed polymer than in the case of disproportionation, although the specific value of f is still the predominant factor. In a heterogeneous system this becomes even more complex, as there is a second efficiency factor that needs to be accounted for, that is, the efficiency by which radicals enter particles, in the case of an aqueous phase initiated heterogeneous polymerization. In many systems with low initiator concentrations and low efficiencies, it is possible to discount this effect and still maintain an accurate prediction of molecular weight in the system. RAFT systems typically require very low initiator concentrations if block copolymers are required with high block purity.¹¹ This is due to the fact that the initiator-derived chains also lead to substantial termination in the system, and homopolymer of the second monomer will be formed.

4.5.2 Thermal initiation

It is important to note that in some polymerizations, background or thermal generation of radicals by the monomer itself is a significant factor that needs to be considered. This is a highly temperature and monomer dependent process. In the case of styrene, the polymerization occurs via a third order mechanism, which is referred to as the Mayo Diels-Alder radical mechanism for styrene.^{22,23} In the case of styrene polymerization using TEMPO, it is reported that the thermal generation of radicals is not only significant but is indeed critical for the polymerization to proceed.²⁴ There is however some evidence of the polymerization being initiated by TEMPO under certain conditions.²⁵

4.6 Leaving group efficiency

For the RAFT process to be efficient all of the propagating radicals in the system should have comparative leaving group ability.²⁶ Initiating leaving groups should have better leaving group abilities than those of the propagating radicals. This normally implies that leaving groups should have good radical stabilizing abilities, and are either tertiary or secondary radical species with radical supporting substituents, such as aromatic groups or pseudo halogens (such as nitriles). A point that should be noted here is that methacrylonitrile is not a suitable starting material for RAFT agent synthesis due to the anti-Markovnikov product that is formed by the addition of dithiobenzoic acid to the olefinic moiety.²⁷

4.7 Diffusion-controlled transfer

Diffusion of chains is a potential problem in high viscosity media. The RAFT process relies on the interaction of long chain species, and for this reason there are some theoretical issues that still require substantial research to allow a clearer image of how serious a problem this can be. This is substantiated by reports that control of polydispersity is improved in dilute media when higher molecular weight polymers are targeted. This is however similar in techniques such as ATRP which do not have similar theoretical diffusion issues. If chains are unable to interact but monomer is still capable of diffusing, then the movement of the radical chain end is predominantly via chain growth, and the probability of exchange with the macroRAFT species in the system is substantially lower.

4.8 NMR as an analysis technique for RAFT

Nuclear magnetic resonance spectroscopy is a powerful tool for *in situ* investigations of the kinetics of free radical polymerization reactions. NMR allows us to determine concentrations as well as the natures of all species in a reaction at a specific time. The limitations of kinetic experiments are usually associated with the complexity of the system being investigated.²⁸⁻³⁰

In situ NMR investigation of free radical polymerization is normally extremely problematical due to the nature of a conventional free radical polymerization reaction. In a conventional free radical polymerization, high molecular weight polymer forms

very rapidly, resulting in peak broadening in the spectrum. This leads to substantial difficulty in identifying specific species in the spectrum. Polymer NMR spectroscopy has however been used for a number of different purposes, including tacticity assignments as well as copolymerization ratio determinations.³⁰⁻³⁵ Endgroup identification is complicated by the large number of similar endgroups with slight variations that lead to peak overlap, and is also limited by the low relative concentration of endgroups in the systems, which cause detection limit problems.³³

In living radical polymerization, the possible applications of NMR are significantly different. Living radical polymerization is characterized by a linear increase in molecular weight with monomer conversion, and consequently does not usually involve high molecular weight polymer formation early in the reaction. The development of the chains occurs in a uniform manner and leads to a more limited array of species, which decreases the number of peaks in the system, and simplifies analysis substantially.

This section of chapter four addresses ¹H NMR investigations of the early reaction period of RAFT-mediated polymerizations, with specific relation to the period in which RAFT-mediated emulsions become unstable. The investigation starts before complete conversion of the initial RAFT agent to include growing polymer chains and includes the first monomer addition step(s). *In situ* ¹H NMR spectroscopy is used to directly investigate the concentration of several characteristic species, and the rate of polymerization, to determine possible effects that could translate to emulsion instability in a heterogeneous system.

4.8.1 Experimental

4.8.1.1 Chemicals

Styrene monomer (Plascon research centre, University of Stellenbosch, estimated purity ~99% ¹H NMR) was washed with 0.3 M KOH, followed by vacuum distillation under reduced pressure, to remove inhibitor and polymer. Methyl acrylate (Sigma) was passed through an inhibitor removal column prior to use. Azo bis(isobutyronitrile) (AIBN, Riedel-De Haën) was recrystallized from AR grade methanol and found to be ~99% pure by ¹H NMR. Deuterated solvents C₆D₆ (99.6%, 0.1% TMS) and pyrazine (99%) (both Sigma-Aldrich) were used as received. RAFT agents were synthesized as discussed in chapter three.

4.8.1.2 Sample preparation

Samples were prepared by weighing out the reagent masses as given in Tables 4.2 and 4.4. The samples were subsequently transferred to NMR tubes. The tubes were flushed with ultra-high purity nitrogen for 10 minutes. At this point, a sealed glass insert containing the integration reference standard (pyrazine for styrene and formic acid for methyl acrylate) was inserted and the tubes were sealed. The use of the reference standard was solely for integration purposes.

4.8.1.3 Analysis

NMR spectra were recorded on a 600 MHz Varian *Unity*Inova spectrometer. A 5 mm inverse detection PFG probe was used for the experiments and the probe temperature was calibrated using an ethylene glycol sample in the manner suggested by the manufacturer using the method of Van Geet.³⁶ ^1H spectra were acquired with a 3 μs (40°) pulse width and a 4 sec acquisition time. For the ^1H kinetic experiments, samples were inserted into the magnet at 25 $^\circ\text{C}$ and the magnet fully shimmed on the sample. A spectrum was collected at 25 $^\circ\text{C}$ to serve as a reference. The sample was then removed from the magnet and the cavity of the magnet was raised to the required temperature (70 $^\circ\text{C}$ or 84 $^\circ\text{C}$). Once the magnet cavity had stabilized at the required temperature, the sample was re-inserted (time zero) and allowed to equilibrate for approximately 5 minutes. Additional shimming was then carried out to fully optimize the system and the first spectra were recorded approximately 5-10 min after the sample was inserted into the magnet. Integration of spectra was carried out both manually and automatically to allow identification of species during formation. Automated integration was carried out using ACD labs 7.0 ^1H processor®.

4.8.2 Results and Discussion

The NMR data that were obtained during the investigation provides instantaneous concentrations of detectable non-radical species in the RAFT reactions. The effect of chemically induced nuclear polarization on the apparent concentrations of the observed NMR signals in the experiments was found to be minimal under the conditions used. The concentrations and molar ratios of the reaction components used in all of the reactions in this study are summarized in Table 4.2.

Table 4.2: Composition of reaction mixtures for *in situ* NMR analysis. The solvent used was deuterated benzene (99.6%), and the initiator used was azo bis(isobutyronitrile), (AIBN).^a Cyanoisopropyl dithiobenzoate. ^b Cumyl dithiobenzoate. ^c *p*-Methoxy cyanoisopropyl dithiobenzoate. ^d Cumyl phenyl dithioacetate. # Reaction carried out at 84 °C. * Reaction carried out at 70 °C.

Sample	Solvent		Initiator		Styrene		RAFT Agent		[M]/ [R _o]	[R _o]/ 2[I _o]
	Mass (g)	Mol (×10 ³)	Mass (g)	Mol (×10 ⁵)	Mass (g)	Mol (×10 ³)	Mass (g)	Mol (×10 ⁴)		
1*	0.30	3.56	0.010	6.7	0.25	2.4	0.107 ^a	4.84	4.95	3.96
2 [#]	0.30	3.56	0.010	6.1	0.24	2.31	0.100 ^a	4.52	5.11	3.70
3*	0.25	2.99	0.010	6.3	0.26	2.46	0.100 ^b	3.68	6.68	2.92
4 [#]	0.25	2.99	0.010	6.3	0.26	2.46	0.100 ^b	3.68	6.68	2.92
5*	0.30	3.56	0.010	6.3	0.24	2.31	0.100 ^c	3.23	7.15	2.56
6 [#]	0.30	3.56	0.010	6.3	0.25	2.4	0.107 ^c	3.46	6.93	2.74
7*	0.35	4.16	0.010	6.3	0.24	2.31	0.105 ^d	3.67	6.29	2.91
8 [#]	0.32	3.80	0.010	6.3	0.26	2.46	0.100 ^d	3.49	7.04	2.76
9*	0.365	4.34	0.011	6.7	0.38	3.68	0	0	0	0
10 [#]	0.30	3.56	0.010	6.1	0.38	3.68	0	0	0	0
11 [#]	0.50	5.99	0.010	6.3	0.50	4.8	0.050 ^b	1.84	26.0	1.46
12 [#]	0.55	6.59	0.010	6.3	0.51	4.88	0.101 ^b	3.68	13.2	2.92
13 [#]	0.50	5.99	0.010	6.3	0.51	4.88	0.208 ^b	7.4	6.59	5.87
14*	0.50	5.99	0.020	12.6	0.52	4.92	0.200 ^b	7.36	6.68	2.92
15*	0.50	5.99	0.042	25.4	0.50	4.8	0.200 ^b	7.36	6.52	1.45

Figure 4.9 shows the chemical structures of the primary species of interest for this study. For convenience, the following naming convention will be used. Species CD is the initial RAFT agent containing the dithiobenzoate species (D) and the initial cumyl leaving group (C), CSD is the dithiobenzoate species formed by single styrene (S) adduct of a cumyl radical (C[•]) while CS₂D and CS₃D species are formed by the respective second and third styrene adducts of the cumyl radicals. The same naming convention applies for derivatives of the RAFT agent cyanoisopropyl dithiobenzoate (AD), with consecutive monomer adducts ASD, AS₂D, *etc.*, with the cyanoisopropyl group replacing the cumyl group. To differentiate between the phenyl dithioacetate Z group we have used the terminology (CDta) and the para-methoxy dithiobenzoate (ADme). When methyl acrylate is used as monomer the notation AM_nD is used.

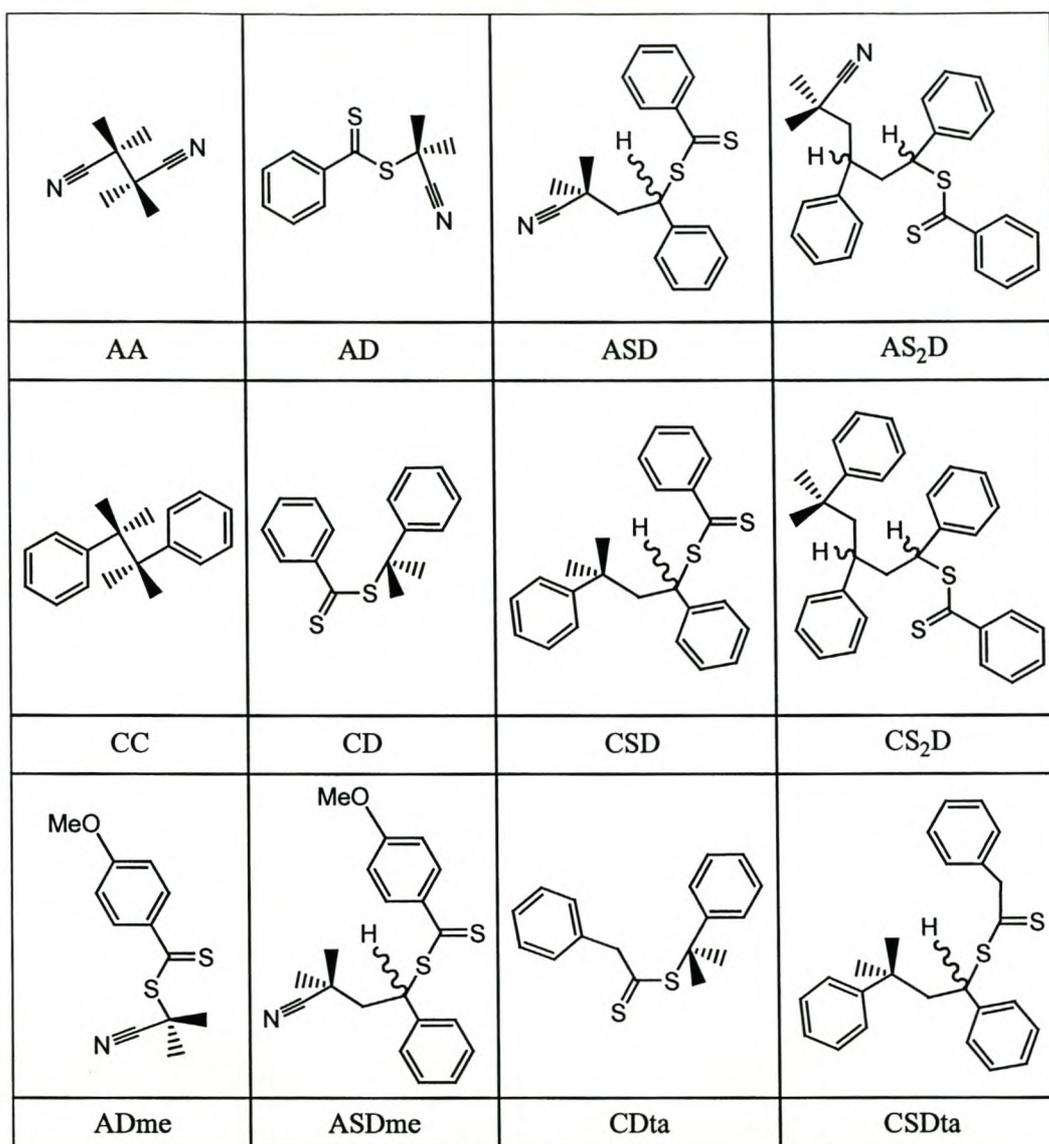


Figure 4.9 The predominant species of interest for the investigation of the early period of the free radical polymerization of styrene in the presence of cumyl or cyano isopropyl radicals using a number of different RAFT agents and AIBN as an initiator.

A representative selection of peaks that were integrated for this study are shown in Table 4.3.

Table 4.3: ^1H NMR chemical shifts of a representation of integrated species relevant to the investigation of initialization in the cyanoisopropyl dithiobenzoate-mediated polymerization of styrene.

Methyl peaks of R groups δ (ppm)	Ortho protons of corresponding dithiobenzoate ring δ (ppm)	Species
Singlet 0.93	N/A	AA
Singlet 1.18	N/A	CC
Two peaks 1.10, 1.08	N/A	AC
Singlet 1.45	Doublet 7.71	AD
Singlet 1.81	Doublet 7.81	CD
Two peaks 1.01, 0.87	Doublet 7.85	ASD
Two peaks 1.25, 1.20	Doublet 7.78	CSD
Two peaks 0.81, 0.65	Doublet 7.90	AS ₂ D
Two peaks 0.95, 1.02	Doublet 7.81	CS ₂ D
Two peaks 0.89, 0.72	Doublet 7.79	AS ₃ D
Two peaks 1.02, 1.14	Doublet (not identified)	CS ₃ D
Singlet 1.49	Doublet 7.84	ADme
Singlet 1.67	Doublet 7.27	CDta
Two peaks 1.02, 0.88	Doublet 7.99	ASDme
Two peaks 1.14, 1.19	Aromatic region	CSDta

A sample spectrum showing the most important peaks after initialization (see below) was completed, in reaction 1 (Table 4.2), is shown in figure 4.10:

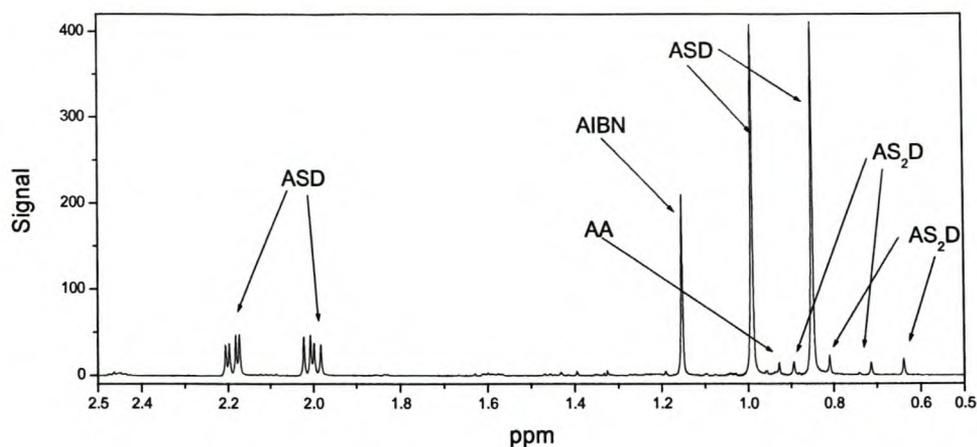


Figure 4.10 A typical ^1H NMR spectrum between 2.5 and 0.5 ppm, directly after initialization, showing the peaks corresponding to several of the important species studied here. AS_nD are the peaks for the n -meric styrene adducts of the cyanisopropyl dithiobenzoate, AA the product of the termination reaction between two cyanoisopropyl radicals, and AIBN is the initiator.

Where two peaks are indicated, diastereotopic groups were present. Where more than two peaks are indicated there were enantiomers in the system. Figure 4.11 shows a spectrum of reaction 3.

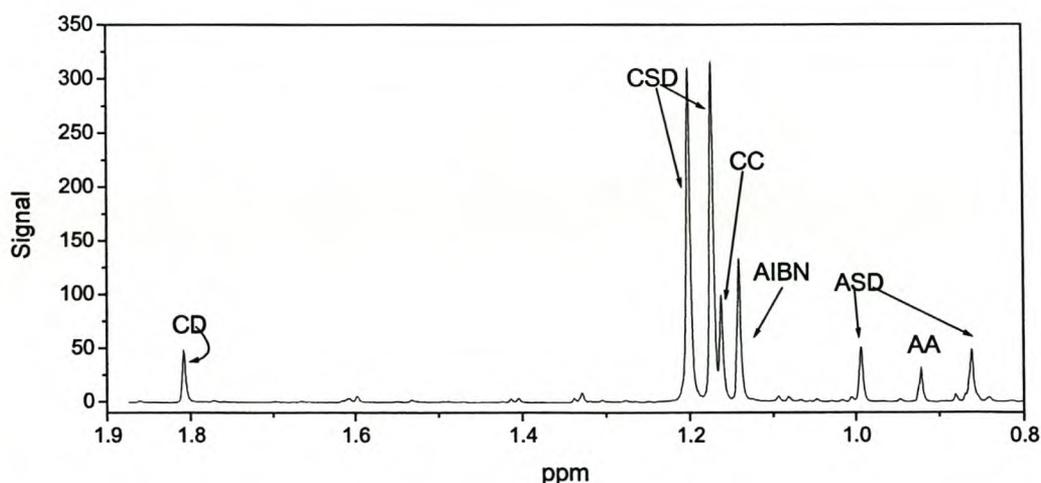


Figure 4.11 A typical spectrum of the reaction of cumyl dithiobenzoate, styrene and AIBN: reaction 3, Table 4.2.

In order to minimize the complexity of the system, we will begin our discussion with the use of cyanoisopropyl dithiobenzoate as the RAFT agent. The use of this agent, styrene monomer and AIBN as initiator, results in a single active tertiary radical species in the system. It should be noted that the choice of styrene as a monomer means that the vast majority of radicals formed from propagation reactions should be secondary radicals.

Temperature plays an important role in the rate of reactions in a RAFT-mediated polymerization. For that reason different temperatures were used to determine if the results could be explained by the same arguments.

The first reaction was carried out for a period of 4 hours at 70 °C, with a reaction mixture containing styrene monomer, cyanoisopropyl dithiobenzoate (species AD) and AIBN initiator (reaction number 1, Table 4.2). Figure 4.12 shows the time dependence of the concentrations of dithiobenzoate species during this reaction. A rapid decrease in concentration of the species AD and a buildup of the species ASD, until the cyanoisopropyl dithiobenzoate had been completely consumed (after 50 min), was observed.

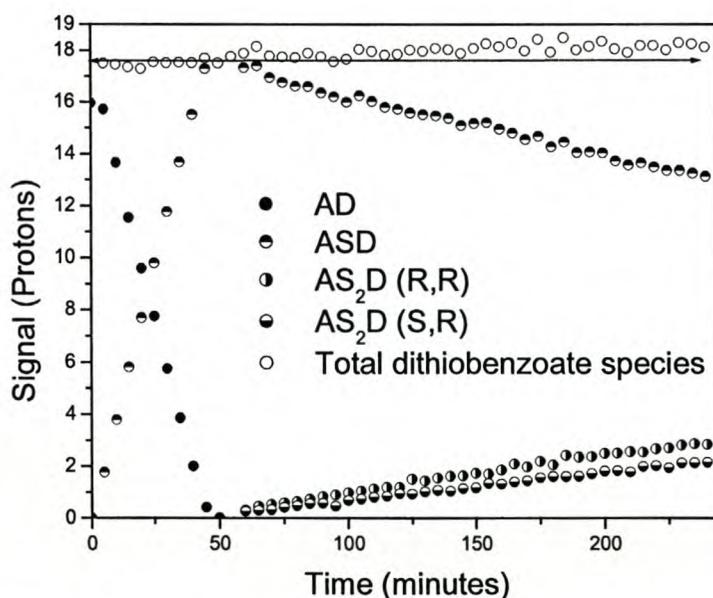


Figure 4.12 Relative concentrations of methyl protons of dithiobenzoate species versus time in the *in situ* free radical polymerization of styrene at 70 °C. Cyanoisopropyl dithiobenzoate was used in the presence of AIBN as an initiator. Table 4.2 Sample 1: 3.56×10^{-3} mol C_6D_6 , 6.75×10^{-5} mol AIBN, 2.40×10^{-3} mol styrene, 4.84×10^{-4} mol cyanoisopropyl dithiobenzoate.

At 50 minutes, the concentration of species ASD had reached a maximum. The nearly linear decrease of [AD] with reaction time is indicative of a pseudo-zero order reaction in [AD]. Once all of the cyanoisopropyl dithiobenzoate has been converted to ASD (and a very small amount of higher species), the second monomer addition to the radical species began to increase in frequency (to form species AS_2D). To determine whether the reaction is truly pseudo-zero order in [AD] it is important to examine the effect of a change in Z group on the reaction. For this purpose the reaction was

repeated using cyanoisopropyl *p*-methoxy dithiobenzoate, which is reported as having significantly less rate retardation when used as a RAFT agent. A sample spectrum of sample 5, table 4.2, is shown in figure 4.13.

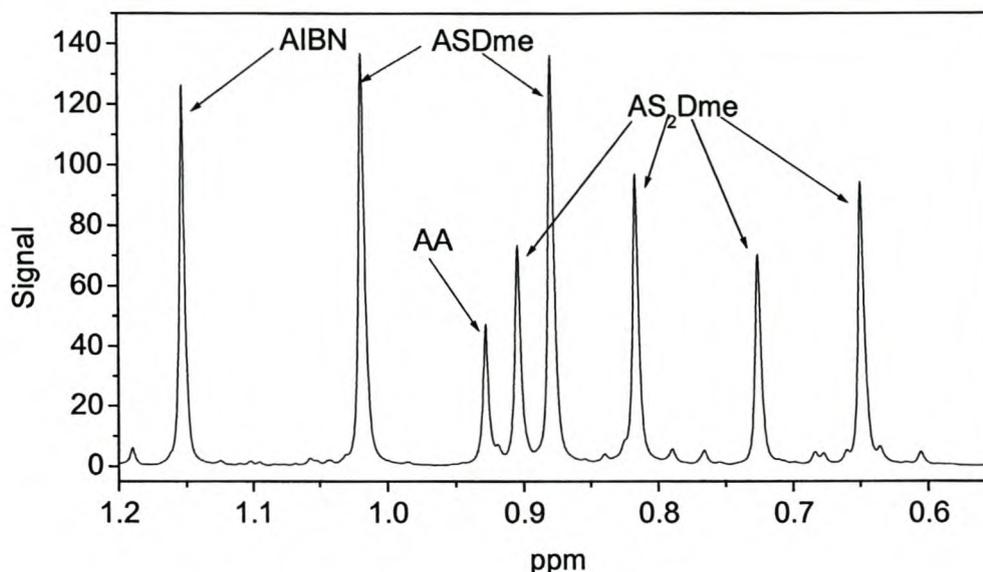


Figure 4.13 A typical ^1H NMR spectrum between 1.2 and 0.55 ppm, showing the peaks corresponding to several of the important species studied here. AS_nDme are the peaks for the *n*-meric styrene adducts of the cyanoisopropyl *p*-methoxy dithiobenzoate, AA the product of the termination reaction between two cyanoisopropyl radicals, and AIBN is the initiator.

The NMR spectrum is very similar to that obtained from the reaction of cyanoisopropyl dithiobenzoate as would be expected from the minimal structural changes in the products formed. If the Z group played a significant role during initialization, the consumption of the initial RAFT agent (AD or ADme) would be expected to occur at different rates. Figure 4.14 shows the consumption behaviour of the respective RAFT agents.

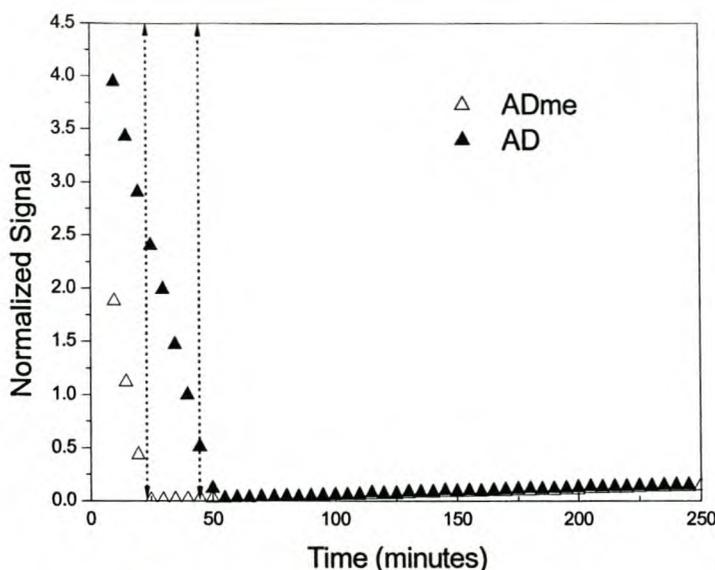


Figure 4.14 The *in situ* polymerization reactions of styrene in the presence of cyanoisopropyl dithiobenzoate and cyanoisopropyl *p*-methoxy dithiobenzoate using AIBN as an initiator at 70 °C. The plots are normalized for initiator concentration (samples 1, 3 Table 4.2). The dotted lines are visual indications of where the initial RAFT agent is consumed.

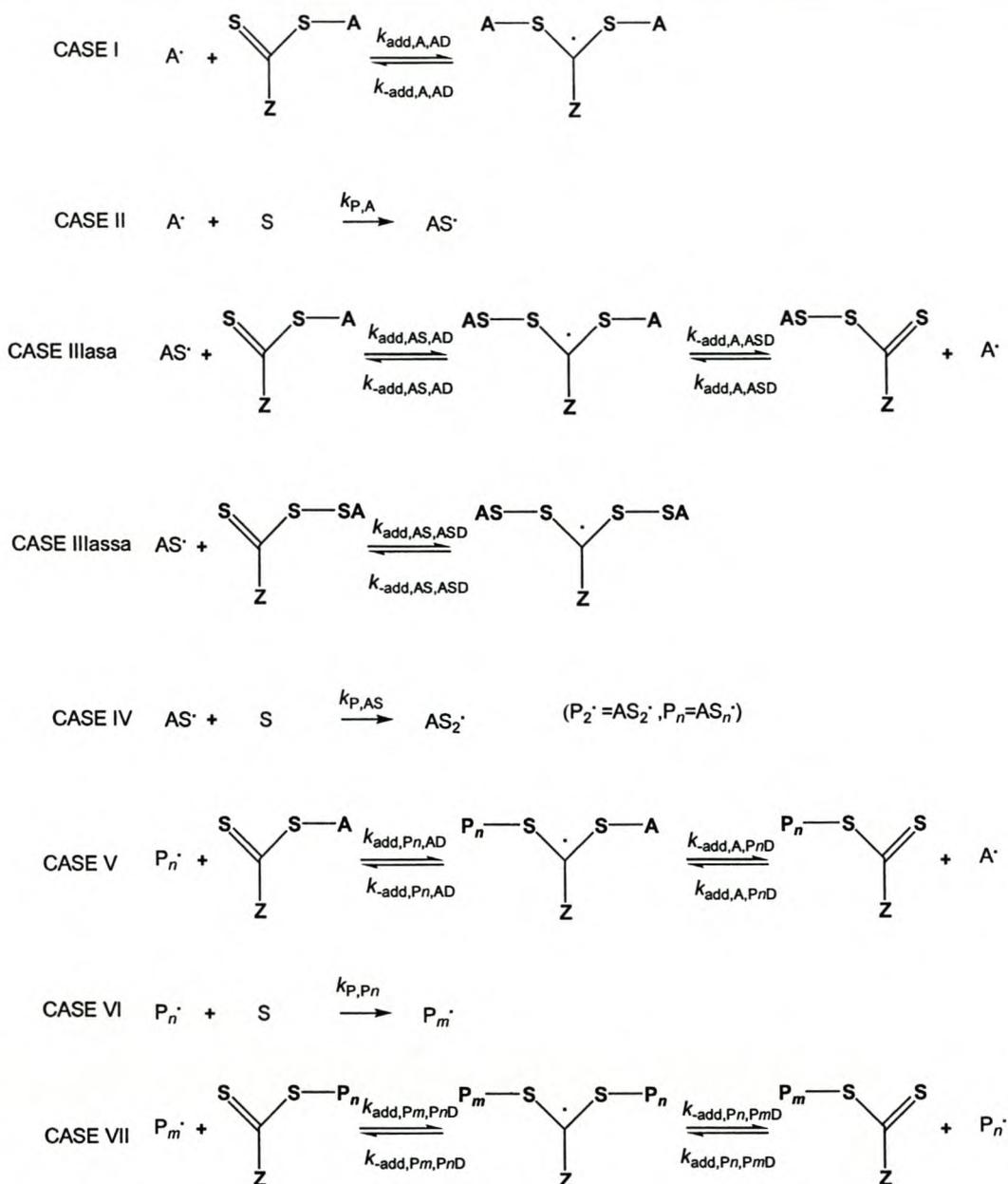
The linear decrease in concentration with time suggests that the rate of consumption of both agents is pseudo-zero order in RAFT agent concentration and that the behaviour is independent of the Z group in the reaction, which substantiates the fact that the propagation of the initiator fragment is rate determining. There are several important points to look at if we consider these reactions. The first is that the conversion of the species AD to ASD or ADme to ASDme is complete, with no detectable “loss” of dithiobenzoate groups to side reactions or the formation of high (detectable) concentrations of intermediate radical species. The termination products for such reactions could not be detected during the course of the reaction (or were below the detection limits of the instrument used), implying that the concentrations of such species were below 10^{-3} M during this reaction. The same was observed for all reactions in this study. The second point to note is that the early reaction is extremely selective. Only one type of radical addition reaction appeared to occur, to any significant extent, during this initial period (before 50 min), i.e., the propagation of cyanoisopropyl radicals. Very little propagation of longer chain radicals occurred until after this initial period. This also implies that the concentration of these other propagating radicals and the corresponding thiocarbonylthio-functional dormant chains was very low during this period.

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

1. *Initialization* is the process by which the starting RAFT agent is consumed.
2. *Initialization period* is the period in which the starting RAFT agent is consumed.
3. *Initialization time* is the time required for the starting RAFT agent to be completely consumed (converted to other forms).

4.8.2.1 Reactions of Radical Species During Initialization

In scheme 4.1, the relevant reactions during the polymerization are represented in a way that allows a qualitative discussion on the rate-determining step; termination events are not displayed.



Scheme 4.1 The steps involved in the initialization period of the RAFT reaction of cyanoisopropyl dithiobenzoate or cyanoisopropyl *p*-methoxy dithiobenzoate, styrene monomer and AIBN initiator.

The relative probabilities of competing reactions occurring are proportional to their overall rates, which are proportional to the concentrations of reactants and the rate coefficients for the competing processes. The reagent concentrations for this system are a function of a combination of the addition, fragmentation and propagation rates of the species shown in scheme 4.1. It is important to note that there are several different types of intermediate radical species in the initialization period, each of which has different stabilities, and (asymmetric) fragmentation rate coefficients. The apparently large differences in addition and fragmentation rate coefficients for the

different species involved in the initialization period are critical to understanding the behavior of the reaction during the initialization period. The most important of these differences is the much faster (preferred) fragmentation rate of intermediates containing a potential tertiary leaving group and a potential secondary leaving group, to form a RAFT agent and a tertiary radical. This will be discussed in more detail later. The competing processes and fates of each of the important species in this initial period are now described in detail. For the purposes of the discussion that follows, Z refers to the Z groups that have been discussed in the preceding reactions.

Cyanoisopropyl radicals (A^\bullet) generated in the system will undergo one of three main reactions. (1) Radical addition to a RAFT agent (relative frequency = $k_{\text{add}}[\text{RAFT}]$, e.g. $k_{\text{add,AZ}}[\text{AZ}]$) to form an intermediate radical (these reactions are depicted in cases I, III_{asa} and V; note that case I gives a degenerate product after fragmentation of the formed intermediate radical). (2) Radical addition to monomer (propagation, with relative frequency = $k_{\text{p,A}}[\text{M}]$, case II), to give radical species AS^\bullet . (3) Termination can occur with other radical species in the system.

The radical species AS^\bullet can participate in reactions that are similar to the reactions undergone by the A^\bullet radicals. These reactions are: (1.) addition (with different addition rate coefficients) to the RAFT agents (cases III_{asa}, III_{assa}, or VII), (2.) propagation, with the relevant propagation rate coefficient, to form radical species AS_2^\bullet (case IV), (3.) termination. The products of these processes are described below.

For the RAFT process to be efficient, propagating radicals must display higher addition rates to the RAFT agent than to monomer.³⁷ This prevents a possible scenario of rapid propagation to form long chains before the addition-fragmentation process can allow exchange (via the intermediate radical species) between growing chains. Depending on the monomer concentration, a portion of initiator-derived radicals adds directly to the RAFT agent. These reactions cannot be distinguished in the reaction under discussion since when A^\bullet adds to AZ, eventually resulting in fragmentation to form A^\bullet , the overall result is degenerate. There is therefore no effect on the NMR spectrum. An example of this behaviour will be shown later. A fraction of A^\bullet species will however eventually add to a styrene monomer, leading to the formation of AS^\bullet in the reaction mixture.

The fragmentation behavior of each of the formed intermediate radical species is the crux in understanding the behavior of the early reaction (assuming that the addition

rate constants remain relatively large). If the possibility of termination reactions of the intermediate radicals is neglected (probably a good approximation here, since their concentrations during initialization are very small),³⁸ then each of these intermediate radicals will soon undergo fragmentation, to again produce a propagating radical and RAFT agent. The fragmentation reaction is generally very asymmetric, with a very strong preference to form the more stable propagating radical.

Secondary radical species are more reactive than tertiary radical species with the same substituents (as the reactivity of radical species is inversely related to their stability) when comparing reactions with the same reagents. When radical species with varied substituents are compared however, care must be taken when making generalizations. Cyanoisopropyl and cumyl radicals have higher addition rate constants to styrene than the long chain propagation rate constant for styryl radicals.^{39,40} These radicals are tertiary and are superior leaving groups, and are thus more likely to fragment when attached to a RAFT agent, than their respective styryl adducts. For example in the case of ASDA*, the fragmentation rate, $k_{\text{-add,ASZ,A}}$ of the tertiary cyanoisopropyl radicals will be much larger than the fragmentation rate, $k_{\text{-add,AZ,AS}}$ of the secondary AS* radical species (case IIIasa in scheme 4.1) due to their higher radical stabilities.⁴¹ The difference in leaving ability between the two attached groups generates a large asymmetry in fragmentation rate coefficients for the same intermediate radical (e.g. ASZA*), with the much greater rate coefficient being for the formation of the more stable leaving radical. The greater rate coefficient implies that the lifetime of intermediate radicals containing at least one tertiary radical will be shorter than for equivalent secondary species, with the large asymmetry in fragmentation rate coefficients leading to a preference for the tertiary radical to result from the fragmentation step. The generated AS* radical species will therefore quickly become end-capped as a thiocarbonyl thio species (ASZ), because addition is very fast, and will displace tertiary radicals (A* in this case) that are attached to the RAFT agent (case IIIasa). The expelled tertiary radicals can then undergo addition (case I, IIIasa, V) or propagation (case II).

The tertiary radicals (A*) will be unlikely to displace the secondary radical species (e.g. AS*) that are trapped in the dormant state (e.g. case IIIasa) (since the rate coefficient for fragmentation to form the secondary species is much lower than that to form the tertiary species). In such a case, they (A*) will instead begin to behave in a similar fashion to a reversible end-capping reaction such as ATRP or SFRP when

encountering an AS_nZ species until such time as they encounter a monomer and propagate. The (A^\bullet) radicals will still encounter AZ species to form an intermediate radical, before again fragmenting (providing a degenerate end-product after fragmentation), or undergo termination. This means that it is still possible to have a controlled process occurring in the system, but the mechanism by which chains are being activated to allow propagation is different to that of the normal RAFT process.

Almost every cyanoisopropyl dithiobenzoate or *p*-methoxy dithiobenzoate molecule (AZ) in the system is converted to an ASZ dormant species before significant concentrations of AS_2^\bullet radicals (and therefore any AS_2Z or higher dormant species) have the opportunity to develop in the system. This selectivity results from a combination of the fast rates of addition of propagating radicals to the RAFT agent, and the extreme asymmetry of the fragmentation step. Accordingly, the formation of AS^\bullet radicals (which quickly form the ASZ species) becomes the rate-determining step in the process of the formation of ASZ from AZ . It has been mentioned above that the decrease in RAFT agent concentration initially occurs according to a pseudo-zero order reaction. ASZ cannot form until AS^\bullet radicals are formed, which implies that the rate determining step is the propagation of A^\bullet to form AS^\bullet (with rate = $k_{p,A}[M][A^\bullet]$), since this is much slower than the addition of AS^\bullet to AZ . The result of this propagation step is visible as the formation of ASZ from AZ .

As it is unlikely that a secondary radical will be displaced by the addition of a tertiary radical to ASZ , the probability of the secondary radical species being reactivated by a transfer step (i.e. case IIIassa, an addition and subsequent fragmentation to form a secondary species) is dependent on the active concentration of the aforementioned secondary radical species. Since radicals are first formed as tertiary species, which will not displace the secondary radical species by addition to RAFT agents, in this system, reactivation of those species depends on both propagation of the cyanoisopropyl radicals, and their consequent addition to a RAFT agent that already contains a dormant secondary species. This will only occur when there is a significant concentration of RAFT agents containing dormant secondary species, which is not the case during the early stages of the initialization period. In the early stages of this period, the rate of addition of AS^\bullet to the initial RAFT agent (containing tertiary species) is too high to allow significant concentrations of AS^\bullet to exist. Thus the dominant propagating radical will be A^\bullet , and the concentration of the secondary radical species (and ASZ) will increase until it reaches a maximum after the end of the

initialization period (when no AZ remains). This has a significant effect on the total concentration of intermediate radical species in the system, since only intermediate radicals with at least two secondary species will be relatively stable. Once a significant concentration of RAFT agents containing dormant secondary species (ASZ) is formed at the end of this period, and a significant fraction of secondary radicals are present (AS^{*}), longer chains may form in significant concentrations, and more stable intermediate radicals will form. This should lead to a buildup in intermediate radical concentration, reaching a maximum some time after initialization has been completed. This has indeed been observed in recent ESR spectroscopic studies of this system.³⁸

For the purposes of this discussion, radical reactivity has been divided into tertiary and secondary radical species. When a system with two tertiary species is considered, the polymerization becomes substantially more complex. The use of cumyl dithiobenzoate, styrene monomer and AIBN as initiator, results in a system in which two different tertiary radical species are present.

The first mixed radical experimental system examined is the reaction of styrene, cumyl dithiobenzoate and AIBN at 70 °C (reaction 3, Table 4.2). Figure 4.15 shows the time dependence of the concentrations of dithiobenzoate species within the first 7 hours of the reaction. It is observed that there is a decrease in concentration of species CD, and a corresponding increase in concentration of the species CSD and ASD as a single monomer unit is added. This trend continues until the cumyl dithiobenzoate and any formed cyanoisopropyl dithiobenzoate (AD) have been completely consumed (after about 250 minutes). At this point the concentrations of species CSD and ASD have reached a maximum. Once the cumyl dithiobenzoate has disappeared from the reaction, the second, third and higher monomer additions to the radical species begin to increase in frequency (species CS₂D, AS₂D and CS₃D, AS₃D, etc.). The implication of this behaviour is that the formation of the CSD and ASD (i.e. propagation of A^{*} and C^{*} to form AS^{*} and CS^{*}) species or the consumption of the starting RAFT agent is the rate-determining step in the initialization process.

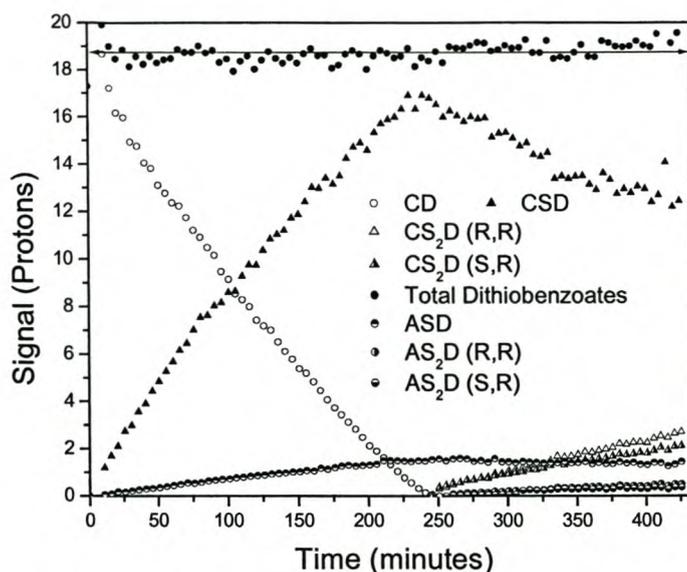


Figure 4.15 Relative concentrations of the methyl protons of dithiobenzoate species versus time in the *in situ* free radical polymerization of styrene in the presence of cumyl dithiobenzoate and using AIBN as an initiator at 70 °C (reaction 3, Table 4.1).

For comparison purposes it was decided to conduct experiments using a cumyl functional R group and an alternative Z group. The RAFT agent used here was cumyl phenyl dithioacetate (CDta or PPPDTA). A sample NMR spectrum for reaction 7 is shown in figure 4.16.

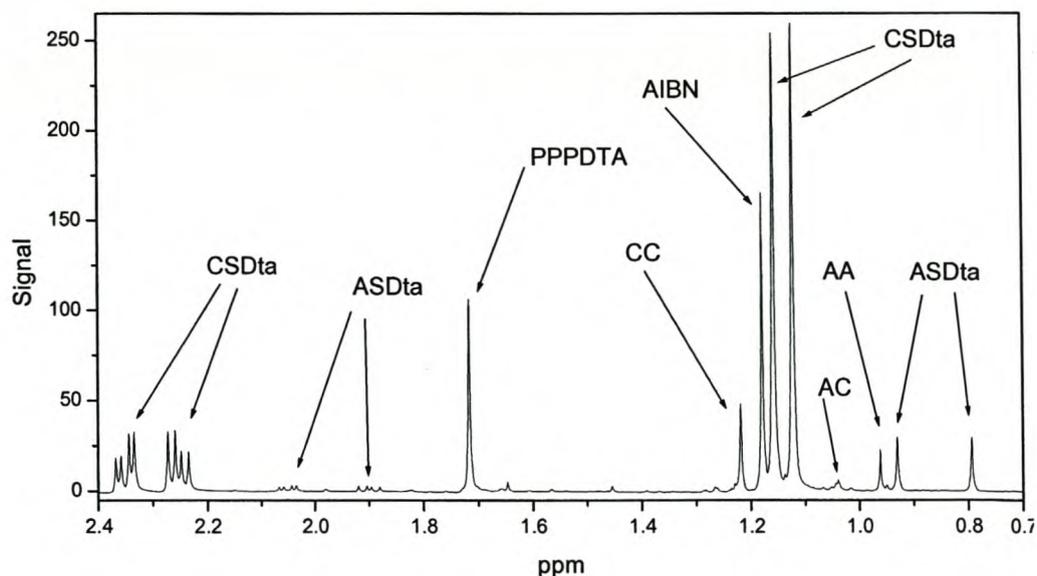


Figure 4.16 An example of the reaction spectrum of cumyl phenyl dithioacetate prior to initialization.

A significant difference in the NMR spectra, when compared to the spectrum in figure 4.11, was that the CC cumyl product was now directly observable in the spectrum at reaction temperature and it was not necessary to subtract peaks. Figure 4.17 shows a comparison of the consumption of the initial RAFT agents in reactions 5 and 7.

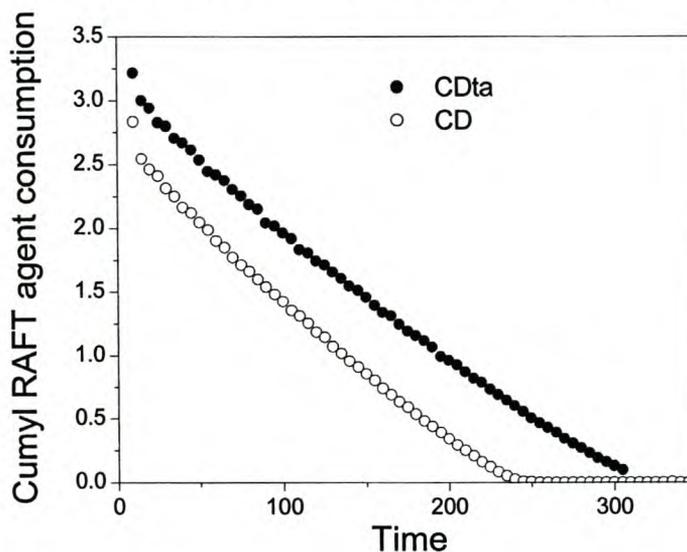
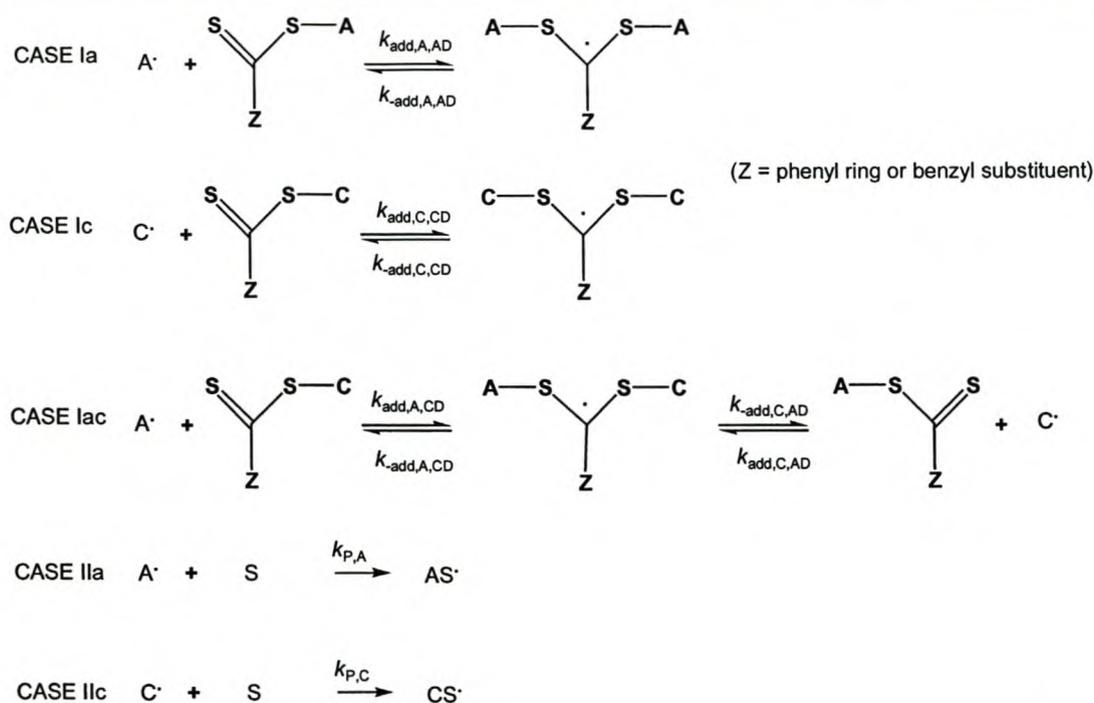


Figure 4.17 The *in situ* polymerization reactions of styrene in the presence of cumyl dithiobenzoate (CD) and cumyl phenyl dithioacetate (CDta), using AIBN as an initiator at 70 °C. The plots are normalized for initiator concentration (reactions 5 and 7, Table 4.2).

Although the reaction data is more complex than in the case of the cyanoisopropyl derivatives, it can be seen that the rate of consumption of the RAFT agent appears to be Z group independent. In this case it should be noted that the use of phenyl dithioacetate Z groups is reported to provide significant increases in polymerization rates.⁴² However, this was not the case during the initialization period. For the purposes of the discussion that follows, Z will be used as a generic description of dithiobenzoate or phenyl dithioacetate.

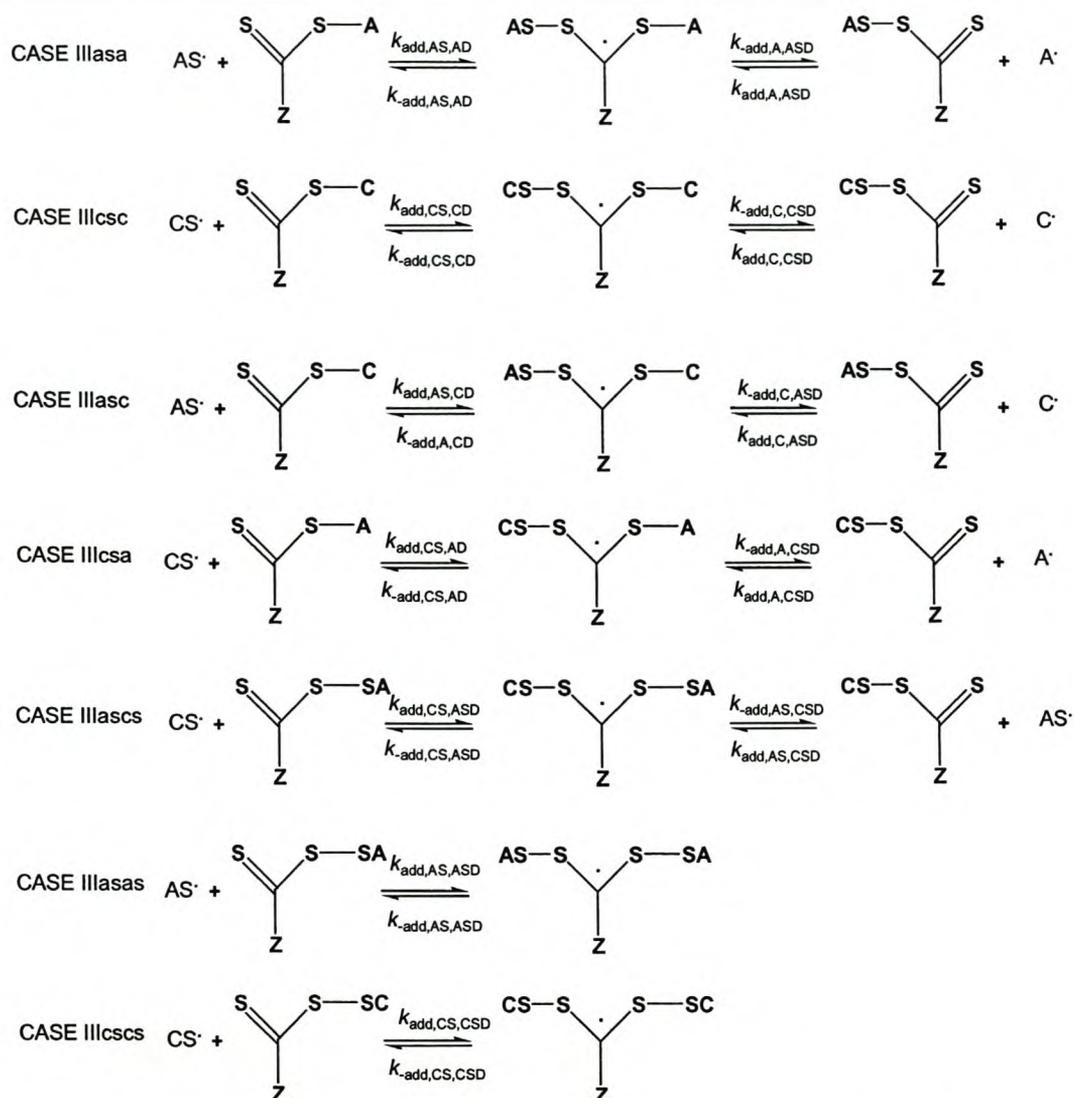
Scheme 4.2 shows the types of reactions that are under consideration at the beginning of the reaction (i.e. prior to monomer consumption). Reaction cases labeled with subscripts **c** and **a** denotes the reactions that are specific to cumyl or cyanoisopropyl radical species, respectively; **as** and **cs** continues in the same fashion.



Scheme 4.2 The steps involved in the beginning of the initialization period of the RAFT reaction of cumyl dithiobenzoate/phenyl dithioacetate, styrene monomer and AIBN initiator.

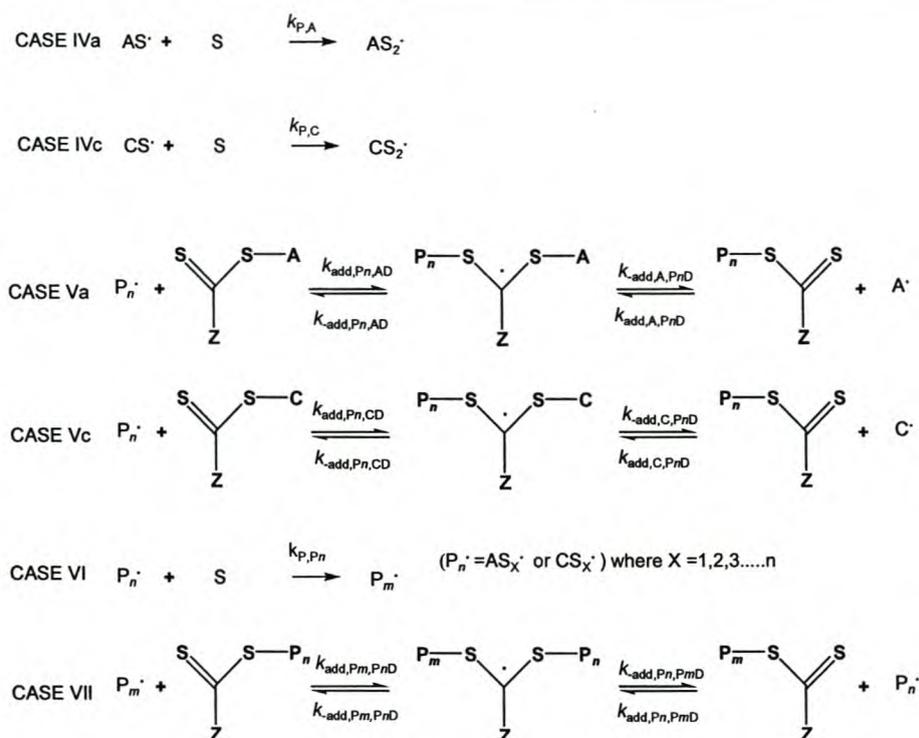
The cyanoisopropyl radicals generated by initiator decomposition will find themselves in one of three situations: (1.) case Ia or Iac - addition to a RAFT agent, (2.) case IIa - monomer addition (propagation), to give radical species AS^\cdot , or (3.) termination. Cumyl radicals generated by case Iac will undergo case Ic or Iac, i.e. addition to a RAFT agent, case IIc monomer addition (propagation), or terminate.

In scheme 4.3 we examine the reaction during the initialization process. At this point, all of the reactions addressed in scheme 4.2 are still possible but a set of new possibilities arises. The new reactions are as follows: the cyanoisopropyl radicals generated by initiator decomposition can now find themselves in one of two extra types of situations, namely case IIIasa or IIIcsa, which are both addition to a RAFT agent. AS^\cdot can add to a RAFT agent in the system, i.e. cases IIIasa, IIIasc, IIIcsas, IIIasas. Cumyl radicals generated by case IIIasc or IIIcsc can likewise undergo case IIIasc or IIIcsc additions, i.e. addition to a RAFT agent. CS^\cdot can add to a RAFT agent in the system in cases IIIcsc, IIIcsa, IIIasc and IIIcscs.



Scheme 4.3 The additional steps involved during the initialization period of the RAFT reaction of cumyl dithiobenzoate, styrene monomer and AIBN initiator.

At the end of the initialization process, the reactions shown in scheme 4.3 begin to dominate. Radical species AS^{\bullet} and CS^{\bullet} formed by case IIa or IIc (scheme 4.2) respectively can add to monomer, i.e. case IVa or IVc respectively (scheme 4.4). Both AS^{\bullet} and CS^{\bullet} can add to a RAFT agent in the system, i.e. case VII. Long chain propagation can occur as shown in case VI (e.g. AS_2^{\bullet} becoming AS_3^{\bullet}). Longer chains can also displace any tertiary leaving groups that are still attached to RAFT agents, i.e. case Va and Vc. This could similarly be an addition of a tertiary radical to a long chain RAFT agent.



Scheme 4.4 The additional steps involved in the initialization period of the RAFT reaction of cumyl dithiobenzoate, styrene monomer and AIBN initiator at the end of initialization.

The occurrence and rates of these initialization reactions will govern the overall reaction mechanism during the early stages of this reaction. The most prominent criteria for the extremely selective and stepwise behavior in the initialization period, as observed here, are firstly that the fragmentation of the formed intermediate radicals is very selective towards radicals that have not yet undergone propagation, and secondly, that addition of propagating radicals, with a degree of polymerization of at least unity, to the RAFT agent, is much faster than to monomer. The first of these criteria will usually hold if the initial leaving group on the RAFT agent is a much better leaving group than that formed after one propagation step, as is the case here. The second criterion will hold if $k_{add}[\text{RAFT}] \gg k_{p,1}[\text{M}]$ (with the appropriate k_{add} for the incoming radical, and for all forms of the RAFT agent), which will typically be the case when efficient RAFT agents are used. $k_{p,1}$ (the propagation rate coefficient for a monomeric radical) is chosen here since $k_{p,1}$ is typically greater than k_p . In these systems, most oligomeric radicals will consist of a single monomer unit added to an initiator or RAFT leaving group fragment. If $k_{add}[\text{RAFT}] \ll k_{p,1}[\text{M}]$, then the selective and stepwise behavior will probably not occur, since chains of degree of polymerization greater than unity will form before all of the initial RAFT agent has been consumed. Scenarios in which this is likely are when k_{add} (e.g. a low activity

RAFT agent, such as a MADIX agent) is small, $[\text{RAFT}]/[\text{M}]$ is small (e.g. a very high target molar mass), or $k_{p,1}$ is very large (which might occur for some initiators, and/or very active monomers). Note that the $[\text{RAFT}]/[\text{M}]$ ratio can be kept high during initialization, and further monomer added, if this problem arises.

4.8.2.2 Effects of temperature

Duplicate reactions were carried out at 84 °C (reactions 2 and 4, Table 4.2). The time dependence of the concentrations of important species in the reaction of cyano isopropyl dithiobenzoate and styrene is shown in figure 4.18.

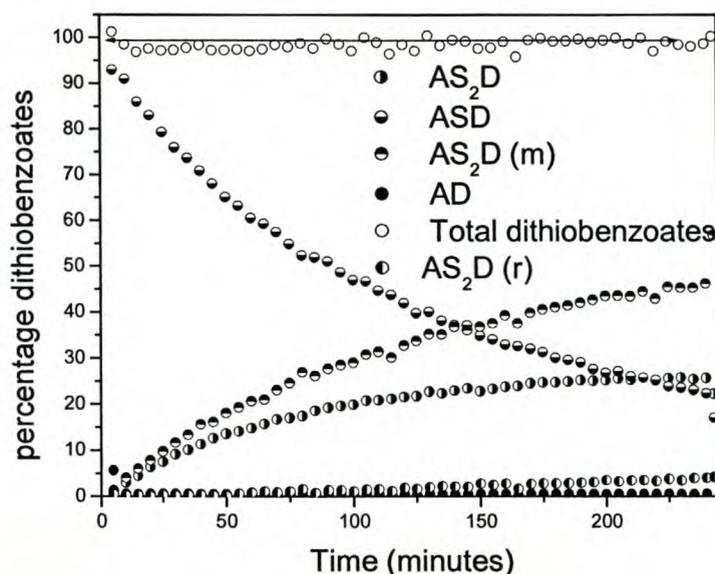


Figure 4.18 Styrene polymerized in the presence of cyano isopropyl dithiobenzoate and AIBN *in situ* at 84 °C (reaction 2, Table 4.2: 3.56×10^{-3} mol C_6D_6 , 6.1×10^{-5} mol AIBN, 2.31×10^{-3} mol styrene, 4.52×10^{-4} mol cyanoisopropyl dithiobenzoate).

As expected, the reaction rate is substantially faster than in the case of the reaction carried out at 70 °C. In fact, the reaction proceeds so rapidly that the cyanoisopropyl dithiobenzoate is consumed prior to the time the first spectrum was collected. This is presumably due to both the higher radical flux due to initiator decomposition, and the higher propagation rate coefficient for the cyanoisopropyl radicals. A similar reaction was carried out using the cyano isopropyl *p*-methoxy dithiobenzoate, and the same results were obtained (this is expected as the same radical species will be present). Overall, the same characteristics were observed at this higher temperature. The reaction showed similar selectivity, with no significant concentrations of AS_2D or higher dormant species formed until after the end of the initialization period, followed by a decrease in rate of styrene consumption after the end of the initialization period.

The products of the reaction of cumyl dithiobenzoate, styrene and AIBN carried out at 84 °C are shown in figure 4.19.

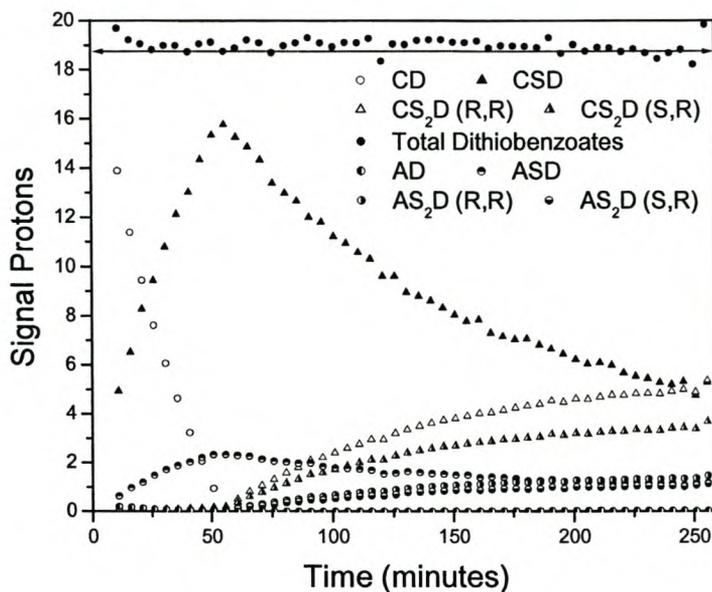


Figure 4.19 Relative concentrations of the methyl protons of the dithiobenzoate species versus time in the *in situ* polymerization of styrene, in the presence of cumyl dithiobenzoate and using AIBN as an initiator at 84 °C (reaction 2, Table 4.2).

The initialization period was shorter than that of reaction 1. The radical flux clearly plays a very important role in the length of the initialization period. In figure 4.20 an enlargement of a portion of the species concentration plot is shown to demonstrate the presence of cyanoisopropyl dithiobenzoate in the reaction.

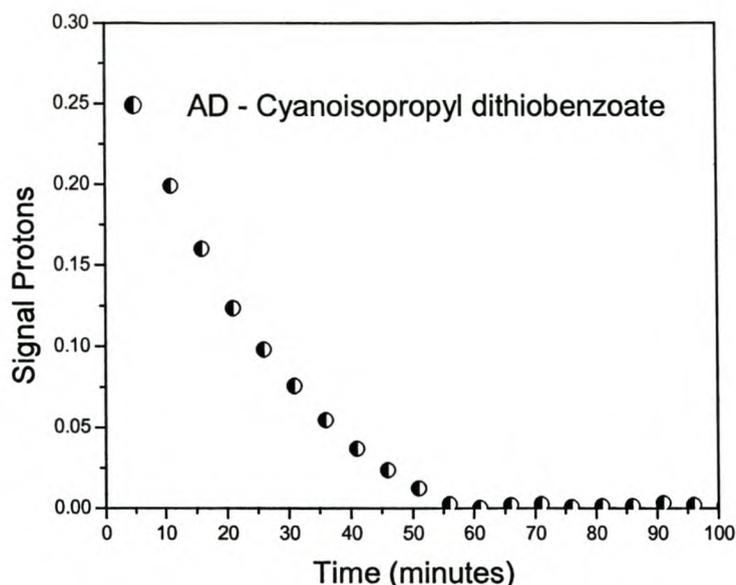


Figure 4.20 The consumption of the AD species in the reaction at 84 °C (Reaction 2, Table 4.2) is enlarged for clarity.

Species AD, which is not an original component of the reaction mixture, reaches a maximum concentration prior to the commencement of spectral data collection at 8 minutes. This implies that a rapid addition-fragmentation equilibration occurs in the reaction, and suggests that there are potentially other periods in the reaction that have interesting behaviour, apart from the initialization period. The preinitialization behaviour is potentially very significant for *in situ* RAFT agent formation.^{43,44}

As expected, the use of a varied Z group continued to result in very similar results as shown in figure 4.21. The similarity in behaviour suggests that the increase in temperature does not lead to stronger Z group effects. It is interesting to note that preliminary room temperature experiments suggest that Z group effects may become important at lower temperatures, which would be expected.

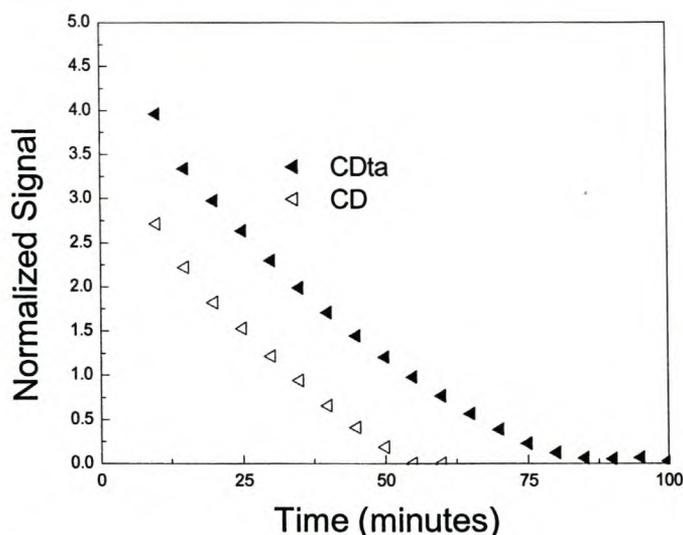


Figure 4.21 The *in situ* polymerization reactions of styrene in the presence of cumyl dithiobenzoate and cumyl phenyl dithioacetate, using AIBN as an initiator at 84 °C. The plots are normalized for initiator concentration (reactions 6 and 8 Table 4.2).

When comparisons of figures 4.18 and 4.19 are made, the same temperature dependence in reaction rate is clear in the case of cumyl dithiobenzoate, as has also been observed in the case of cyanoisopropyl dithiobenzoate. This suggests that the same initialization behavior is followed for both RAFT systems. The time scale is however different and will be discussed later. The reason for this lies in the difference between the R group radicals (radicals formed through fragmenting of the group attached to the dithioester in the original RAFT agent), with conversion of the slowest fragmenting R group radical into its respective mono styrene adduct being the rate determining factor in the initialization period.

4.8.2.3 Monomer Consumption

Some interesting observations can be made when comparing the fractional conversion for reactions 1 and 2 in the first-order kinetic plot in figure 4.22.

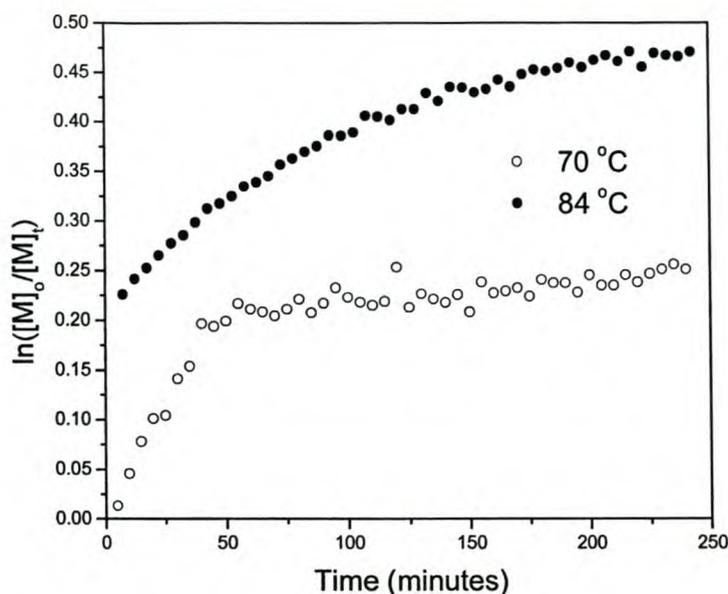


Figure 4.22 Logarithmic plot of fractional conversion versus time in the reactions of cyanoisopropyl dithiobenzoate with AIBN and styrene in deuterated benzene at 84 and 70 °C. Reactions 1 and 2, Table 4.2. Reaction 1: 3.56×10^{-3} mol C_6D_6 , 6.75×10^{-5} mol AIBN, 2.40×10^{-3} mol styrene, 4.84×10^{-4} mol cyanoisopropyl dithiobenzoate; Reaction 2: 3.56×10^{-3} mol C_6D_6 , 6.1×10^{-5} mol AIBN, 2.31×10^{-3} mol styrene, 4.52×10^{-4} mol cyanoisopropyl dithiobenzoate.

The rate of monomer consumption is substantially higher during the initialization period than after this period. The substantial decrease in the rate of the reaction after the initialization period at 70 °C is so extreme that polymerization appears to almost cease (although it must be noted that it does not, the rate is simply so slow that it might not be noticed by most analysis techniques). This is consistent with reports of systems that show little polymerization especially at lower temperatures, even though initiating radicals are being generated in the system.⁴⁵ The rates of polymerization in the reactions, normalized to monomer concentration, are equal to the sum of $k_p[P^*]$ for all propagating species present. The dominant propagating species in the two periods of the polymerization (i.e. initialization and equilibrium) are quite different, namely A^* (cyanoisopropyl radicals) during initialization, and AS_n^* (oligostyryl or polystyryl radicals) after initialization. The propagation rate coefficient for the addition of cyanoisopropyl radicals to styrene is $5200 \text{ L mol}^{-1} \text{ s}^{-1}$ at 70 °C,⁴⁰ and the propagation rate coefficient for addition of polystyryl radicals to styrene is $480 \text{ L mol}^{-1} \text{ s}^{-1}$ at 70 °C,⁴⁶ and possibly higher for short oligomeric radicals. The decrease in rate immediately following the end of the initialization period is by a factor of approximately 20. The difference in propagation rate coefficients alone is unable to account for the difference in rates. The only other possibility is that the propagating

radical concentration must also have decreased rapidly after initialization, leading to rate retardation that was not present during the initialization period.⁴⁷ Thus, the decrease in rate is probably due to a decrease in both the propagating radical concentration (corresponding to the rate retardation commonly observed in dithiobenzoate-mediated free radical polymerization reactions), and the propagation rate coefficient for the dominant propagating radicals in the system. It is important to note that for this reaction there was no apparent inhibition period at the beginning, but that the rate of reaction was much higher in the initialization period.

If we examine the monomer consumption of the cumyl dithiobenzoate mediated reactions in samples 3 and 4, as seen in figure 4.23, we can see that the monomer consumption is faster during the initialization period for both reactions than after the leaving groups have been converted to P_m species, i.e. the period after initialization.

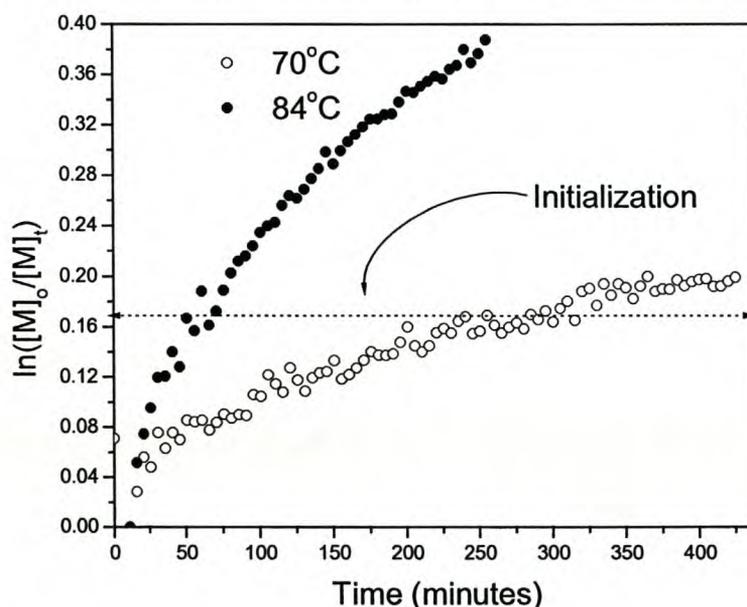


Figure 4.23: Semi-logarithmic plot of fractional conversion versus time in the reactions of cumyl dithiobenzoate with AIBN and styrene in deuterated benzene at 84 and 70 °C (reactions 3 and 4, Table 4.2).

When comparisons are made between the monomer consumption of the cumyl and cyanoisopropyl dithiobenzoate reactions presented in this dissertation, it is clear that the rate of monomer consumption during the initialization period of the cumyl dithiobenzoate reaction is slower than in the case of cyanoisopropyl dithiobenzoate. The rate of reaction is dependent on the propagating radical concentration, and the rate of propagation (k_p) of the cumyl and cyanoisopropyl radicals. Thus, there are a number of different possibilities for the different rates of reaction. The first possibility

is that there are differences in k_p for the cumyl and cyanoisopropyl radicals; accurate data at the actual reaction temperatures is unfortunately not available. Data for these radicals at lower temperatures suggest that the propagation rate constants are similar in magnitude.^{39,40}

The second possibility is that there is a rate retardation phenomenon occurring in the cumyl dithiobenzoate system, which would imply that there is a substantial concentration of intermediate radical species in the system. This would be suggested if the cumyl and cyanoisopropyl radical species have similar addition rates to styrene monomer but differing addition (and fragmentation) rates to the thiocarbonyl thio moiety.²⁶ However, preliminary ESR spectroscopic data of intermediate radical concentrations suggest that there is no significant difference in the intermediate radical concentrations during the initialization period in the reactions discussed in this chapter.³⁸

The third possibility is that there is a difference in the average termination rate constants for the cyanoisopropyl and cumyl radicals.

Some authors have observed shorter “inhibition” periods when using cyanoisopropyl dithiobenzoate as a RAFT agent.^{10,11} It is clear from the results presented above that this is consistent with *in situ* NMR results. The cyanoisopropyl radical provides a shorter initialization time, giving cyanoisopropyl dithiobenzoate reactions a “head start”. Once radical flux corrections have been made, the rates of polymerization would be the same in the two reactions only *if* termination rates were similar in the initialization and equilibrium phases of the reaction.

In RAFT polymerizations, in which initiator-derived initiating radicals and initial leaving group radicals (R^\bullet) are different, the number of different *propagating* (and intermediate) radicals during the early (and later) stage is increased (specifically, here we have now A^\bullet and C^\bullet radicals in significant quantities, whereas before only A^\bullet radicals were present in significant quantities). In these cases, the rate of monomer consumption in the initialization period becomes a composite term to compensate for the fractions of the two types of radicals active in the system. This will substantially increase the difficulty in resolving different influences on the propagating radical concentration. The reactions where cumyl radicals were present (reactions 3 and 4, figure 4.23) are complicated by the fact that there are two different tertiary radicals

consuming monomer in the system, and the rate of monomer consumption is therefore not as obviously interpreted as in the case of the cyanoisopropyl radicals.

4.8.2.4 Inhibition?

One of the consequences of the initialization period is that the rate of monomer consumption is governed by the rate of conversion of the starting RAFT agent (AD) into the single monomer adduct analog (ASD). The rate of RAFT agent conversion controls the amount of time taken to change the dominant type of propagating species from that during the initialization period (A^* here) to a different dominant form (AS_n^* here) later. This in turn is governed by the addition rate constants of the R-derived radical (or initiator fragment radical, which is the same in this case) groups to monomer.^{39,40} Here it becomes clear that much experimental evidence that has been presented for inhibition in RAFT polymerization^{10,48,49} is actually evidence of the initialization period.

In free radical polymerizations, the propagating radical concentration is dependent on the overall rates of initiation and termination, and rapidly reaches equilibrium. In a RAFT system there is an extra radical species (intermediate radicals) whose concentration is potentially very significant.^{9,50,51} The potential for termination of the intermediate radical, whether reversible or irreversible, has been shown.⁴⁷ For the purposes of simplification it is assumed that the termination of the intermediate radicals does not significantly change the equilibrium concentration of propagating radicals. This simplification is valid during the initialization period, due to the very low concentrations of intermediate radicals in the initialization period; after initialization this assumption may be poor, dependent on the RAFT agent concentration.⁴⁷ The discussion will also only consider the case in which the intermediate radical lifetime is not so extensive as to cause rate retardation.

As mentioned earlier, the rate of reaction is significantly faster in the initialization period than after the initialization period for styrene. In contrast, some of the most significant inhibition times that have been reported have been in methyl acrylate (MA) systems.¹⁰ If the methyl acrylate RAFT system using the same RAFT agents used in this study is examined, the following relationship can be derived from literature values:^{39,40,52}

$$\frac{k_{p,MA}}{k_{p,A,MA}} \gg 1 \gg \frac{k_{p,STY}}{k_{p,A,STY}} \quad (4.7)$$

Here $k_{p,MA}$ and $k_{p,STY}$ refer to the long chain propagation rate coefficients for MA and STY, and $k_{p,A,MA}$ and $k_{p,A,STY}$ to the rate coefficients for the addition of the cyanoisopropyl radical to MA and STY. Assuming, as a first approximation, similar propagating radical concentrations before and after initialization (this is apparently not true here, and usually the propagating radical concentration will be lower after initialization), the relative reaction rates will be primarily dependent on the relevant k_p values. For styrene this gives a higher rate during initialization than for the period afterwards. For MA, a somewhat different rate behavior is predicted as $k_{p,MA}$ is $13100 \text{ L mol}^{-1} \text{ s}^{-1}$ at $25 \text{ }^\circ\text{C}$,⁵³ and $k_{p,A,MA}$ is $367 \text{ L mol}^{-1} \text{ s}^{-1}$ at $25 \text{ }^\circ\text{C}$,⁴⁰ i.e. the rate of reaction will be much slower during initialization. To test the hypothesis, the reactions in table 4.4 were carried out.

Table 4.4: Composition of reaction mixtures for *in situ* NMR analysis. The solvent used was deuterated benzene (99.6%), and the initiator used was azo bis(isobutyronitrile), (AIBN).^a Cumyl dithiobenzoate (CD).^b Cumyl phenyl dithioacetate (PPDTA).[#] Reaction carried out at $84 \text{ }^\circ\text{C}$. * Reaction carried out at $70 \text{ }^\circ\text{C}$

Reaction	Solvent		Initiator		Methyl Acrylate		RAFT Agent		[M]/ [R _o]	[R _o]/ 2[I _o]
	Mass (g)	Mol ($\times 10^3$)	Mass (g)	Mol ($\times 10^5$)	Mass (g)	Mol ($\times 10^3$)	Mass (g)	Mol ($\times 10^4$)		
16*	0.25	2.99	0.011	6.7	0.25	2.90	0.103 ^a	3.79	7.65	2.82
17 [#]	0.25	2.99	0.011	6.7	0.25	2.90	0.103 ^a	3.79	7.65	2.82
18*	0.25	2.99	0.011	6.7	0.25	2.90	0.115 ^b	4.02	7.21	3.00
19 [#]	0.25	2.99	0.011	6.7	0.25	2.90	0.115 ^b	4.02	7.21	3.00

Figure 4.24 shows the concentration changes with time of the initial RAFT agent as well as the monomer in reactions 16 and 18 (Table 4.4.).

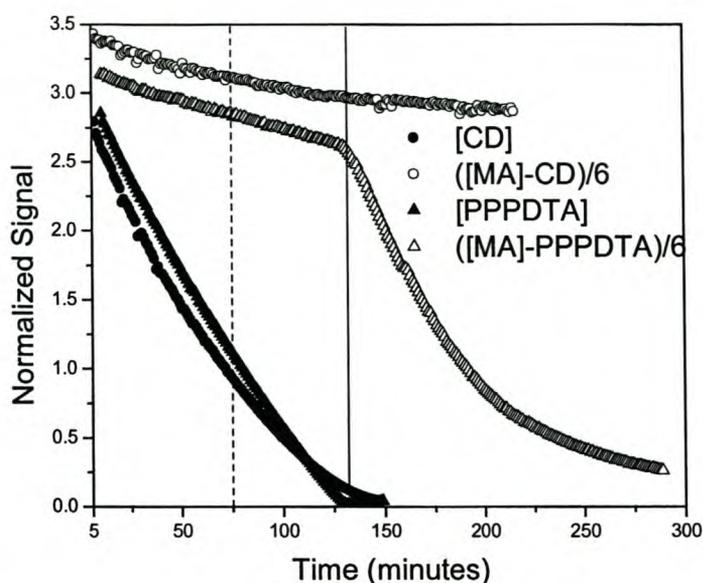


Figure 4.24 The consumptions of methyl acrylate (MA) in the presence of cumyl dithiobenzoate and cumyl phenyl dithioacetate at 70 °C are presented normalized to the initiator concentration in the system. The vertical lines are visual indications of the point where deviation from linearity in RAFT agent consumption is observed (dotted) and initialization time (solid).

The slight differences in starting concentrations are due to slight variations in concentration between the samples (see table 4.4.) in figure 4.24. The principle presented is however unaffected. The reaction shows quite clearly that there is significant variation between the two systems, but it should be noted that for a significant period of time, the pseudo zero-order consumption of the RAFT agent appears to hold. There is far more deviation from this behaviour in the case of the cumyl dithiobenzoate RAFT agent, which would be expected in the case of a stronger Z group retardation effect.

The pseudo zero-order behaviour is monomer dependent as would be expected. Every different monomer system will provide different leaving group behaviour and this will lead to a change in the lifetimes of intermediate radical species, and in this way affect the rate of the reaction.

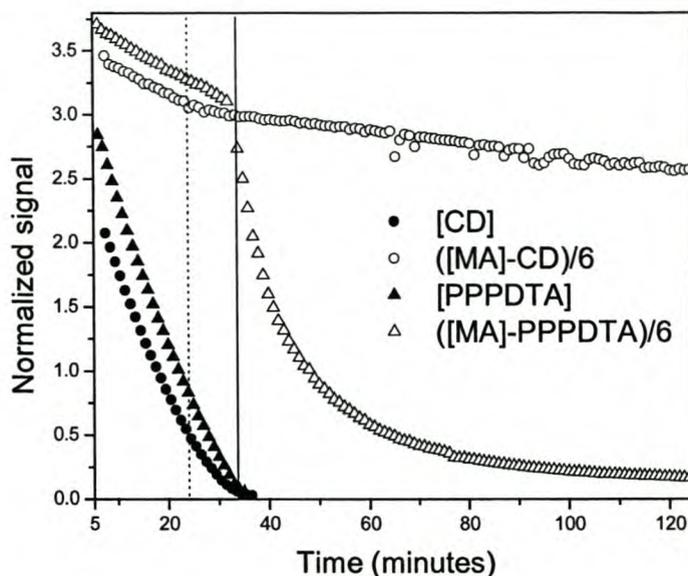


Figure 4.25 The consumption of methyl acrylate in the presence of cumyl dithiobenzoate and cumyl phenyl dithioacetate at 84 °C are presented normalized to the initiator concentration in the system versus time. The vertical lines are visual indications of the point where deviation from linearity is observed (dotted) and initialization time (solid).

The data for figure 4.25 was collected in one minute intervals and it is clear that in the case of the phenyl dithioacetate agents that this rapid data collection is almost insufficient. In the case of the cumyl dithiobenzoate RAFT agents, the concentration of RAFT agent in the system is such that retardation becomes overwhelming after the initialization period. This means that the propagating radical concentration has changed to such a large extent that the rate of polymerization in the case of dithiobenzoates is decreased to the point that even the very high k_p values (typical in acrylate polymerizations) do not lead to an increase in polymerization rate. However, when a RAFT agent is used that does not cause significant rate retardation, it becomes clear that the behaviour predicted by equation 4.7, and illustrated by figure 4.26 is indeed occurring.

When there is a relatively small amount of RAFT agent present in a reaction (i.e. long chains are targeted), then a very small percentage of the monomer will be consumed during the initialization period. This would be difficult to distinguish from complete inhibition if the target molar mass is high. RAFT agent to monomer concentration ratios that have been used in the literature are commonly very high,¹⁰ often of the order of a thousand to one. Figure 4.26 demonstrates this point for both cases where $k_p/k_{p,I}$ (where I is the initiating radical) is greater and less than unity, for different target molar masses.

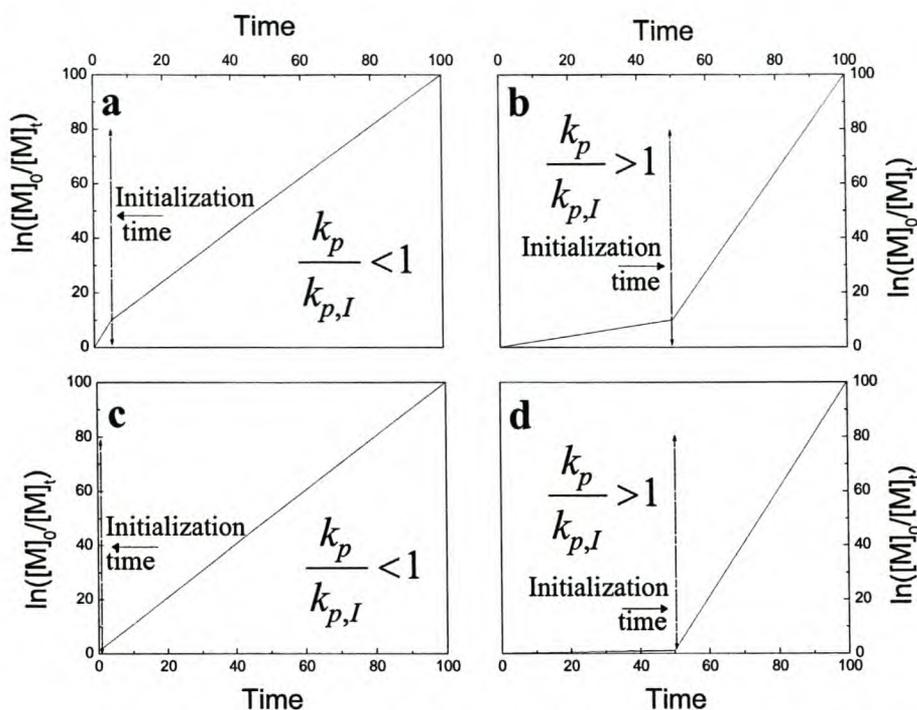


Figure 4.26 The relationships of the rate of monomer consumption in the two phases of the reaction is indicated in the figures with subscript I, referring to initialization: (a) the rate of monomer consumption in the equilibrium part of the reaction is higher than in the initialization period (monomer to RAFT agent molar ratio 10:1), (b) rate of monomer consumption in the equilibrium part of the reaction is lower than in the initialization period (monomer to RAFT agent molar ratio 10:1), (c) rate of monomer consumption in the equilibrium part of the reaction is higher than in the initialization period (monomer to RAFT agent molar ratio 100:1), (d) rate of monomer consumption in the equilibrium part of the reaction is lower than in the initialization period (monomer to RAFT agent molar ratio 100:1).

In figures 4.26 (a) and (b), molar ratios of 1:10 RAFT agent to monomer are presented, and in 4.26 (c) and (d), molar ratios of 1:100 RAFT agent to monomer, assuming constant propagating radical concentrations, in which case the relative reaction rates are proportional to the relevant k_p value. For systems in which the monomer to RAFT agent ratio is not so extreme as to allow for the addition of two monomer units per transfer and in which case the transfer rate constant is sufficiently greater than the propagation rate constant, approximately one mole of monomer is consumed per mole of RAFT agent during the initialization period. This would be almost indistinguishable from total inhibition (i.e. less than 0.1 percent conversion would occur during this time), as would cases in which there are oligomers present, e.g. four monomer additions prior to transfer would still be substantially less than one

percent of conversion in many systems. It is important to note that examples of systems in which there is supposed to be total inhibition are reported to show color change, which is a well-known indication of polymerization in RAFT mediated polymerizations. This is consistent with the suggestion that these systems have an initialization period.⁴⁵ Due to the ratios of reagents used in the present study, the initialization period is accentuated.

The same behaviour can be observed in longer chain targeted reactions, as can be seen in figure 4.27 for styrene polymerizations.

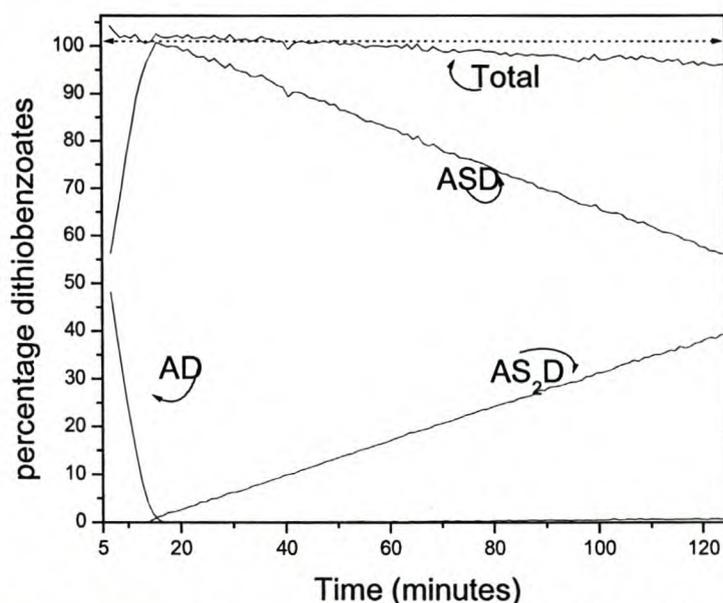


Figure 4.27 The formation and consumption of species AD, ASD and AS₂D at 60 °C, with a target chain length of 50 monomer units i.e. a 1:50 ratio of monomer to RAFT agent.

The relative speed of formation and consumption of the agents is due to the concentration of the RAFT agent as well as initiator. The accuracy of the integrations is poorer than with short chain targets but the trends can easily be identified. Data was gathered at one minute intervals. Similar reactions were carried out using cyano isopropyl dithiobenzoate and methyl acrylate with higher degree of polymerization (DP) targets. The reaction data displayed in figure 4.28 is derived from a MA polymerization with a DP target of 50. The rate retardation in the case of the dithiobenzoate agent is high enough that it is possible to follow the individual monomer additions to the growing dithiobenzoate species. This would be substantially complicated in the case of reactions with cumyl phenyl dithioacetate, due to the excessive exotherm and rate of polymerization. To avoid potential damage to the

instrument it was decided not to carry out high DP experiments with RAFT agents that did not exhibit rate retardation.

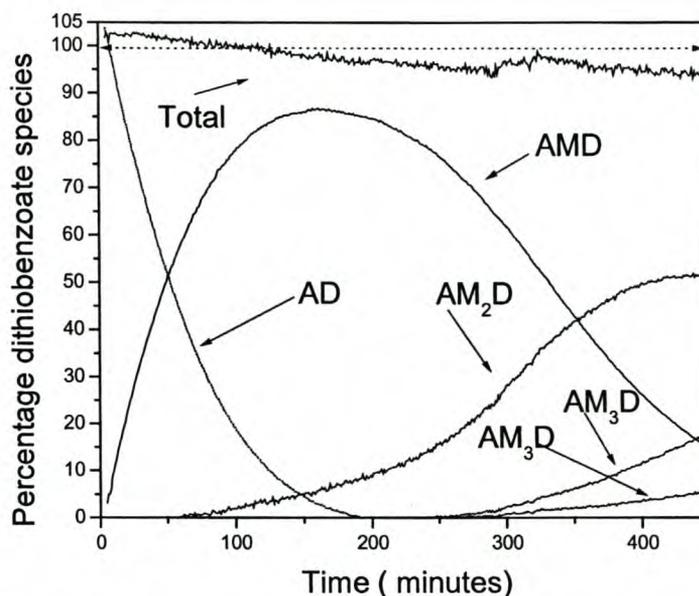


Figure 4.28 The reaction of methyl acrylate using cyano isopropyl dithiobenzoate as a RAFT agent and AIBN as an initiator with a 50 DP target molar mass. The reaction temperature used was 60 °C. Data was gathered at one minute intervals. Methyl protons are plotted for all species.

The reaction is quite rapid, but the use of cyanoisopropyl dithiobenzoate does not provide the increase in rate during initialization as seen in the styrene polymerizations. This behaviour suggests that the differences in behaviour in the styrene system are more likely to be due to the addition rate constant differences to the specific monomers than because of an inherent difference in the intermediate radical species produced by the cyanoisopropyl radical's interaction with the RAFT agent. (The curvature in the consumption of the AD species in the reaction using methyl acrylate as a monomer is indicative of the fact that acrylates are poor leaving groups and will serve to increase the intermediate radical concentration in the system when compared to styrenic monomers). A second factor is the fact that the addition rate constant to monomer for the single monomer adduct species will be substantially higher than for the cyanoisopropyl radical and curvature, being dependent on the competition between addition to monomer and addition to RAFT agents, will be more favoured. In this case, once a fair number of the radicals are of the form AMDA, there is clear retardation of the polymerization rate in the system. The suggested behaviour in figure 4.26 appears quite consistent with the observed experimental data, and

suggests that there is no reason to conclude that the extreme concentrations of RAFT agents in the studied reactions led to different initialization behaviour in the reactions.

4.8.2.5 Radical generation and termination products

The formation of the AA (tetramethyl succinonitrile, TMSN) species in the studied systems was examined in the context of a conventional free radical reaction and initiator (AIBN) decomposition. The AA product is formed by mutual termination of cyanoisopropyl radicals. In figure 4.29, the time dependences of the concentrations of AA and AIBN at 84 °C are presented.

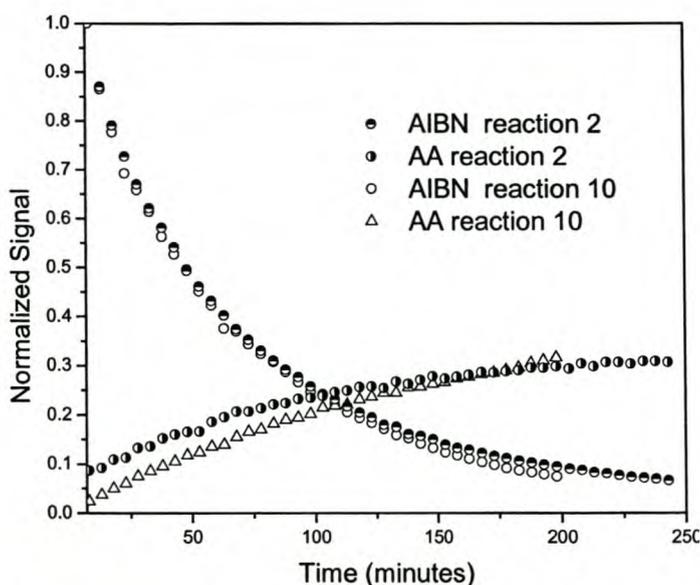


Figure 4.29 The concentrations of AIBN and AA of reactions 2 and 10 carried out in deuterated benzene at 84 °C. Reaction 2 contains RAFT agent cyanoisopropyl dithiobenzoate and Reaction 10 is a conventional free radical polymerization. Reaction 2: 3.56×10^{-3} mol C_6D_6 , 6.1×10^{-5} mol AIBN, 2.31×10^{-3} mol styrene, 4.84×10^{-4} mol cyanoisopropyl dithiobenzoate; Reaction 10: 3.56×10^{-3} mol C_6D_6 , 6.1×10^{-5} mol AIBN, 3.68×10^{-3} mol styrene.

In reaction 2, the concentration of the AA product shows a slight increase when compared to a control polymerization (reaction 10). The concentration difference appears to be due to an event that generated significant amounts of this product prior to the time of the first scan. This deduction can be made, as the formation of the AA product in reaction 2 appears to be occurring at a slower rate than in reaction 10, suggesting that some event prior to observation caused the different initial concentrations. The higher initial concentration was probably due to the termination behavior of cyanoisopropyl radicals in the initialization period, which could not be

examined at the reaction temperature, since initialization was completed before the first scan could be made. The results suggest that the presence of the RAFT agent does not increase the amount of TMSN formation after initialization is complete, i.e. the RAFT agent does not directly promote termination in the system (although it alters the relative populations of propagating radicals, which can change the termination kinetics). The difference in the formed amounts of AA (TMSN) in the RAFT-mediated polymerization and the control lies in the nature of the radical species and the length of the initialization period. Comparisons between the RAFT-mediated reaction (reaction 2) and the control (reaction 10) at 84 °C (figure 4.29) also indicate that the presence of a RAFT agent does not increase the rate of AIBN decomposition. Figure 4.30 presents the AIBN and AA product concentrations as determined at 70 °C. The formation of the AA product in reaction 1 occurs at an increased rate throughout the initialization period (lasting approximately 60 min).

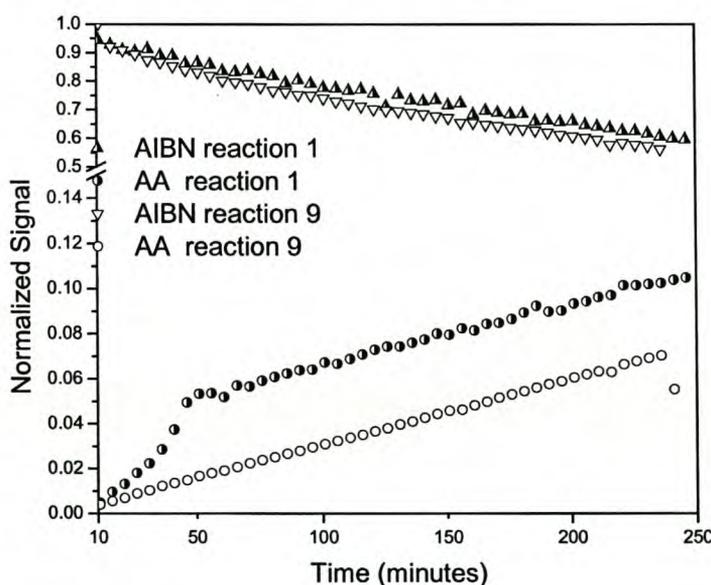


Figure 4.30 The concentrations of AIBN and AA of reactions 1 and 9 carried out in deuterated benzene at 70 °C. Reaction 1 contains RAFT agent cyanoisopropyl dithiobenzoate and Reaction 9 is a conventional free radical polymerization. Reaction 1: 3.56×10^{-3} mol C_6D_6 , 6.75×10^{-5} mol AIBN, 2.40×10^{-3} mol styrene, 4.84×10^{-4} mol cyanoisopropyl dithiobenzoate; Reaction 9: 4.34×10^{-3} mol C_6D_6 , 6.71×10^{-5} mol AIBN, 3.68×10^{-3} mol styrene.

Excess AA product is produced during initialization. Following the initialization period, the AA product is formed at a similar rate as in a conventional free radical polymerization, as evident from comparisons of reactions 1 and 9. The increased concentrations of the respective termination products in the RAFT-mediated

polymerizations are due to an unusual process that occurs during the initialization period in which active chains are kept short (see Figure 4.31).

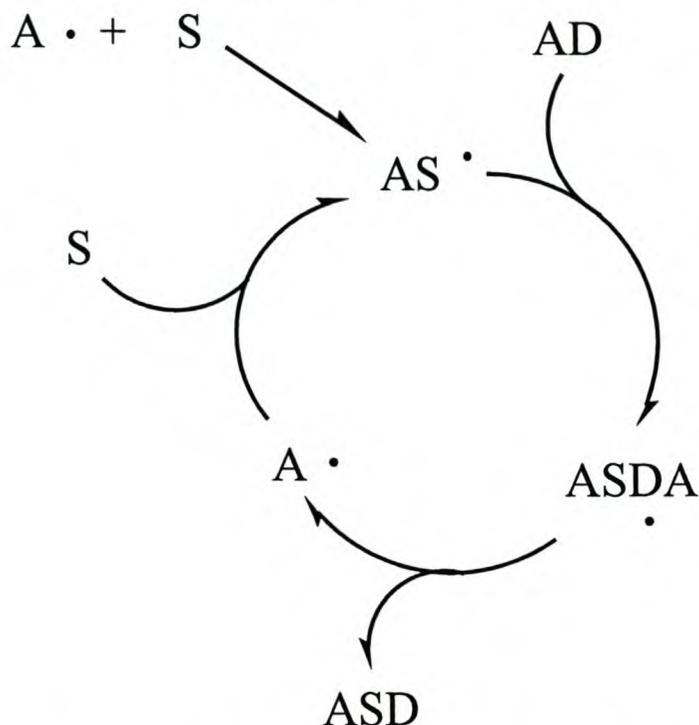


Figure 4.31 The cycle by which cyanoisopropyl radicals (A^\bullet) are rapidly regenerated by addition-fragmentation through a dithioester mediating species, during the early stages of the cyanoisopropyl dithiobenzoate-mediated polymerization of styrene.

During the initialization period, the A^\bullet will add to a monomer unit to form AS^\bullet . When these species undergo efficient transfer, a short A^\bullet will be expelled. This means that, unlike a conventional radical polymerization, the initialization period replaces the slower terminating AS^\bullet species with faster terminating A^\bullet radical species. A^\bullet adds to styrene (S) to form AS^\bullet . AS^\bullet adds to AD to generate intermediate radical $ASDA^\bullet$ that rapidly fragments to produce A^\bullet , which is then once again able to cycle through by adding to styrene. There are significantly higher concentrations of these termination products compared with those in a control reaction because of this replacement during the initialization period. After the initialization period, the usual geminate recombination process dominates the formation of the AA species, as can clearly be observed in figures 4.29 and 4.30. The concentration curves for AA are roughly parallel in figure 4.30, although in figure 4.29 there is a deviation at higher temperature. The reactions at higher temperatures will result in higher conversions and viscosities in the control reaction, leading to a decrease in initiator efficiency and an increase in the geminate recombination product being produced at longer reaction

times in reaction 10. A weaker corresponding increase in viscosity is expected in the RAFT system, since both overall conversion and average chain length (on which viscosity depends) are both much lower than in the conventional system.

The chain length dependence of the termination rate coefficients^{12-15,54} means that short species will have a higher rate of termination. The overall termination rate will be higher during initialization than that in a control reaction in which the short chains are quickly converted into longer chains. The higher rate of radical loss through termination implies that reactions with longer initialization periods will consequently have a lower propagating radical concentration after the initialization period, leading to a slower rate of reaction after the initialization period than comparable reactions with shorter initialization periods. Examining the terminated species gives insight into the reactions that govern the RAFT mechanism during the earlier stages of the polymerization process. We can do this in two ways: firstly by examining the relative concentrations of all the dithiobenzoate species with cumyl and cyanoisopropyl endgroups and secondly, by examining the formed terminated species directly.

Figure 4.32 shows the time dependence of the relative concentrations of all dithiobenzoate species with cumyl (CD, CSD, CS₂D, CS₃D, etc.) and cyano isopropyl (AD, ASD, AS₂D, AS₃D, etc.) endgroups in reaction 1. It is clear that there is a gradual displacement of the cumyl endgroups from the living polymer. The termination of cumyl radicals as well as cumyl-ended oligomeric radicals is responsible for this change in endgroups. It can be seen that approximately 10% of chains with cumyl endgroups are lost to termination during the reaction. The concentration of dithiobenzoate chains with cyanoisopropyl endgroups increases throughout the reaction as more initiator decomposes. A constant concentration of chains with dithiobenzoate endgroups throughout the reaction indicates that very little (below the detection limit of the NMR equipment) loss of these types of chains occur (due to intermediate radical termination or degradation) throughout the length of the reaction.

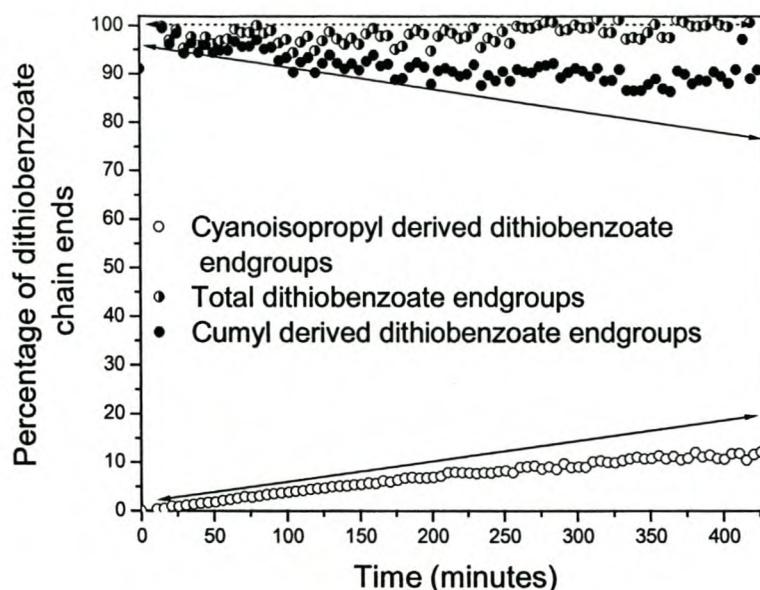


Figure 4.32 A plot of the cumulative integrated endgroups of the dithiobenzoate species in the polymerization of styrene, in the presence of cumyl dithiobenzoate and using AIBN as an initiator at 70 °C. The lines are simply guides for the eye.

Figure 4.33 shows us the time dependence of the relative concentrations of all dithiobenzoate species with cumyl and cyanoisopropyl endgroups within the first 3 hours of reaction 2 (84 °C). This shows a gradual increase of cyanoisopropyl endgroups during the reaction – the rate of which is at a maximum early in the reaction. This is to be expected, as the number of radicals generated by AIBN decomposition is highest early in the reaction (first order decay of AIBN). The probability of displacing cumyl radicals is also higher than that of displacing cumylstyryl radicals, which implies that direct displacement of cumyl endgroup leaving groups later in the reaction requires an addition to styrene monomer, and the rate determining reaction may change.

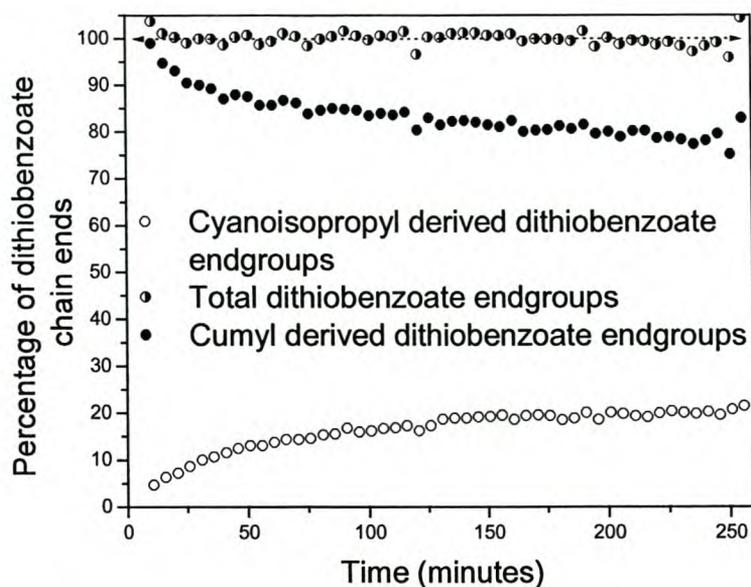


Figure 4.33: A plot of the cumulative integrated endgroups of the dithiobenzoate species in the polymerization of styrene, in the presence of cumyl dithiobenzoate and using AIBN as an initiator at 84 °C.

The number of active (propagating and dormant) chains with a cyanoisopropyl endgroup increases with time due to two factors: (1) “transfer” is efficient, therefore species CD will be displaced with species AD, allowing termination of expelled C^{\bullet} , (2) there is a limited supply of cumyl groups, whereas A^{\bullet} are continually supplied. The total number of chains with cyanoisopropyl endgroups *must* therefore increase. As all of the dithiobenzoate species with cumyl endgroups are introduced into the reaction from the start, we expect to see a maximum in the beginning of the reaction and a gradual decrease in the concentration of the dithiobenzoate species with cumyl endgroups, as some of the cumyl groups are involved in termination. This was observed. It is also interesting to note that the highest rate of decrease is during the earlier part of the reaction, i.e. during the initialization period. This is evidenced by the high level of cumyl-cumyl (CC) termination seen during the initialization period as shown in figure 4.34.

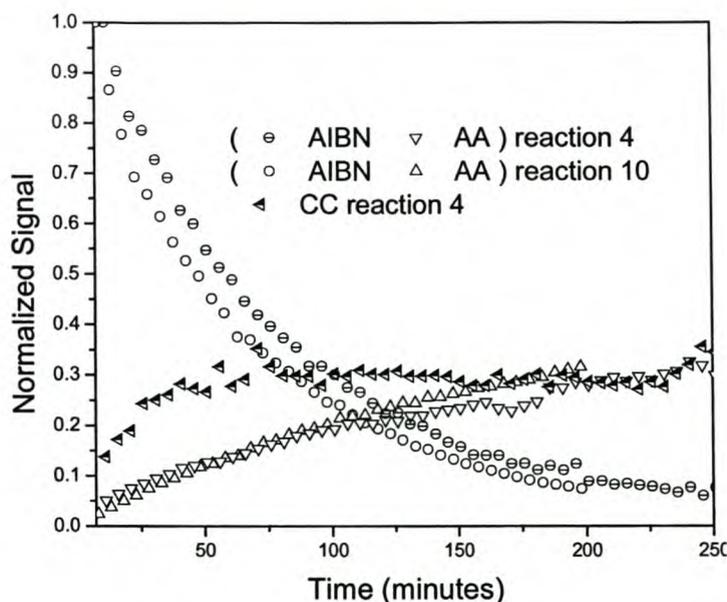


Figure 4.34 The termination products of reactions 4 and 10 (Table 4.2) carried out in deuterated benzene at 84 °C.

The increased temperature in reaction 4 increased the radical flux in the system, leading to a higher rate of displacement of cumyl endgroups from the dithiobenzoate species. The net result was approximately 20% of endgroup interchange by the end of the monitoring period. The interchange of endgroups is especially important for applications in which specific endgroups are required. By directly following the concentration of the termination products formed during reaction 4, it is seen (figure 4.34) that there are significantly more cumyl-cumyl (CC) termination products than products of other termination processes. Other termination reactions do occur (i.e. AC, CSC) but the concentrations of these termination products were too small to be integrated accurately and are therefore not shown in figure 4.33. If it is assumed that the rate coefficients for termination for the short chain radicals present in the reaction at this stage are similar, then this implies that the transfer process is very efficient, leading to a predominance of cumyl radicals in the system during the early stages of the polymerization. This is due to displacement of cumyl radicals by AS^* , CS^* and A^* (A^* are the other dominant propagating species) radicals, although the concentration of the generated species AD is low relative to that of the CD species. When we examine this in the context of the monomer consumption data (figure 4.22), we can see that the concentration of propagating species is at a maximum during the early part of the reaction. Consequently, termination will also be at a maximum. The other termination product that may be expected in the initialization period, species AC, is

present only in very low concentrations with respect to CC species in the reaction. This would suggest that very low concentrations of A^\bullet species are present in the reaction in relation to the C^\bullet species.

The formation of the AA species in reaction 4 can be examined in comparison with the AA termination that would occur in a conventional free radical polymerization (figure 4.34). The concentration of the AA (tetramethyl succinonitrile) termination product is quite similar to that found in a control reaction (reaction 10, Table 4.1) at early reaction times, suggesting that the AA termination product is predominantly a geminate recombination product as in the case of the control reaction. In figure 4.35 the respective termination products for reaction 1 at 70 °C are shown. The very small amounts of termination at the lower temperature complicated analysis, but the same trends were observed as at the higher reaction temperatures. The CC termination product is dominant until the end of initialization, at which time the termination of the CC radicals comes to an end.

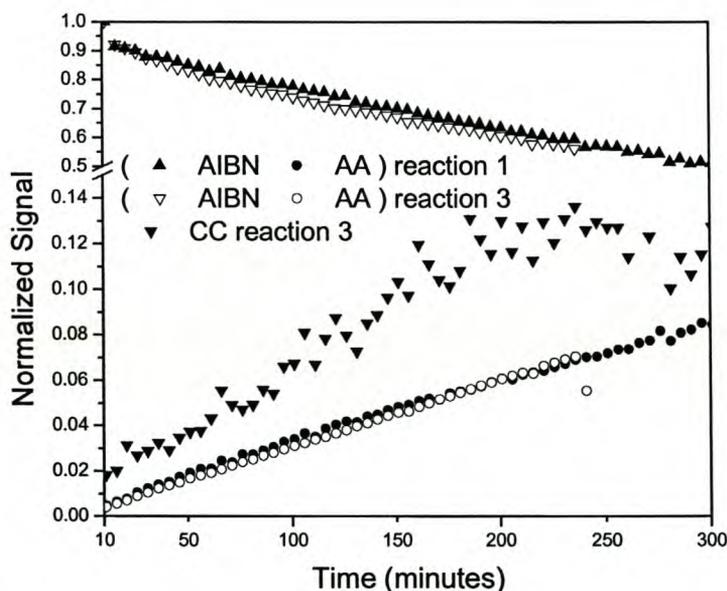


Figure 4.35 The termination products of reactions 3 and 9 (Table 4.2) carried out in deuterated benzene at 70 °C

The increased concentrations of the respective termination products in the RAFT-mediated polymerizations during initialization are due to the unique process that is taking place, in which active chains are kept short. During the initialization period the A^\bullet or C^\bullet will add to a monomer unit to form AS^\bullet and CS^\bullet . When these species undergo efficient transfer, a short A^\bullet or C^\bullet will be expelled. This means that unlike a conventional radical polymerization, the initialization period replaces the slower

terminating AS^{\bullet} and CS^{\bullet} species with faster terminating A^{\bullet} and C^{\bullet} radical species. There are significantly higher concentrations of their termination products compared with a control reaction because of this replacement during the initialization period. After the initialization period the geminate recombination process dominates the formation of the AA species as can clearly be observed in the figure 4.34 and 4.35. The chain length dependence of the termination rate coefficients means that short species will have a higher rate of termination, and the overall termination rate will be higher than that in a control reaction in which the short chains are quickly converted into longer chains.^{12,54} The higher rate of radical loss through termination during initialization implies that longer initialization periods will require significantly higher radical fluxes to allow reactions to proceed at the same rates after the initialization period, as shorter initialization time reactions which will not have had the increased radical loss for as long a period of time. As most termination occurs during the initialization period, reactions with pronounced initialization periods will consequently have a lower propagating radical concentration after the initialization period, leading to a slower rate of reaction after the initialization period. This behaviour could be a contributing factor to reported increased retardation in cases where cumyl dithiobenzoate has been used as a RAFT agent.¹¹

4.8.2.6 Beyond Initialization

To minimize the length of the initialization period, it is important that the propagation rate constant of the homolytic leaving group of the original RAFT agent with respect to the monomer in use be as high as possible. The only caution is that it should remain a better leaving group than the incoming monomer-adduct radicals. To minimize the effect of propagation rate constant differences between initialization and the equilibrium phase of the reaction, a polymeric RAFT agent of the same monomer can be used. In this case, the propagation of the initiator fragment, which is unable to displace the polymeric chain until it has propagated, will result in an immediate increase in intermediate radicals, which is equivalent to the end of initialization, as has been seen by ESR spectroscopy.³⁸ The experimental implication of using the polymeric agent is that the RAFT equilibrium period should be reached very quickly.

To minimize termination in a polymerization process, it is important to limit the radical flux in the system. The effect of initiator concentration on RAFT-mediated polymerizations has been difficult to understand in the past. The correlation between

initiator concentration and polymer polydispersity has been difficult to quantify and many authors have used rough ratios of reaction components that do not give easy access to the reality of the radical concentrations in the system. These ratios have been commonly used in the reversible endcapping living techniques such as ATRP and SFRP, where the radical flux has been minimized to decrease termination, but are not as relevant in a system such as RAFT, in which initiation continues throughout the reaction and the rate termination is relatively high (in comparison to radical fluxes in ATRP and SFRP).

To examine the effect of the concentrations of initiator and RAFT agent in the initialization period, different concentrations and different ratios of these components were used. The effect of changing the RAFT agent concentration on the initialization time is shown in figure 4.36.

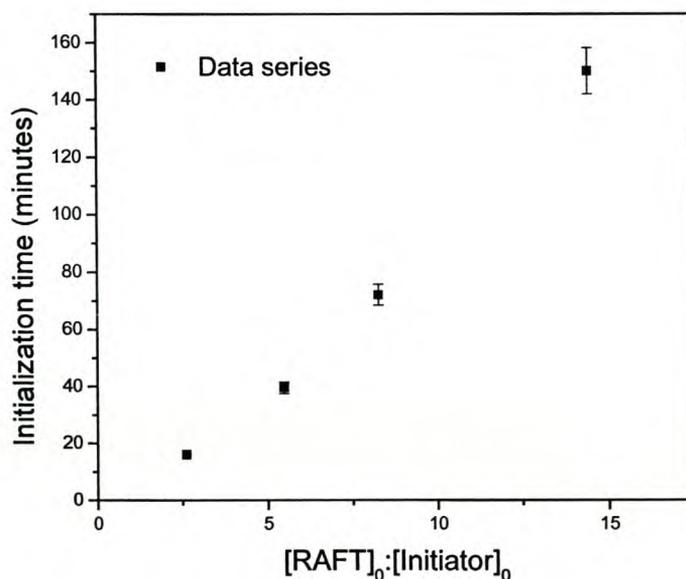


Figure 4.36 The effect of varying the RAFT agent concentration while holding the initiator concentration constant at 84°C.

The dependencies on RAFT agent and initiator concentration as well as temperature affect the length of the initialization period. The fact that the initiator and RAFT agent concentrations show different dependencies in their effects on the initialization time implies that the RAFT to initiator ratio quoted so frequently in the literature should only be used in specific conjugation with the monomer concentration in the system.

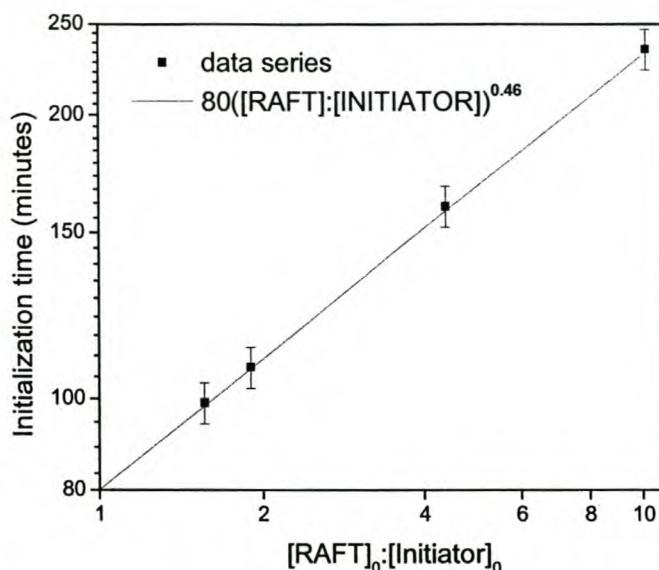


Figure 4.37 The double log plot of initialization time versus initial RAFT agent to initiator concentration at 70 °C. A power law fit of the data is shown.

In the case of an initiator that provides radicals that are unable to displace initial R groups, the process of initialization will be begun by the propagation of the initiator-derived radicals prior to exchange. In the reactions of cumyl dithiobenzoate with AIBN as initiator, the relative addition and fragmentation abilities of the radicals are such that some displacement can occur before the first propagation step, as has been seen by the formation of the AD species in reactions 1 and 2. The amount of AD produced was however very small and made very little difference to the system described here. The use of very active radical initiator species should be carefully monitored, as it may be possible to create a situation in which the incoming polymer chain is unable to displace the initiator fragment from the RAFT agent, preventing or retarding the RAFT process and therefore leading to a potential increase in polydispersity.

It should be noted that the effects of the ratio changes on the polydispersity of the reactions was small but detectable. Further investigations of the concentration dependencies of polydispersity should be considered to provide more insight into these relationships.

4.8.2.7 Implications for emulsion systems

The implications of initialization behaviour for an emulsified system are unknown at this point and some possibilities will be discussed in chapter five. The change in

emulsion stability in a RAFT mediated emulsion system is reported as occurring after a short period, typically in the vicinity of 15-30 minutes into a reaction and after initiation.⁵⁵ It is important to note that destabilization appears to occur after initialization. At this point phase, separation of oligomeric species occurs, destabilizing the emulsion. If this occurs via a superswelling mechanism, as will be discussed in chapter five, the nature of the oligomers may play a very important role in the destabilization process. From ESR results in a parallel study it has been shown that intermediate radical species begin to dominate the radical population some time after initialization.³⁸ These species grow in length at twice the rate of the dormant chain population. Termination of these species leads to oligomers of up to three times the length. This leads to a mixture of oligomeric species in the emulsion that appear to be significant role players in latex destabilization.

4.9 Conclusions

This chapter has provided new direct evidence for details of the mechanism of the initialization period of the RAFT process. It was found that the addition-fragmentation process was extremely selective during this period, and because of this, significant quantities of RAFT adducts of degrees of polymerization greater than one were formed only after complete conversion of the initial RAFT agent to its monomeric adducts. The critical process in the initialization of a RAFT-controlled polymerization was found to be the formation of the single monomer-adduct dithiobenzoate species, and by implication, the propagation of the leaving and initiator-derived radical groups.

In the first system studied, i.e. styrene monomer, the poorest leaving group was the styryl (i.e. AS[•] and CS[•]) radical, although the “long chain” value of addition, propagation, and fragmentation rate coefficients need to be achieved before the system is at equilibrium. This could be two or more monomer units for both addition and propagation.

The reasons for the behaviour observed for the RAFT system are suggested as being dependent on the relative reactivities and radical stabilities, and therefore the related addition and fragmentation rate coefficients of the tertiary radical species in the systems and their monomer adducts. This can be extended to all efficient RAFT

systems, where multiple radical species are present, and should not be considered as solely an explanation of the cumyl dithiobenzoate system.

In situ ^1H NMR spectroscopy shows that the first interval of polymerization that could be observed in the studied systems is an initialization period, which has been defined as the period prior to the complete consumption of the initial RAFT agent. In the case of styrene this initialization period shows a more rapid rate of reaction than during the RAFT equilibrium. The rate of polymerization is a function of the values of the propagation rate constants for the initiator and leaving group fragments as well as of all the radical concentrations in the system. It has been shown that a slower rate of reaction during the initialization period compared to the equilibrium period is expected in the case of methyl acrylate and this has been shown to be the case. The initialization period has largely been mistaken for inhibition in the RAFT literature for homogenous reactions. The lack of previous reports of the rapid rate of reaction during this period is suggested as being due to the long chain lengths targeted in other studies, which means that the initialization period would have been completed before significant conversion had occurred, and thus this period may have gone unnoticed in many systems.

The main reasons for the extremely selective and stepwise behavior observed in the initialization period are:

- The fragmentation of the formed intermediate radicals is very selective towards the tertiary radicals used in the experimental section.
- Addition of propagating radicals of degree of polymerization of at least unity to the RAFT agent was much faster than to monomer.

Cases where this behavior might not occur include the use of RAFT agents with low addition rate coefficients, the use of very high initial ratios of $[\text{M}]/[\text{RAFT}]$, or systems in which $k_{p,1}$ is very large. In Chapter five, the potential implications of the initialization process for heterogeneous media will be discussed in more detail.

4.10 References

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Chapter 5: RAFT reactions in Miniemulsions

This chapter is largely based on:

**Controlled, Radical Reversible Addition–Fragmentation Chain-Transfer
polymerization in High-Surfactant-Concentration Ionic Miniemulsions**
McLeary JB, Tonge MP, De Wet-Roos D, Sanderson RD, Klumperman B.
J Polym Sci Part A: Polym Chem; 42: 960-974.

Abstract

Latex stability in living miniemulsions is discussed, followed by a development of a stable miniemulsion system for RAFT. Particle nucleation is discussed in terms of the RAFT mechanism, and NMR spectroscopy is used as a tool to further the understanding of the role of an oil soluble initiator in a RAFT-mediated miniemulsion. Particle size is discussed with reference to the particle formation mechanism. Chain extension of emulsion polymer is examined by 2-dimensional chromatography to examine the degree of living character present.

5.1 Introduction

Controlled and living radical polymerization techniques have traditionally proven difficult to apply to heterogeneous systems.¹⁻³ The agents used to control the polymerization process must be soluble in the locus of polymerization (usually the dispersed, organic phase), but may have more than insignificant solubility in the other phase (typically the continuous, aqueous phase). In cases where the solubility of the agent is low in the phase where little polymerization takes place, transport problems may occur. Surface activity of the RAFT agent has also been reported for heterogeneous RAFT systems,⁴ which may lead to possible changes in colloidal stability, and interfacial polymerization.

Transfer is presumed to be a superior mechanism for controlled polymerization in water-borne organic dispersions, since the agents for reversible end-capping are often relatively small species and may be capable of exiting latex particles throughout the reaction. This would result in loss of the mediating species from the locus of polymerization, and therefore loss of control over the chain growth. Transfer-based systems only involve a significant concentration of short chain species during the early stages of the reaction.⁵

Some of the theoretical aspects of living systems in miniemulsions have been explored by Luo *et al.*⁶ Monomer diffusion in an emulsion system is governed by the monomer chemical potential difference between droplets and particles. After nucleation, the monomer chemical potential of a particle is lower than that of a monomer droplet due to the formation of polymer in the particle. The rate at which monomer diffusion occurs in the system will affect the rate at which particles increase in size, and the sizes that are reached in the system. Based on this model, Luo *et al.*⁶ predicted that emulsion systems would exhibit a super-swelling state if no early equilibrium was reached with respect to the chemical potential of droplets and particles. The model uses two concepts to explain instabilities in the reaction system.

- *Super-swelling, which is the swelling of a droplet or particle in a rapid fashion to a size many times that of the original droplet.*
- *Swelling capacity, which is a measure of the relative amount of swelling in a system, i.e. a ratio of the droplet swollen size to unswollen size.*

Super-swelling could occur if the particle chemical potential was kept low (i.e. by the formation of oligomers rather than high molar mass polymer, which would have a lower free energy of mixing).

For the development that follows compounds i are defined where 1 is monomer, 2 is hexadecane, 3 is oligomer, starting conditions are given as subscript 0, the nucleated and unnucleated oilphases k are given by subscript d for droplet and subscript p for particle. In all of the following equations v_1 is the molar volume of the monomer in m^3/mol , Φ_{ki} is the volume fraction of compound i in phase k , γ gamma is the interfacial energy in N/m; R is the gas constant (J/K mol), $\chi_{i_a i_b}$ is the interaction parameter between compound i_a and i_b , j_i is the ratio of the molar volume of compound i to that of the monomer, and T is the temperature in Kelvin. The interfacial energies for the phases are given by μ_j in equation 5.1 and 5.2.

$$\mu_d = RT \left[\ln \Phi_{d1} + \left(1 - \frac{1}{j_2}\right) \Phi_{d2} + \Phi_{d2}^2 \chi_{12} + \frac{2v_1 \gamma}{r_d RT} \right] \quad (5.1)$$

$$\mu_p = RT \left[\ln \Phi_{p1} + \left(1 - \frac{1}{j_2}\right) \Phi_{p2} + \left(1 - \frac{1}{j_3}\right) \Phi_{p3} + \Phi_{p2}^2 \chi_{12} + \Phi_{p3}^2 \chi_{13} + \Phi_{p2} \Phi_{p3} \left(\chi_{12} + \chi_{13} - \frac{\chi_{23}}{j_2} \right) + \frac{2v_1 \gamma}{r_p RT} \right] \quad (5.2)$$

Where r_i is the radius of phase i , r_0 is the unswollen initial droplet radius, x is the fractional conversion of the monomer, Y is the swelling capacity, y is the weight percent of droplets that have been nucleated (to form particles), ρ_i is the density of compound i , f_2 is the initial weight ratio of ultrahydrophobe to monomer in a particle. In equation 5.3, r_d is the droplet radius.

$$r_d = \left[1 - \frac{y(Y-1)}{100-y} \right]^{1/3} r_0 \quad (5.3)$$

In equation 5.3 the value 100 is derived from the percentage ratio of particles to droplets. In equation 5.4, r_p is the particle radius.

$$r_p = \left(Y - x + \frac{x\rho_1}{\rho_2} + \frac{f_2\rho_1}{\rho_2} \right)^{1/3} r_0 \quad (5.4)$$

The volume fractions of the compounds in the respective phases of both the droplets and the particles are given by equations 5.5-5.9.

$$\Phi_{d1} = \frac{\left(1 - \frac{y(Y-1)}{100-y}\right) \frac{1}{\rho_1}}{\left(1 - \frac{y(Y-1)}{100-y}\right) \frac{1}{\rho_1} + \frac{f_2}{\rho_2} + \frac{x}{(Y-x)}} \quad (5.5)$$

$$\Phi_{p1} = \frac{\frac{\rho_1}{(Y-x)} + \frac{f_2}{\rho_2} + \frac{x}{\rho_3}}{\frac{\rho_1}{\rho_1} + \frac{f_2}{\rho_2} + \frac{x}{\rho_3}} \quad (5.6)$$

$$\Phi_{p2} = \frac{\frac{\rho_2}{(Y-x)} + \frac{f_2}{\rho_2} + \frac{x}{\rho_3}}{\frac{\rho_1}{\rho_1} + \frac{f_2}{\rho_2} + \frac{x}{\rho_3}} \quad (5.7)$$

$$\Phi_{d1} + \Phi_{d2} = 1 \quad (5.8)$$

and

$$\Phi_{p1} + \Phi_{p2} + \Phi_{p3} = 1 \quad (5.9)$$

The model of Luo *et al.* accurately predicted the colloidal instability that occurred in living radical emulsion systems, and suggested recipe improvements to avoid this colloidal instability in a miniemulsion system. To differentiate between living and conventional particles, the assumption is made that j_3 is proportional to degree of polymerization, which will be a function of the ratio of the conversion and controlling agent concentration, which is reasonable in an efficiently controlled system. In a conventional polymerization the degree of polymerization, will however not be related to conversion in the same fashion, and a limiting value can be used. For the purposes of the simulations presented here j_3 was set to 100000, representing high molecular weight polymer. The droplet diameter was chosen as 60 nm. The weight percentage ultrahydrophobe was set at 4% and for figure 5.1, the fractional conversion in the particles was set at 0.1%. The temperature was set to 75 °C. The interaction parameters were taken from the literature, and the given system is that of methyl methacrylate and hexadecane.⁶ The RAFT agent to monomer ratio was set at 0.01.

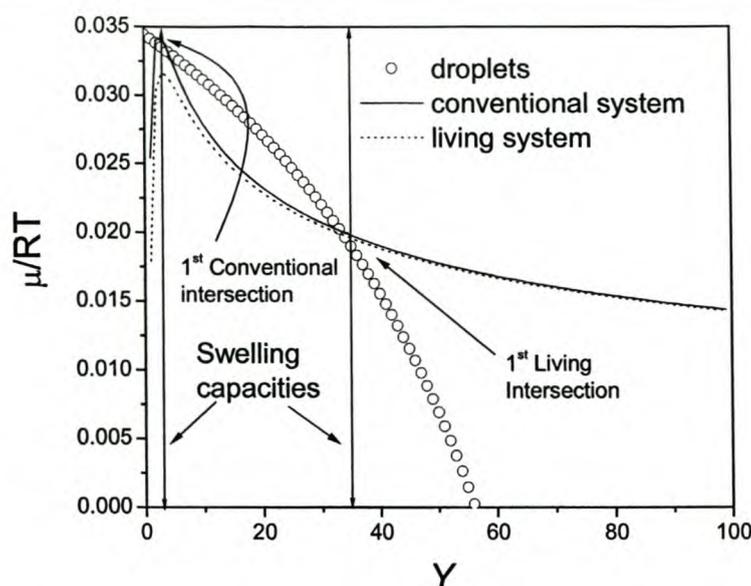


Figure 5.1 The chemical potential versus swelling capacity of droplets, conventional and living particles of 60 nm diameter containing 4 weight % cosurfactant at 0.1% conversion.

If we examine the chemical potential plot produced by the model under the aforementioned conditions (figure 5.1), there are three intersections of the chemical potentials of the conventional polymerization without a controlling agent, and the droplet chemical potential as the swelling ratio Y increases. When the system arrives at the first intersection, the monomer transport is effectively stopped, as there is no longer a potential difference between the particles and the droplets. This was denoted as the normal swelling state.

In the case of a living system however, the lower mixing energy in the case of the oligomeric chains produced in the living system leads to a lower chemical potential, and only a single intersection point is observed. An equilibrium swelling is reached at a much higher swelling capacity. This leads to a large amount of monomer transport between unnucleated droplets and particles. This “super swelling” effect could lead to particles large enough to be shear sensitive ($1-10 \mu\text{m}$),⁶ as well as a range of particle sizes making coagulation between particles by a heterocoagulation mechanism more probable.

Luo *et al.* concluded that larger particles, higher cosurfactant levels and lower molecular weight controlling agent concentrations would all lead to a more stable latex. The most effective method for forming a stable miniemulsion is the inclusion of a very hydrophobic species such as hexadecane prior to homogenization.⁷ The

hydrophobic species or co-stabilizer acts to prevent net monomer diffusion by decreasing the monomer chemical potential of the droplets in a system. Luo *et al.*⁶ suggested that the concentration of this hydrophobe played a critical role in stabilizing the initial droplets in controlled radical miniemulsion systems. The hexadecane levels used are critical, as shown in the simulation results in figure 5.2.

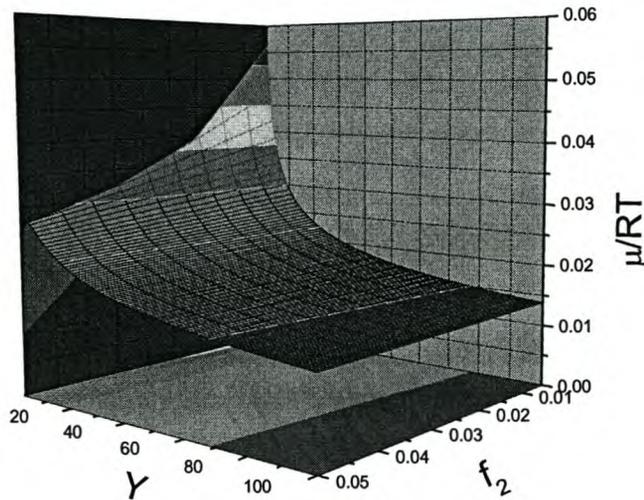


Figure 5.2 The particle chemical potential as a function of the ultrahydrophobe content (f_2) and swelling capacity (Y) of the particle.

It can be seen that below a hydrophobe weight ratio of 0.03, controlled particles with a radius of 30 nm the particle chemical potential plane inverts and the increasing chemical potential of the particles will lead to immediate particle instabilities. Figure 5.3 shows the droplet chemical potential for the corresponding reaction.

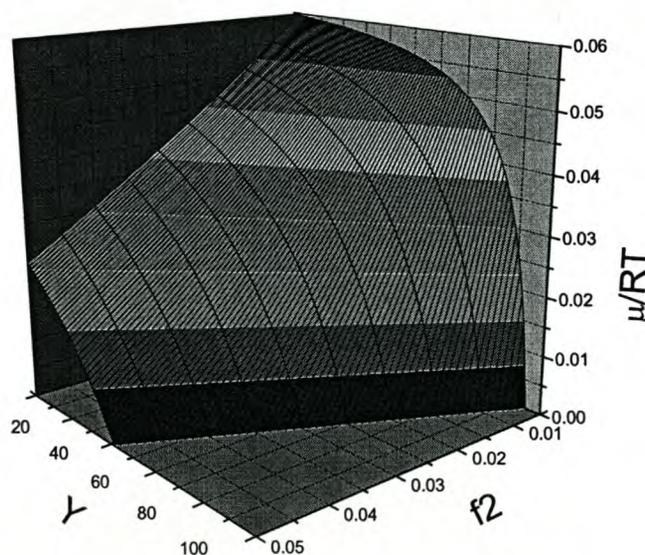


Figure 5.3 The droplet potential for conditions modelled in figure 5.2.

When the two planes are examined and their intersections calculated, It can be shown that below a hexadecane weight ratio of 0.03, controlled particles with a radius of 30 nm are predicted to show only a single potential curve intersection with the droplet chemical potential at high swelling (Y values). Thus, for the conditions shown in figures 5.2 and 5.3, superswelling is predicted at low hexadecane levels. There will be no early intersection of the planes. Luo *et al.*⁶ predicted particle size effects on destabilization. The model suggests that small particle sizes should inevitably lead to destabilization if a costabilizer such as hexadecane is not used at sufficiently high concentrations. However, the model does not take kinetic considerations into account. The number of nucleated particles is a function of time, which should be taken into account for a full description of the systems. Luo *et al.* predicted that with effective nucleation of the particles there would be a lower equilibrium swelling capacity. Figure 5.4 shows the effect of increasing the number of particles nucleated to 10%.

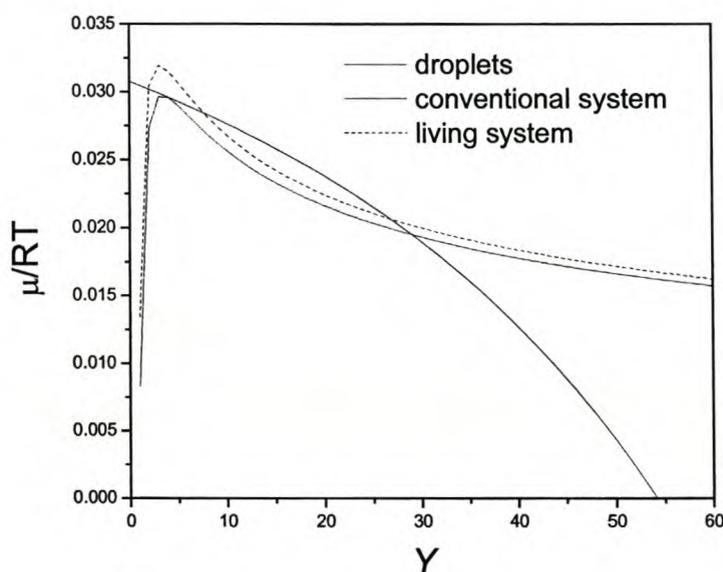


Figure 5.4 The chemical potential versus swelling capacity of droplets, conventional and living particles of 60 nm diameter containing 4 weight % cosurfactant at 10 % particle nucleation.

Comparisons of figure 5.1 and figure 5.4 show that increasing the weight percentage of particles nucleated from 0.1% to 10% causes a decreased equilibrium swelling and may remove the superswelling state, even at 60nm particle sizes. The effect of monomer conversion within the particles also has a substantial influence on the superswelling behaviour predicted by the model. This is very significant in the light of the retardation behaviour shown in RAFT mediated polymerizations.⁸⁻¹⁰

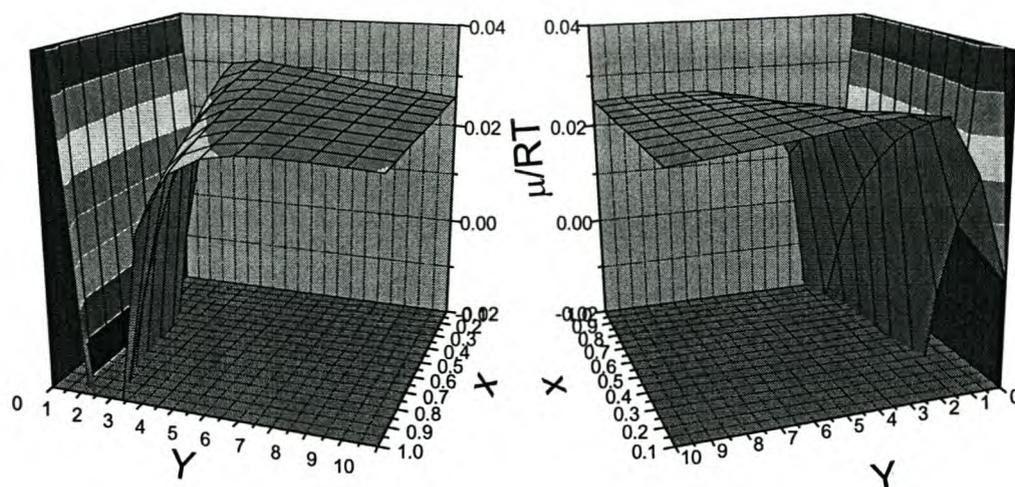


Figure 5.5 The particle chemical potential as a function of the superswelling capacity and conversion in the particles.

In figure 5.5 it can be seen that if the fractional conversion in the particles is above 10%, then a saddle point occurs, which predicts that at the conditions discussed above, particles above 10% conversion will behave in a stable fashion, and will not undergo superswelling. The intersection of the particle chemical potential plane with the droplet chemical potential plane (fig 5.3) will occur at low swelling capacity, similarly to figure 5.4.

It has been shown that surface packing of surfactant in miniemulsions is dependent on the particle size and surfactant type.^{7,11} A dense ionic surfactant monolayer, where the particle surface area per surfactant is approximately equal to the area of the surfactant headgroup, simulates the packing that occurs in polymeric surfactant systems. The dense monolayer occurs under high surfactant concentration conditions and after optimal homogenization.¹²

De Brouwer *et al.*¹³ have shown that the use of polymeric non-ionic surfactants, which might limit the exit of oligomeric species,¹⁴ are suitable for the prevention of phase separation, while maintaining good control of the reaction. The possibility that these conditions inhibit super-swelling is also high because of this possible barrier to exit. Super-swelling can also be prevented by ensuring that polymer is present in particles from the beginning of the reaction with sufficient costabilizer. Vosloo *et al.*¹⁵ followed this approach with some success.

In this chapter, high ionic surfactant concentration miniemulsions have been explored to determine if super-swelling, along with the subsequent destabilization, can be overcome by using systems that are expected to reduce exit rates,¹⁴ and by using sufficiently high co-stabilizer concentrations. The results show that under the correct conditions, traditional RAFT agent systems achieve mediating performance that is very similar to RAFT-mediating performance in homogenous media, while having the advantages of a heterogeneous environment.

5.2 Experimental

5.2.1 Chemicals

The surfactant cetyl trimethylammonium bromide (CTAB, ACROS, 99%+), hexadecane (ACROS, 99%), azo bis(cyanovaleric acid) (ACP, Sigma-Aldrich, 75%), and sodium dodecyl sulfate (SDS, Sigma-Aldrich, 90%) were used as purchased. Styrene (Protea Chemicals 99.5%) and methyl methacrylate (ICI Chemicals and Polymers) were washed with 0.3 M KOH, and distilled under vacuum prior to use to remove inhibitor and polymer. Azo-bis(isobutyronitrile) (AIBN, Riedel de Haen) was recrystallized from AR grade methanol and found to be ~99% pure by ¹H NMR.

5.2.2 Analysis

Molar masses were determined using Size Exclusion Chromatography (SEC). The SEC instrument consisted of a Waters 717plus Autosampler, Waters 600E System Controller (run by Millennium³² V3.05 software) and a Waters 610 fluid unit. A Waters 410 differential refractometer was used at 35 °C as detector. Tetrahydrofuran (THF, HPLC-grade) sparged with IR-grade helium was used as eluent at a flow rate of 1 mL min⁻¹. The column oven was kept at 30 °C and the injection volume was 100 µL. Two PLgel 5 µm Mixed-C columns and a pre-column (PLgel 5 µm Guard) were used. The system was calibrated with narrow polystyrene standards ranging from 800 to 2×10⁶ g mol⁻¹. All molar masses are reported as polystyrene equivalents. Particle sizes were determined by dynamic light scattering using a Malvern Instruments Zetasizer 1000 HAS with a fixed scattering angle of 90° at 25 °C assuming a monomodal distribution. TEM images were obtained from a JEOL 200 CX instrument at the University of Cape Town's electron microscopy unit.

5.2.3 Sample preparation

Polymer samples for SEC analysis were dried, dissolved in THF at a concentration of 5 mg mL^{-1} and filtered through a $0.45 \text{ }\mu\text{m}$ filter. For light scattering determinations, latexes were diluted with 0.01 M NaCl solution.

5.2.4 Miniemulsion Preparation and Polymerization

Miniemulsions were prepared by dissolving water-soluble components in deionized water and separately dissolving oil soluble components in monomer. The separate solutions were stirred to homogeneity and then combined, followed by thorough mixing with a magnetic stirrer for one hour to provide a pre-emulsion.

During the course of the investigation a number of different sonication vessels, times and conditions were used to determine the effect of preparation on the system. All of the reported emulsions were prepared in such a way as to arrive at a homogeneously dispersed system. From the significant number of variables in the method of preparation, it is quite conceivable that many research groups that have difficulty preparing stable latexes via this method have simply not achieved the correct laboratory conditions. Each instrument, amplitude, tip depth, vessel width, viscosity (i.e. surfactant, particle size and monomer) used provided different behaviours. Some methods used successfully even involved multiple sonication sessions with short recovery intervals.

A typical example of a preparation procedure used to homogenize a 100 mL latex sample would be the following: The pre-emulsion was sonicated at 50% amplitude (44 Watts) for 30 minutes in a temperature-controlled vessel to minimize heating of the pre-emulsion (using a Sonics and Material Vibra cell Autotune series high intensity ultrasonic processor 750 VCX), with no pulse. Despite the attempts at temperature control, some heating of the dispersions occurred during this period, although this was typically less than $10 \text{ }^\circ\text{C}$. It should be noted that no detectable polymerization occurred during the sonication process, which in itself is quite unusual, considering some of the more aggressive conditions used (i.e. 30 minutes sonication). In general, it was found that $\sim 80\text{-}100 \text{ kJ}$ was sufficient to prepare homogenized latexes of $50\text{-}100 \text{ mL}$.

Heating, under nitrogen, at the indicated temperatures, polymerized the resulting miniemulsions. Samples were periodically removed via a septum and needle and dried for analysis. Conversions were determined gravimetrically. Oil phase and water phase components are reported as concentrations in the respective phases.

5.3 Simplifications

To simplify the following discussion we are going refer to 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid (**1**) and cumyl dithiobenzoate (**2**) as agents (1) and (2).

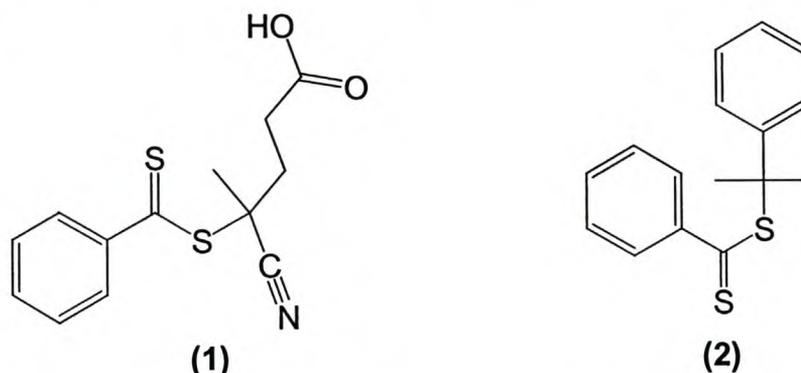


Figure 5.6 Chemical structures of RAFT agents 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid (1) and cumyl dithiobenzoate (2).

5.4 Surfactant concentration effects

The effect of surfactant concentration on the particle size of a RAFT miniemulsion using (1) and polymeric dithiobenzoates (see 4.3.1) was investigated. Particle size was analyzed and area per surfactant group was calculated as show below. In Table 5.1, the reactions and results obtained for the particle size determination are tabulated, showing compositions and characteristics of styrene miniemulsions in the presence of dithiobenzoates used in the testing of particle size of polymerized miniemulsions.

Table 5.1: Reactions used for size analysis. w_m and w_s are weight fractions of monomer and surfactant respectively, and v_{oil} and v_{water} are the respective volumes of the oil and water phases. Conditions: reaction 1: RAFT agent (PMMA) dithiobenzoate ($7200 \bar{M}_n$, \bar{M}_w/\bar{M}_n 1.07); reactions 2- 5,7: RAFT agent (PBMA) dithiobenzoate ($6600 \bar{M}_n$, \bar{M}_w/\bar{M}_n 1.07); 6: RAFT agent (1). Oil phase and water phase components are provided as concentrations in the respective phases.

Reaction	RAFT (10^3) mol.dm ⁻³	Temperature (°C)	Hexadecane mol.dm ⁻³	CTAB (10^2) mol.dm ⁻³	diameter (nm)	$\frac{v_{oil}}{v_{water}}$	$\frac{W_m+W_s}{W_s}$	$\frac{\text{area}}{\text{chain}}$ nm ²
1	1.57	80	0.371	41.09	34	0.29	2.77	0.18
2	1.56	80	0.216	16.97	38	0.26	5.09	0.41
3	1.64	80	0.408	8.61	57	0.27	9.23	0.53
4	1.56	80	0.227	3.39	86	0.26	21.45	0.92
5*	1.58	80	0.383	4.13	75	0.26	17.61	0.82
6**	9.30	70	0.192	6.85	62	0.24	11.04	0.63
7	1.05	70	0.193	1.47	130	0.25	47.74	1.30

*Final latex $\bar{M}_n = 90200$ $\bar{M}_w/\bar{M}_n = 1.42$ **Final latex $\bar{M}_n = 29600$ $\bar{M}_w/\bar{M}_n = 1.31$.

The surface area per surfactant molecule was calculated using the model of Antonietti *et al.*¹² (Table 5.1) from the stoichiometry, particle size, and the assumption that all surfactant molecules are located at the droplet surface for this system, creating, a more or less, dense packing of surfactant as seen in figure 5.8.

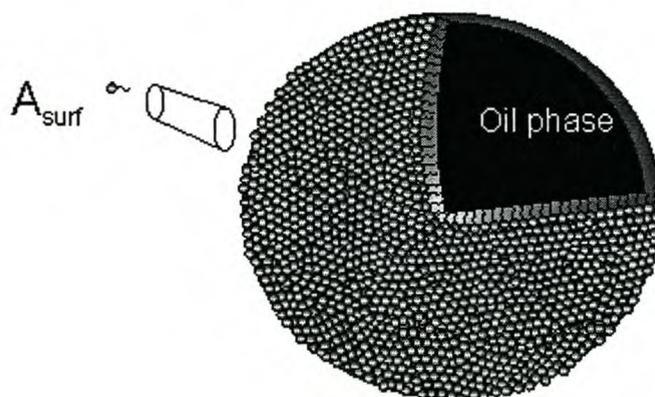


Figure 5.8 Schematic representation of the surfactant packing and headgroup area per surfactant on an emulsified droplet with a dense packed surfactant layer.

This means that the total area of the dispersed particles is:

$$A_{tot} = 3(W_m + W_{surf}) / (\rho R_h) \quad (5.9)$$

Where the weight fractions of oil W_m and surfactant W_{surf} are divided by the average density of the droplet ρ multiplied by the hydrodynamic radius of the droplet R_h . When we correct for the absolute number of surfactant molecules N_{surf} i.e.

$$N_{surf} = N_A W_{surf} / M_{surf} \quad (5.10)$$

Where M_{surf} is the molecular weight of the surfactant and N_A is Avogadro's number. Then it is possible to calculate that the area per surfactant A_{surf} is:

$$A_{surf} = \left(\frac{(W_m + W_{surf})}{W_{surf}} \right) \cdot \left(\frac{3M_{surf}}{N_A \cdot \rho} \right) \cdot \left(\frac{1}{R_h} \right) \quad (5.11)$$

Although this is only strictly true for ideal systems, it gives an indication of the behaviour of the systems in question. The very small particle sizes generated imply that the total droplet surface area is substantially higher than for a comparable emulsion system with similar component concentrations. In a conventional system, there would be a larger number of micelles present, and a much smaller number of large droplets. In a miniemulsion system, the free surfactant concentration is lower, and the number of micelles that form in the system is much lower than might be expected for the same surfactant concentration when used in a conventional emulsion. Landfester *et al.*⁷ reported that in most correctly prepared miniemulsions, the aqueous surfactant concentration is below the critical micelle concentration until at least *ca.* 50 wt% surfactant with respect to monomer. This was taken as a limit to the range in which miniemulsions can successfully be formed. Figure 5.7 shows the effect of surfactant concentration on particle size and area per surfactant in the systems.

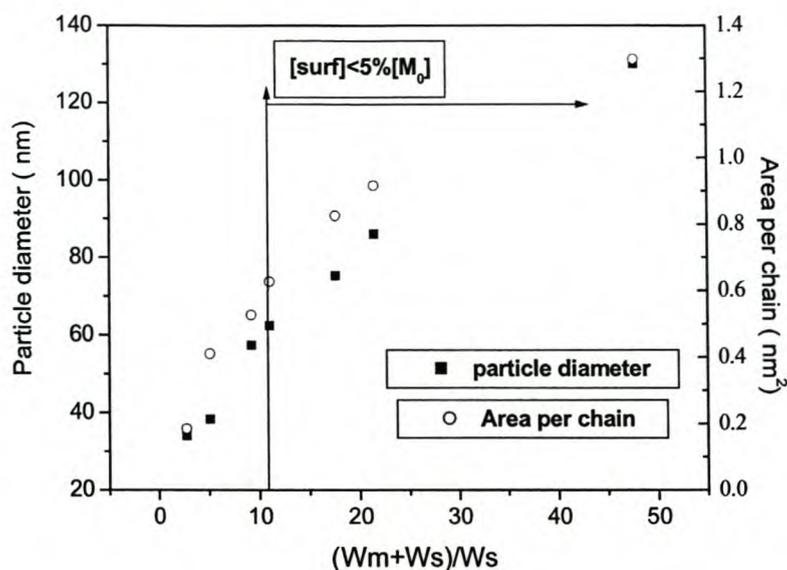


Figure 5.7 The effect of surfactant concentration and solids content on the particle diameter for CTAB-based miniemulsions prepared and polymerized under identical conditions (see Table 5.1). Typical stable formulations provided particles sizes of less than 80 nm.

In the work presented here, it was found that RAFT-styrene miniemulsion systems in which the CTAB concentration was less than 5% of the styrene concentration (this concentration is marked by a vertical line on Figure 5.7) tended to form a separate deep red monomer layer within the first 10% of conversion. The monomer layer which has been reported previously, ultimately led to a red polymeric coagulum in the reactor.¹⁶ The coagulum was usually between 10 – 20% of total solids at final conversion. The molar mass of the polymer in the final latex in such cases showed a slight degree of control, but was not in accordance with predictions, in agreement with the results of previous studies.^{17,18} The reasons for the stability problems at lower surfactant concentrations are unclear but the dense packing of surfactant is thought to be an important factor.

In RAFT-styrene miniemulsions in which the CTAB concentration was greater than 5% of the monomer concentration the polymerized miniemulsions did not show the red coagulum. The final amount of coagulum in these cases was found to be approximately 1% or less of the original monomer concentration. Separation of a red-coloured monomer phase was not observed. The stability of the polymerized miniemulsions was excellent, with latexes typically stable for more than six months. The stability is significantly different to systems that have been reported in the literature with lower surfactant and ultrahydrophobe concentrations, which are often

destabilized by polymerization.¹⁶ The simulations carried out by Luo *et al.*⁶ predict destabilization at relatively small particle sizes due to the super-swelling effect. In this case however, it should be noted that the concentration of co-stabilizer or ultrahydrophobe is significantly higher than what was used in the simulations where destabilization occurred. As also indicated by the simulations, this higher concentration will prevent a super-swelling state, and should remove the shear sensitivity that is observed in literature systems. The lower surfactant and hydrophobe concentrations used by Tsavalas *et al.*,¹⁶ who were unable to prepare stable dithiobenzoate mediated latexes, and the stability of the miniemulsions obtained here, are consistent with the predictions of these simulations.

It is important to note that particle size also plays a substantial role in the rate of polymerization and that varying the concentration of the surfactant will therefore have a substantial influence on the rate of the polymerization. The rate at which chains grow is also a potential factor in the formation of stable latex.

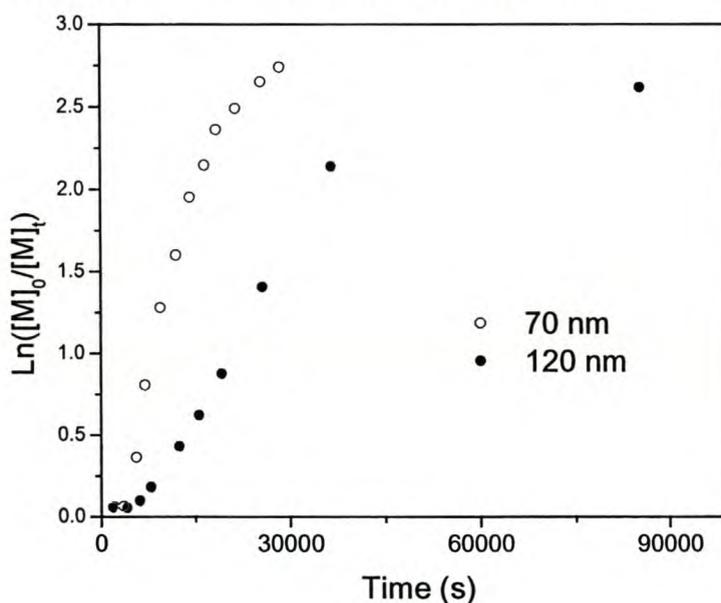


Figure 5.9 The rate of polymerization of styrene for two reactions in which cumyl phenyl dithioacetate (PPDDTA), initiated by AIBN in the presence of CTAB as surfactant. The oil phase and aqueous phase ratios are identical and the surfactant concentration of the 70 nm particles was twice that of the 120 nm particles.

Figure 5.9 illustrates the difference in polymerization rate that is obtained by doubling the surfactant concentration in the system. The particle sizes that were determined were measured after polymerization. In principle, the particle size should be maintained, and a one-to-one copy of the droplets should be produced. This is

however only possible with 100% nucleation efficiency, which is rare.¹⁹⁻²¹ The determination of droplet size prior to polymerization is a difficult process due to the transient nature of droplets, and it will be shown below that the use of techniques that require dilution are rather inefficient due to the rapid change in particle size that occurs in the system. The reliability of particle size measurement using dynamic light scattering was tested to determine the effect of the presence of polymer. A model emulsion was prepared and light scattering was used to determine particle size with conversion in the reaction. The particle size was monitored during the experiment. To make use of the light scattering apparatus it is necessary to first dilute the latex in a salt solution and the ionic latexes were found to show large instabilities under these conditions. This led to substantial variation in the results that were determined. The measured particle size dropped substantially once significant polymer was formed in the system, this is most probably an artifact of the determination procedure. In principle, a miniemulsions droplet should not show much change in size during polymerization, except in the case of low nucleation efficiency, in which case the particle size should increase with conversion. The dilution of the latex with salt solution is expected to explain the artifact due to disruption of the surfactant packing. Figure 5.10 shows the experimental effect of increasing conversion on the determined particle sizes via light scattering.

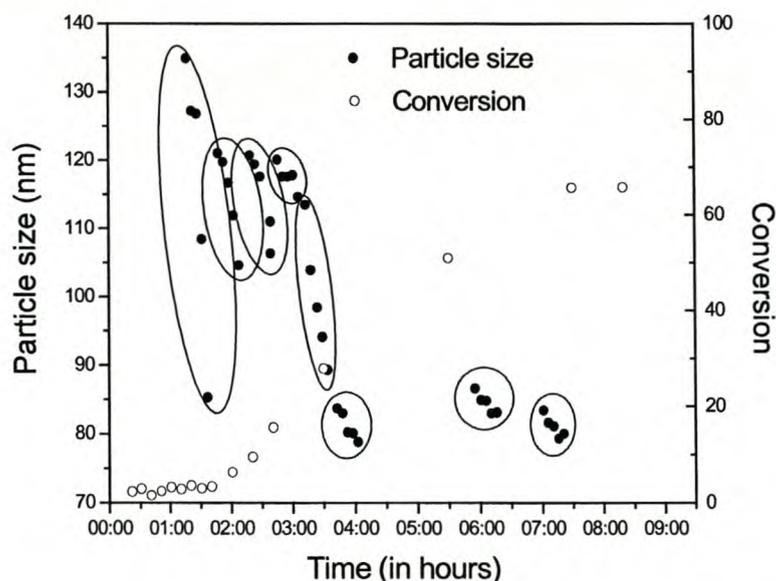


Figure 5.10 Droplet size versus time in the zetasizer. Data was acquired in 5 data point series and the individual points are displayed.

Within each analysis, there are substantial changes in particle size value determined, and the change in particle size within each set of five determinations demonstrates the change in droplet size in the presence of salt dilution. Once conversion in the samples reaches ~20%, the readings become stable and quite repeatable. The unreliability of the technique for samples that contain low amounts of polymer is quite clearly illustrated.

5.5 General behaviour

Having developed a method for preparing miniemulsions that were stable in the presence of a dithiobenzoate RAFT agent during polymerization, investigations were carried out to determine the degree of control of molecular weight that could be obtained in these miniemulsion systems. Figure 5.11 shows molar mass distributions for reaction 15, the miniemulsion polymerization of styrene (20g, 0.191 mol) in the presence of hexadecane (3.93×10^{-3} mol) with AIBN initiator (6.70×10^{-5} mol) in SDS (3.46×10^{-3} mol) and water (81.2 g) at 75 °C, total volume ~100mL. Reaction details for the miniemulsion reactions carried out with dithiobenzoate agents are shown in Table 5.2.

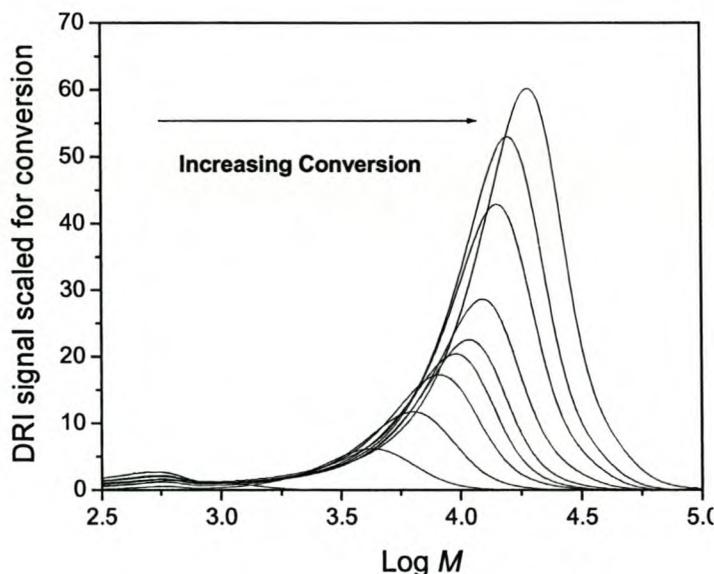


Figure 5.11 Evolution of molar mass distributions with conversion for reaction 15 (Table 5.2) for the miniemulsion polymerization of styrene (0.191 mol) in the presence of hexadecane (3.93×10^{-3} mol) with AIBN initiator (6.70×10^{-5} mol) in SDS (3.46×10^{-3} mol) and water (81.2 g) at 75 °C.

Table 5.2: Miniemulsion compositions and characteristics for testing molar mass control using RAFT agent (1) unless otherwise stated. Temperature of polymerization was 85 °C for reactions 8, 18; 70 °C for reactions 9, 10, 12; and 75 °C for reactions 11, 13 – 17. Oil phase and water phase components are provided as concentrations in the respective phases.

Reaction	$\frac{v_{oil}}{v_{water}}$	HD mol. dm ⁻³	Initiator/ (10 ³) mol.dm ⁻³	RAFT mol.dm ⁻³	Surfactant (g.dm ⁻³)	diameter (nm)	Conversion	SEC \bar{M}_n	Predicted \bar{M}_n	\bar{M}_w/\bar{M}_n
8*	0.23	0.18	AIBN/7.62	0.045	SDS/ 24.4	86.9	0.74	18000	13100	1.34
9*	0.22	0.37	ACP/39.29	0.094	CTAB/ 33.5	69.6	0.82	9700	8300	1.22
10*	0.24	0.19	AIBN/3.05	0.057**	CTAB/ 25.3	73.3	0.57	12700	10300	1.2
11*	0.23	0.18	AIBN/15.2	0.045	CTAB/ 26.3	65.7	0.84	21100	13100	1.26
12 [#]	0.23	0.18	AIBN/15.2	0.045	SDS/ 25.3	102	0.83	15700	18400	1.19
13*	0.24	0.18	ACP/3.36	0.044	CTAB/ 24.6	81.0	0.80	16200	14200	1.35
14*	0.23	1.2	AIBN/3.36	0.046***	SDS/ 26.3	--	0.59	9800	12000	1.42
15*	0.23	0.19	AIBN/3.36	0.045	SDS/ 26.3	--	0.59	11700	12300	1.50
16*	0.24	3.85	AIBN/4.58	0.083***	SDS/ 25.0	--	0.63	6900	7500	1.32
17*	0.24	0.18	AIBN/3.00	0.045	SDS/ 25.0	--	0.43	9700	9900	1.14
18*	0.24	0.18	AIBN/3.00	0.045	SDS/ 25.0	--	0.77	15500	16500	1.21

* The monomer used here was styrene. ** (PMMA)dithiobenzoate ($\bar{M}_n = 910$ $\bar{M}_w/\bar{M}_n = 1.41$) was used as RAFT agent here. [#] The monomer used here was MMA. *** RAFT agent (2).

Figure 5.12a shows \bar{M}_n and PDI versus conversion for reactions 14 (RAFT agent 2) and 15 (RAFT agent 1) both carried out at 75 °C (0.045 mol.dm⁻³ RAFT, 3.0 × 10⁻⁴ mol.dm⁻³ AIBN) and figure 5.12b shows \bar{M}_n and PDI versus conversion for reactions 17 and 18 (0.045 mol.dm⁻³ RAFT agent (1), 3.0 × 10⁻⁴ mol.dm⁻³ AIBN) carried out at 75 and 85 °C. The monomer in all cases is styrene, the surfactant is SDS, and specific polymerization conditions are stated in Table 5.2.

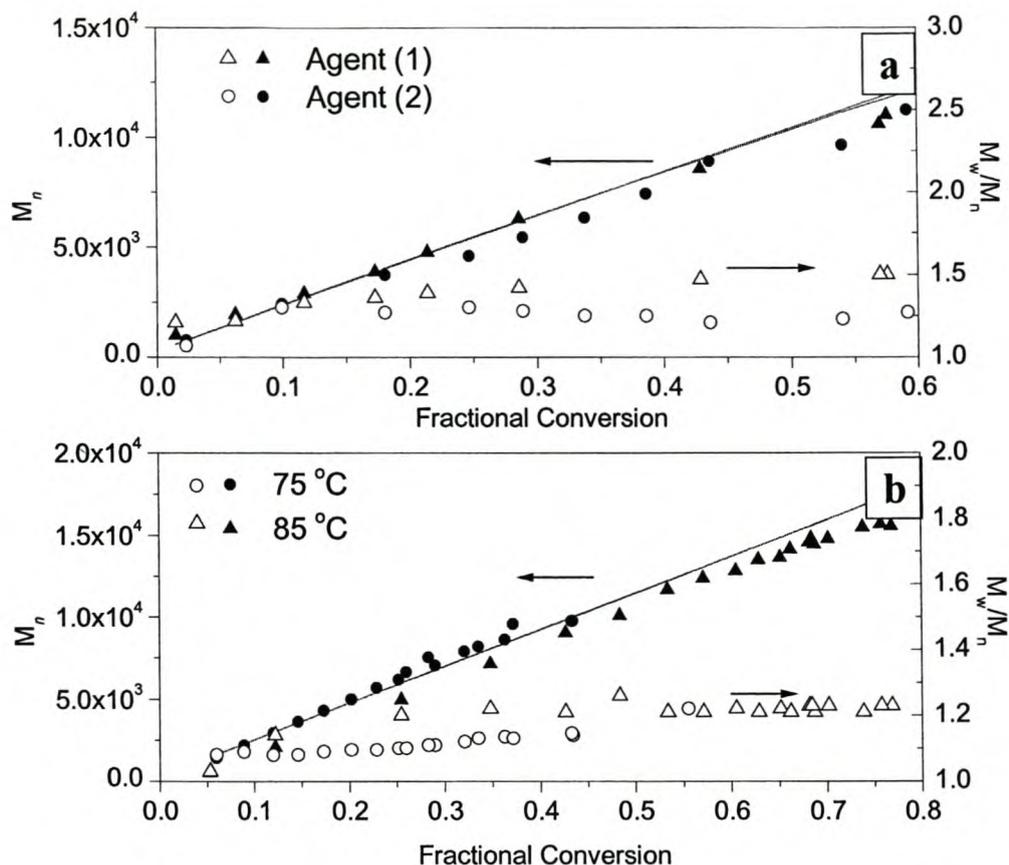


Figure 5.12 Evolution of \bar{M}_n and PDI for RAFT miniemulsion polymerizations: (a) reactions 14 (RAFT agent (2)) and 15 (RAFT agent (1)) both carried out at 75 °C (0.045 mol.dm⁻³ RAFT, 3.0 × 10⁻⁴ mol.dm⁻³ AIBN); (b) reactions 17 and 18 (0.045 mol.dm⁻³ RAFT agent (1), 3.0 × 10⁻⁴ mol.dm⁻³ AIBN) carried out at 75 and 85 °C. The monomer in all cases was styrene and the surfactant was SDS. Specific polymerization conditions are stated in Table 5.2.

The lines indicating the predicted number average molar masses were calculated using equation 5.12:

$$\bar{M}_n = M_{\text{RAFT}} + \frac{x[M]_0 M_M}{[\text{RAFT}]_0} \quad (5.12)$$

Where \bar{M}_n is the predicted molar mass, M_M is the monomer molar mass, M_{RAFT} the molar mass of the RAFT agent, $[M]_0$, $[\text{RAFT}]_0$ are the initial concentrations of the monomer and RAFT agent. Equation 5.12 was chosen, rather than the more complete expression shown in chapter four (equation 4.5), which includes chains originating from the RAFT agent and chains originating from the primary (initiator-derived) radicals. Equation 4.5 can also be made more complete by the inclusion of the radical

particle entry efficiency, given in chapter two by equation 2.17. The latter approach, which is given by equation 5.13 is for example used by Monteiro *et al.*¹³

$$\bar{M}_n = M_{\text{RAFT}} + \frac{x[M]_0 M_M}{[\text{RAFT}]_0 + \left(\frac{k_{tc} + 2k_{td}}{k_t}\right) \left(\left(\frac{\sqrt{f_{aq} k_d [I] (k_{tc} + 2k_{td})_{aq}}}{k_{p, aq} C_w} + 1 \right)^{1-z} \right)} f[I]_0 (1 - e^{-k_d t}) \quad (5.13)$$

For the work covered in this chapter, equation 5.12 provided a better fit to the data. Although it is strictly correct to consider all chains generated by both the RAFT agent and initiator when calculating \bar{M}_n , equation 5.12 will provide a good fit for the evolution of \bar{M}_n if the contribution from initiator-derived chains is negligible (e.g. if the efficiency of radical entry multiplied by the efficiency of radical generation is very small). The contribution from initiator-derived chains will be small when the initiator concentration is very low with respect to the RAFT agent concentration, or when few initiation events produce polymer in a measurable mass range, such as when initiator efficiency is low. Presumably, initiator efficiency is low in the current system, probably due to only a small fraction of initiator-derived radicals resulting in a true initiation (e.g. entry) event, in which case, equation 5.12 provides a good fit to the data. The slight deviations from linearity in the data are due to the role of initiator. A direct comparison of oil-soluble (RAFT agent (2)) and water-soluble (RAFT agent (1)) leaving radicals is shown in Figure 5.12a. The only difference between the reactions is the type of RAFT agent leaving group. Under precisely the same conditions it can be seen that the control is slightly better with the water insoluble leaving radical, while the correspondence with predicted values is slightly better with the water-soluble leaving radical. The behaviour may be indicative of entry efficiency differences, but these deviations are within the experimental error for this system, and so no significant conclusion can be drawn.

The pH stability of dithioesters has been examined by Thomas *et al.*²² who found that in the pH range of the latexes synthesized in this study (~pH 4.5), significant degrees of degradation of the dithioester functionality takes days, and thus cannot be responsible for the observed deviations of molar mass from predictions. In Figure 5.12b, two reactions with the same leaving group (RAFT agent (1)) are presented at different temperatures. The polydispersity of the polymer in the reaction carried out at 85 °C is slightly higher at lower conversions than that of reaction carried out under duplicate conditions at 75 °C. It should be kept in mind that initiator decomposition is

temperature-dependent, and the radical fluxes in the reactions will differ substantially. The reactions are labelled in Table 5.2 as reactions 17 and 18 (0.045 mol.dm⁻³ RAFT, 0.0003 mol.dm⁻³ AIBN). It should be noted that although some broadening of the distributions occurred at higher conversions (this increase in PDI at higher conversions is possibly due to bimolecular termination via combination, giving a high M shoulder, with very little chain growth per unit time occurring), the linearity of \bar{M}_n versus conversion and PDI remain excellent. The PDI data is superior to the published results of Butté *et al.*¹⁷ and Lansalot *et al.*¹⁸ Comparisons between these and the current system will be discussed further in section 5.9. Figure 5.13 shows semilogarithmic plots of monomer conversion *versus* reaction time. The monomer and surfactant are styrene and SDS respectively in all cases and the concentrations are 22% v/v oil-to-water and 25 g.dm⁻³ surfactant, which provided latexes that were of similar particle size.

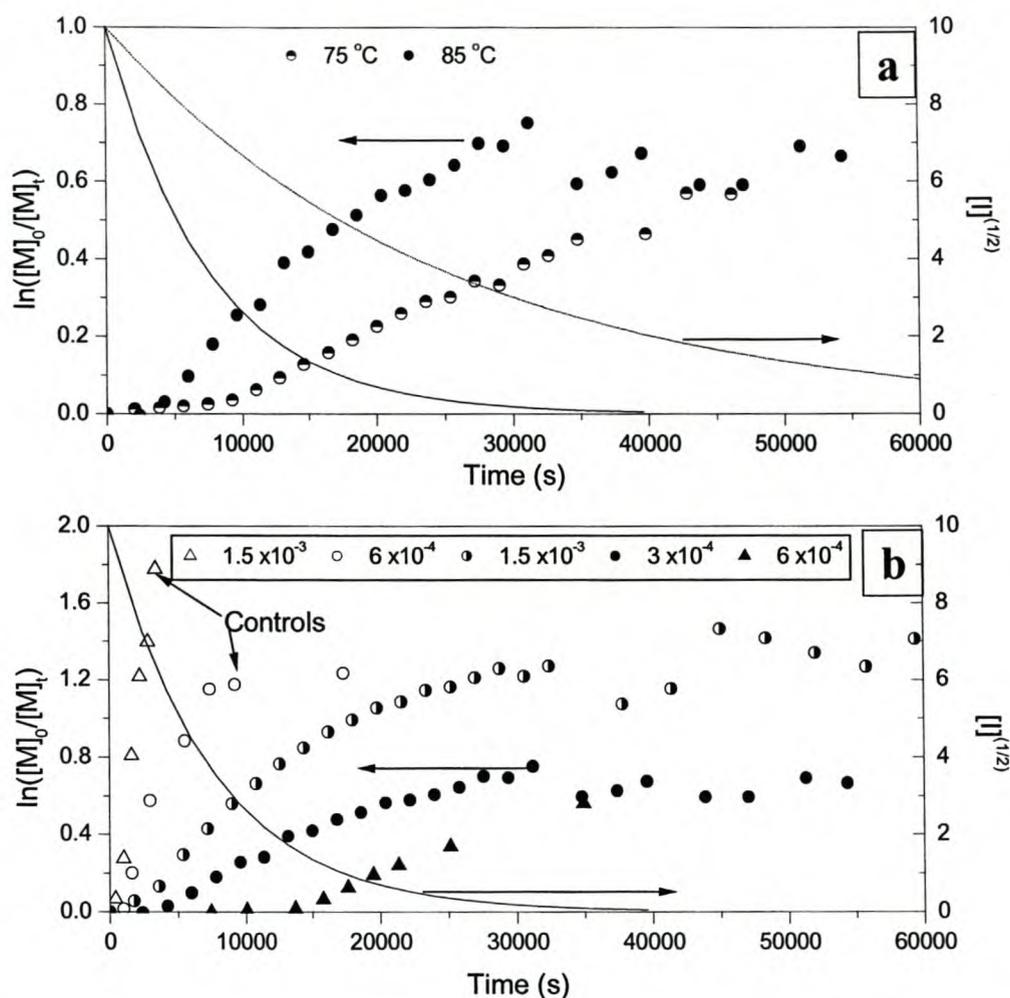


Figure 5.13 Semilogarithmic plots of monomer conversion *versus* reaction time (points) (a) A comparison of temperatures (75 and 85 °C) holding the concentrations of the RAFT agent (1) constant at 4.5×10^{-2} mol. dm^{-3} and the initiator constant at 3.0×10^{-4} mol. dm^{-3} (b) A comparison of initiator concentrations carried out at 75 °C holding the concentration of the RAFT agent (1) concentration constant at 0.045 mol. dm^{-3} (closed symbols). The open symbols are duplicate reactions in the absence of RAFT agent. The monomer and surfactant are styrene and SDS respectively in all cases and the concentrations are 22% v/v oil-to-water and 25 g. dm^{-3} surfactant. Initiator decays are plotted (lines) to show the radical generation in the systems.

The comparison of temperatures holding the concentrations of the RAFT agent (1) constant at 4.5×10^{-2} mol. dm^{-3} and the initiator constant at 3.0×10^{-4} mol. dm^{-3} in Figure 5.13a shows the effect of increased radical flux on the rate of polymerization at the same reagent concentrations by increasing the temperature. It can be seen that the rate is substantially increased at higher temperatures, and the apparent inhibition period in the reaction is decreased. The comparison of initiator concentrations carried out at 75 °C, holding the concentration of the RAFT agent (1) concentration constant at 0.045 mol. dm^{-3} in Figure 5.13b shows the effect of initiator concentration on the

rate of polymerization. Increasing the initiator concentration causes a substantial increase in the rate of the reactions. Two control experiments that did not contain RAFT agents are shown for comparison purposes to show the rate retardation that occurs when a dithiobenzoate agent is added to a reaction. The control experiments are of precisely the same composition apart from the AIBN concentration; both contain SDS as surfactant, but have a RAFT agent concentration of zero. The final conversion in the controls is superior to that of the RAFT reactions, but do not reach full conversion. The large improvement in behaviour at higher initiator concentrations for the RAFT systems, in terms of both the conversion reached and the rate of polymerization, did not result in significant loss of control.

The observed maximum rate (and corresponding maximum propagating radical concentration) early in the miniemulsion reactions is quite significant in terms of the mechanism of the overall reaction. The slopes of the plots in Figure 5.13 for the miniemulsions are proportional to the overall propagating radical concentrations in the reactions. For a miniemulsion (or emulsion) system where the locus of polymerization is the latex particles, the radical concentrations are proportional to the product of the number of nucleated latex particles and the average number of propagating radicals per particle in each of these latex particles (\bar{n}). The early maximum propagating radical concentration implies an early maximum in either or both of these quantities. In the context of the model developed by Luo *et al.*⁶ this is quite significant as efficient particle nucleation will prevent the superswelling state and allow the formation of a stable latex as we saw in section 5.1. Interpretation of the value of \bar{n} depends to some extent on whether these systems display “pseudo-bulk” or “zero-one” kinetics, which mainly depends on the fate of radicals entering a latex particle. To provide more insight into the early polymerization kinetics it was decided to return to *in situ* NMR.

5.6 NMR spectroscopy as an analytical tool for the analysis of emulsions

The use of *in situ* ^1H NMR for the analysis of polymerizations in homogeneous media can be very successful, as discussed in chapter four. However, the use of NMR in a heterogeneous system is not as easily achieved. To determine whether the behaviour of the systems is more akin to pseudo-bulk or zero-one conditions, and determine whether initialization occurs in emulsion systems in the same fashion as in solution

polymerizations, as seen in chapter four, it was decided to attempt a similar investigation as was carried out in the case of homogeneous polymerizations.

In the case of predominant aqueous phase initiation, we might expect to see a poor correlation between the monomer consumption and the RAFT agent consumption, due to the minimal concentration of RAFT agent in the aqueous phase. The typical polymerization behaviour in free radical emulsion polymerization, as has been discussed in chapter two, is that a number of units (precisely how many depends on monomer and initiating radical fragments) are added in the aqueous phase prior to droplet entry. Oil phase initiation is reported to be an inefficient process in very small particles, such as those typical of this study.²³ It could conceivably be possible that multiple monomer units are added to the growing radicals prior to transfer, due to aqueous phase propagation events, such as those that occur with an aqueous phase soluble initiator. The length of chain required to achieve surface activity with an oil-soluble initiator is however unclear, and this should be considered as a possible complicating factor.

The first issues that need to be dealt with to obtain usable spectra were the viscosity of the emulsion medium and the heterogeneous chemical environment that occurs in emulsions. Solid particles or particles with relatively high viscosity, e.g. emulsion droplets, result in T_2 relaxation times being reduced, and leads to line broadening in NMR samples. Low solids latexes (<1%) provided an environment in which it was possible to produce a spectrum with reasonable peak separation that could be integrated with enough accuracy to provide useful quantitative information about the species in the system. It should however be noted that broad line widths prevented high resolution from being achieved. Figure 5.14 shows the spectrum obtained from a 1% solids styrene emulsion prepared using sodium dodecyl sulfate as surfactant, and cyanoisopropyl dithiobenzoate as RAFT agent, with the oil phase soluble initiator AIBN, and hexadecane as the ultrahydrophobe. Pyrazine was used as an internal standard, diluted in deuterated benzene, in a separate insert. The spectrum shown was acquired at the end of initialization.

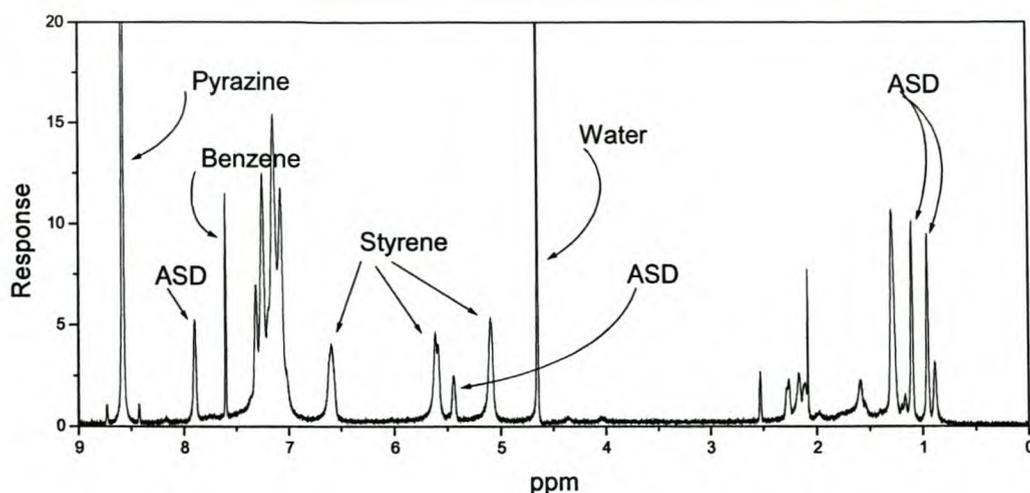


Figure 5.14 Miniemulsion *in situ* ^1H NMR spectrum of the reaction of cyano isopropyl dithiobenzoate in the presence of styrene and AIBN. The reaction was carried out at 70 $^\circ\text{C}$.

The spectrum was complicated by the use of sodium dodecyl sulfate and hexadecane, which both have peaks in the methyl region. The internal standard (pyrazine), the deuterated solvent in which the pyrazine was diluted, and the water in the spectrum have narrow line widths due to the homogeneous environments that these components experience. The behaviour observed in the reactions was RAFT agent specific and very similar to that observed in the solution studies. Monomer conversion showed specific and clear rate changes in the case of cyanoisopropyl dithiobenzoate. The evidence suggests that oil phase initiation is very significant in these systems or that z , the length required for particle entry is low, and that the overwhelming majority of particles are nucleated very early in the reaction, as the initial RAFT agent is consumed in the same fashion as in homogeneous experiments.

It is clear from the spectrum that the styrene concentration in the system was quite low, target DP in the system was ~ 3 -4. This was typically due to both design and nature of the preparation process, as the sonication process tended to decrease the styrene concentration in the system for the volume of latex that was prepared (approximately 1 mL). The experimental setup did not allow for sealed homogenization and the sonication time of 5-8 s (6000-6500 J) did not allow much scope for modification due to the rapid heating of the preemulsion that occurs at such low volumes. This factor could be examined in the future. The problem with increasing the monomer content in the starting mixture is that the particle size and stability is dependent on the size of the oil phase to surfactant ratio. Figure 5.15 shows

the time dependence of the signals corresponding to the three olefinic styrene peaks that were followed in the reaction of cyanoisopropyl dithiobenzoate.

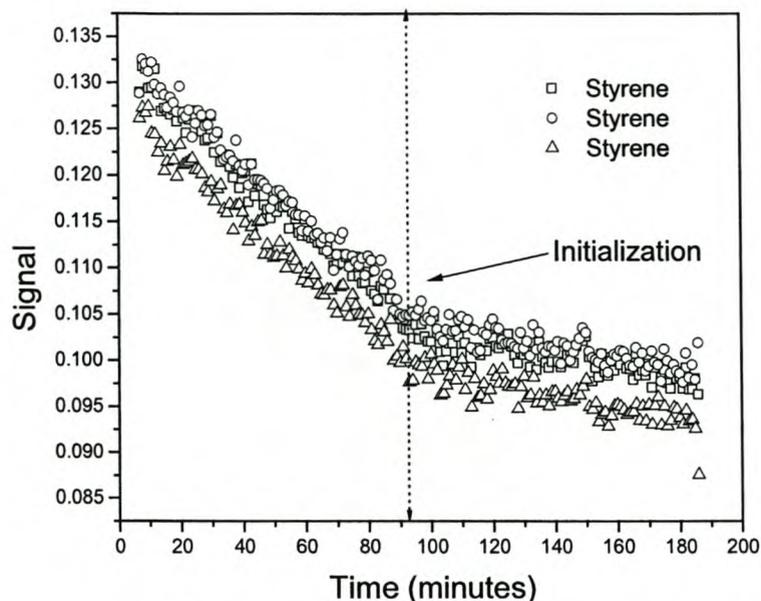


Figure 5.15 The monomer consumption in the emulsion polymerization of cyanoisopropyl dithiobenzoate, AIBN and styrene as a function of time at 70 °C.

Initialization occurs in the systems, with a significant change in rate in the case of cyanoisopropyl dithiobenzoate, while a smaller change in rate occurs at 70 °C when cumyl dithiobenzoate is used as a RAFT agent, as shown in figure 5.16.

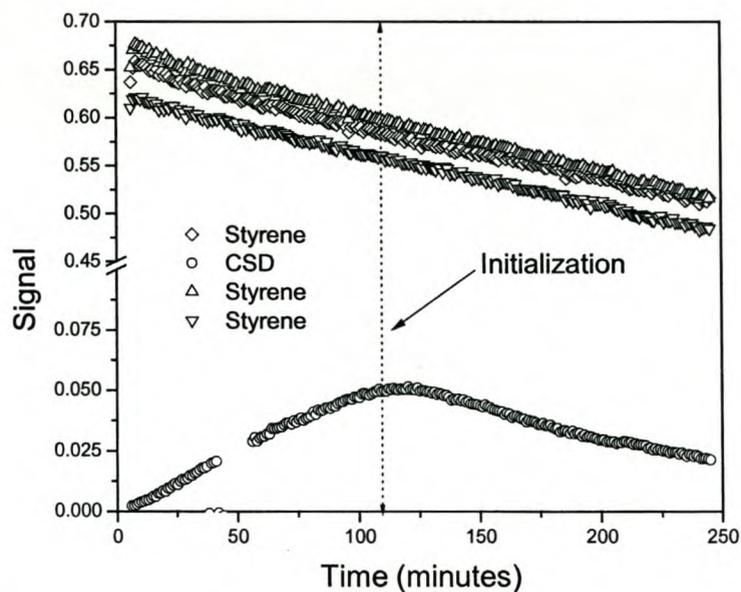


Figure 5.16 The monomer consumption in the emulsion polymerization of cumyl dithiobenzoate AIBN and styrene as a function of time at 70 °C.

As discussed in chapter four, the reason for the small change at the end of initialization is due to the probable similarity in the addition rate constants for the cumyl radical to styrene and the cumyl styryl radical to styrene at the specific reaction temperature. For the solution polymerization of cumyl dithiobenzoate, it has been observed that there are few intermediate radicals present during the initialization process, and for this reason it is unlikely that the intermediate radical species have a significant role in the rate of formation of ASD or CSD. However, after initialization, the high rate of addition to the RAFT agent may be a process that could conceivably compete with radical exit, providing more opportunities for radicals to be contained in a particle. This can be seen as a pseudo zero-one polymerization in that there would only be a single propagating radical present, but large numbers of intermediate radicals. The increased populations of intermediate radicals would potentially increase the probabilities of intermediate radical termination.

The chain lengths that could be examined suggest that the RAFT process has no competing processes, other than those observed in the homogeneous polymerizations in chapter four, during the initialization period in the miniemulsion systems studied. This corresponds well to both laboratory observations and published reports, which suggest that a period of heating, typically in the range of 20-30 minutes, which may correspond to initialization, is required before destabilization becomes obvious in *ab initio* RAFT polymerizations.^{16,24} From ESR studies in a companion project,²⁵ it is known that the intermediate radical concentration only begins to climb near or after the initialization period in the case of styrene polymerizations in homogenous media. From the NMR studies in miniemulsion, it appears that there are no obvious reasons to consider the reactions as behaving in a different fashion. If we work from the premise that the reactions behave similarly, this suggests that intermediate radical oligomeric species could have a role in the destabilization of latex particles, potentially as part of superswelling behaviour. The experimental limitations of this study have disadvantages, in that the system is not directly comparable to other miniemulsions in this chapter, and advantages in that phase specific behaviour is easier to determine. The preparation and dilution of the latexes for NMR leads to a substantial decrease in the aqueous phase concentration of species that were original aqueous phase components, and this is a factor that should be examined in follow up studies.

The slow rate of polymerization when a water-soluble initiator (KPS) is added to the system is shown in figure 5.17.

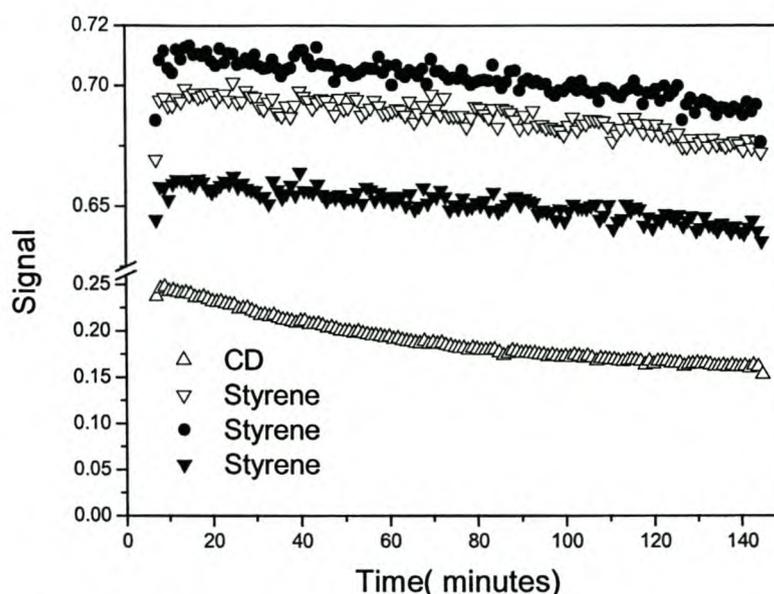


Figure 5.17 The rate of polymerization in the KPS initiated cumyl dithiobenzoate mediated low solids styrene miniemulsion at 70 °C.

Figure 5.17 suggests indicates that the oil phase initiation seen in figures 5.16 and 5.15 is significant, as the aqueous phase initiation appears low. Dilution of the aqueous phase would lead to a much lower initiator concentration in the case of a water-soluble initiator, while dilution of the aqueous phase will not have a large effect on the oil phase soluble initiator concentration in the oil phase. The initialization times in the reactions are comparable to solution systems, which suggests that the decreased number of droplets in the system behave as nanoreactors polymerizing independently, and do not rely on aqueous phase radicals for initiation. The system is far from commercial latex, with solids contents being less than 1%. The length of a z-mer in an AIBN initiated polymerization should be determined to allow a more exact conclusion, but it seems likely that oil phase initiation is very significant in RAFT mediated miniemulsions. The fact that polymerization rates were similar to homogenous polymerizations under similar oil phase conditions, suggests that termination of oil phase radicals is potentially not as significant here and that pseudo bulk conditions may apply during initialization and pseudo zero-one conditions after initialization. This is a topic for future study.

5.7 Rate of the reactions

In the discussion that follows, it will be shown that the primary factors controlling the maximum rate of reaction are probably independent of whether or not this system obeys zero-one kinetics. For a conventional emulsion or miniemulsion system it is relatively easy to predict whether a system will obey zero-one kinetics,²⁶ as this depends on the relative probability of the entering species propagating, or terminating with another radical inside the entered particle. These relative probabilities are strongly dependent on the particle size and the propagation rate coefficient for the monomer. However, for a system containing a RAFT agent the situation is further complicated by the fact that at least two distinct types of radicals exist, and the fates with respect to both types of radicals must be considered.

The fundamental point is whether the intermediate radicals also undergo rapid termination reactions when an entering radical encounters these species, which is discussed in detail in Tonge *et al.*²⁷ At this stage, the fates of these radicals are not known, and whether a system that would obey zero-one kinetics in the absence of a RAFT agent always does so in the presence of a RAFT agent is uncertain. There is some evidence from *ab initio* quantum chemical calculations to support long enough intermediate lifetimes to permit reactions involving the intermediate radicals to become significant, but that is outside the scope of the current discussion.²⁸ For the purposes of this discussion zero-one kinetics are concerned with propagating radical species only, while intermediate radicals are considered as unreactive species.

5.7.1 Zero-one

If the assumption is made that these systems behave in a similar manner to conventional emulsion systems, then, with the small particle sizes for styrene-containing latexes observed here, the systems are predicted to obey zero-one kinetics. The very low \bar{n} values observed (usually < 0.1) are consistent with zero-one kinetics. In such a case, the value of \bar{n} will depend on the rate coefficients for entry and exit of radicals from the particles as well as the addition rate of propagating radicals to RAFT agents and the fragmentation rate of the intermediate radicals. The rate coefficient for entry will be at a maximum early in a reaction, with a slow decrease with time and conversion. The rate coefficient for exit is mainly dependent on particle size, which in an ideal case would be approximately constant throughout the reaction. The

intermediate radical concentration is expected to be constant with time as observed in homogeneous experiments²⁵ during the equilibrium period of the RAFT-mediated polymerization. Since none of the events that are expected to dominate \bar{n} in a zero-one system change significantly with time, it is expected that \bar{n} will be approximately constant over a short time interval, with a slow decrease due to loss of initiator.

5.7.2 Pseudo-Bulk

For a pseudo-bulk system, the situation is much simpler, with the value of \bar{n} being dominated by a similar balance of initiation and termination events (again, with the same time dependence) and the particle size, which is approximately constant. The same prediction can be made for a pseudo-bulk system, i.e. the value of \bar{n} should be at a maximum early in the reaction, followed by a slow decrease. Both models that have been discussed predict an early maximum in \bar{n} , followed by a slow decrease, which is exactly as is observed for the overall propagating radical concentrations through large sections of the miniemulsion reactions.

A factor that might also influence the rate of reaction is the locations of the reactants. For a miniemulsion system, this could be quite important, since early in the reaction there are two main organic phases (the nucleated and non-nucleated droplets), which initially contain very similar concentrations of all reactants (including monomer and RAFT agent). The rate of reaction (and propagating radical concentration) for a pseudo-bulk system depends on the rates of initiation and termination events in the locus of polymerization, which for a pseudo-bulk system are roughly independent of particle size. The rate of termination is primarily dependent on the propagating radical concentration in the locus of polymerization: the higher this concentration, the higher will be the rate of termination (all other factors being equal). If the locus of polymerization is smaller than the entire organic phase, such as will be the case with a significant number of non-nucleated droplets, then the propagating radical concentration will indeed be higher in the locus of polymerization, leading to an enhanced rate of termination. If a significant number of droplets have not been nucleated, then the *overall* propagating radical concentration (and \bar{n}) will be decreased due to the enhanced termination rates, since a significant amount of monomer is unavailable to the reaction (both nucleated and non-nucleated droplets must be considered). For a pseudo-bulk system under such conditions, the presence of non-nucleated droplets would lead to a *lower* rate of reaction than would otherwise occur

if all droplets are nucleated. That is, an early maximum in the rate of polymerization is likely to be the result of most of the initial miniemulsion droplets being nucleated early in the reaction, as for a zero-one system. A wide range of nucleation times is also likely to result in a broad particle size distribution and high PDI of the molar mass distribution. The results presented here suggest that this is not the case in the systems studied.

There are further reasons why it is likely that most droplets are nucleated early in the reaction and that monomer transport is slow. The most significant of these is that if monomer transport from non-nucleated to nucleated droplets is rapid, transport of the RAFT agent must be of a similar speed. If this is not the case, the RAFT agent will be isolated from the locus of polymerization, and the possibility of the formation of particles containing primarily or only RAFT agent is high, and a wide range of RAFT agent concentrations would be observed in particles. A wide range of RAFT agent concentrations would lead to very broad molar mass distributions, probably also of significantly higher molar mass than predicted, which is not observed (see table 5.2). Previous studies¹⁶ suggest that transport of the RAFT agent cumyl dithiobenzoate is much slower than monomer transport, which implies that particle nucleation must be an efficient process in the studied systems.

The argument in favor of rapid efficient nucleation is supported by the fact that there would be little thermodynamic driving force (other than the super-swelling mentioned earlier, which is neither predicted nor observed under the conditions used) for net migration of the monomer or RAFT agent between non-nucleated and nucleated droplets at low conversions. The reason being that these droplets and pre-particles are almost identical in radii, polymer content, and concentrations of monomer and RAFT agent. The scenario is different from that of an emulsion polymerization, where monomer droplets and latex particles are very different, especially in terms of radius and surface area per unit volume, which leads to the rapid migration of monomer from droplets to particles. The slower monomer migration that would occur in the miniemulsion systems would allow more time for particle nucleation.

A second reason for the expected early nucleation of particles is supported by kinetics and based on the rate of radical production. The time required for nucleation of every droplet (droplet/particle number here is typically 10^{18} dm^{-3}), assuming 100% initiation efficiency, under current reaction conditions is estimated to be less than a

few minutes, which is much less than the observed induction periods (at least 20 minutes). Complete nucleation would therefore be expected by the time significant polymerization is observed.

Regardless of whether the current system obeys zero-one or pseudo-bulk kinetics, it would appear that the number of nucleated particles reaches its maximum, long-term value very early in the reaction, although some particle (and rate) loss due to coagulation is possible. That is, most of the miniemulsion droplets are entered (and nucleated) early in the reaction, with little expected coagulation or new particle formation during the remainder (majority) of the reaction. There is also a strong chance that there is fairly good reproduction of the original droplet size distribution in the final latex, although a perfect “one-to-one” copy is not expected. Polydispersity in the particle size distribution would then likely be a reflection of the characteristics of the original droplet dispersion and the preparation method, as discussed earlier, it is however difficult to verify this hypothesis.

The observed rapid cessation of reaction later in some of the reactions appears to be different from what is expected in terms of the above discussion. The point at which this loss of propagating radicals occurs appears to be independent of conversion, time, type of monomer, temperature and particle size and appears to be somewhat random, although there may be a dependence on initiator concentration.

A thorough investigation into the dependence of the rate of reaction on particle size and entry events may in the future yield more insight into the dominant mechanisms controlling the rate of reaction in these RAFT miniemulsion systems. Understanding of the mechanism of the RAFT process for this system is also necessary for a complete interpretation of the kinetics for this system; this understanding is still somewhat limited.^{8,29-32}

5.8 Particle size and distributions

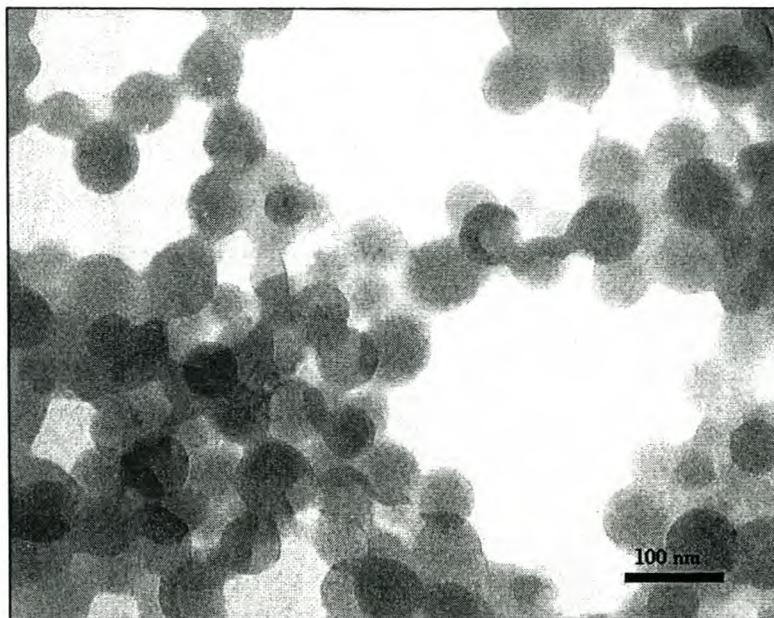


Figure 5.18 TEM micrograph of the final polystyrene latex from reaction 13 (0.18 mol.dm^{-3} hexadecane, $3.36 \times 10^{-3} \text{ mol.dm}^{-3}$ ACP, RAFT agent (1) $0.044 \text{ mol.dm}^{-3}$, 24.6 g.dm^{-3} CTAB) see Table 5.2 for composition).

Transmission electron microscopy (TEM) of samples of the final miniemulsion latexes shows fairly broad distributions of particle sizes (Figure 5.18), which is typical of living radical polymerization miniemulsions.^{18,33} So-called one-to-one copies in miniemulsion polymerizations are rare and only found in ideal systems. The reasons for the broadness of the distributions in these systems are probably related to deviations from the ideal miniemulsion mechanism, and preparation of the original dispersion. The possible deviations include the possibilities of diffusion of monomer between particles and a range of nucleation times (although both of these appear to have relatively little importance in light of the above discussion if the system is zero-one), or lack of nucleation in some particles. Particle coagulation could also occur, leading to more variation in particle size. The variation in particle size is likely to be exacerbated, since the rate of reaction is slow, and the droplets/particles spend a long time being monomer-rich. Monomer-swollen latexes are often very sticky, and as the RAFT process first forms oligomeric species, which grow slowly with time, and therefore the latexes remain sticky for a long period, rather than forming high polymer rapidly, as would happen in a conventional free radical polymerization.

5.9 Comparisons to similar processes in the literature

The fact that Butté *et al.*¹⁷ and Lansalot *et al.*¹⁸ were able to obtain stable miniemulsion systems with dithiobenzoate agents should be discussed in terms of their exact systems. Butté *et al.*¹⁷ were able to obtain stable systems with controlled characteristics when using dithiobenzoates that had been prepolymerized in homogeneous media. Lansalot *et al.*¹⁸ found that dithiobenzoates gave conversions below 40% and PDI data above 2 after 30% conversion when used directly in miniemulsion, which is similar to the results obtained by Tsavalas *et al.*¹⁶ Miniemulsions with dithiobenzoates had limiting molar masses for these systems, which were explained in terms of radical exit from particles and poor nucleation of the initial miniemulsion droplets. The use of a polymeric radical that significantly exceeded the critical length for water solubility as carried out by Butté *et al.*¹⁷ (in this case polystyrene at a degree of polymerization ~ 15) is similar to the work of Vosloo *et al.*¹⁵ The use of the prepolymerized RAFT agents in the above studies did however have some disadvantages, as low molecular weight tailing due to inactive chains and high molecular weight shoulders were evident in the SEC traces.

Lansalot *et al.*¹⁸ were able to obtain some control when using RAFT agents with radical supporting groups of different structure. They found improved conversion when using RAFT agents of a phenyl dithioacetate functionality but still were unable to maintain PDI values below 1.5. The use of polymeric radicals in phenyl dithioacetate systems was found to improve the polymerization rate, indicating a more efficient nucleation of particles. They concluded that the structure of the RAFT agent played a critical role in the formation of a stable polymerized miniemulsion. The control obtained using phenyl dithioacetate functional RAFT agents was typically poor, with PDI increasing substantially with conversion.

In both the work of Butté *et al.*¹⁷ and Lansalot *et al.*¹⁸, the concentration of hexadecane was well below the levels recommended by Luo *et al.*⁶ Low concentrations of hexadecane would lead to predicted super-swelling, resulting in shear sensitivity, and to a broad range of particle sizes, which was observed in the TEM images published by Lansalot *et al.*¹⁸ It should be noted that the particle sizes in this study are substantially smaller than those of Lansalot *et al.*, due to the high surfactant concentrations used, and it is difficult to make direct comparisons as to the difference in particle size polydispersity as a result. The distributions in their study do

however appear to be broader than those observed in this study. Low concentrations of hexadecane would also allow a number of mechanisms by which control of polymer molar mass could decrease with time, including higher monomer diffusion gradients and less stable droplets. The most important of these would be variation in the concentration of the RAFT agent in the particles due to migration of monomer between droplets/particles (also observable by the variety in particle size), caused by super-swelling in conjunction with a variation in nucleation times.

The key differences between the systems in the literature and the current study are firstly that dithiobenzoate RAFT agents have been shown to be effective in providing living characteristics in miniemulsion with leaving groups (in this case cumyl and cyano valeric acid radicals) that are capable of exiting latex particles. The important implication of this fact is that no prepolymerization is required. Secondly, reasonable conversions and excellent stability can be obtained using dithiobenzoates. The most important implication of the second result is that miniemulsions are capable of reproducing the polymer that has been prepared in homogeneous systems, with the only difference being the increase in rate of polymerization in the case of the miniemulsion polymerizations.

5.10 Disadvantages of high surfactant concentrations

There is a possibility that the high surfactant concentration used could lead to significant amounts of micellar nucleation. The polymerization in these secondary particles would then take place via a conventional free radical mechanism, as very little or no RAFT agent would be present in these secondary particles, due to the RAFT agents' poor water transport abilities, leading to a fraction of high molecular weight polymer in the system. This will be discussed in chapter six, and may be significant when different classes of RAFT agents are used. In the case of dithiobenzoate agents, this phenomenon appears to occur to such a small extent that a significant high molecular weight fraction was not observed by size exclusion chromatography. Moreover, as stated earlier, there appeared to be few micelles present in the current system. Homogenous nucleation, which is normally a potential competing process to droplet nucleation, especially in the case of more hydrophilic monomers such as methyl methacrylate, is considered insignificant in these systems because there is no evidence of an uncontrolled molecular weight distribution in these reactions.

5.11 General disadvantages of RAFT in miniemulsion with AIBN

There are a number of disadvantages to RAFT polymerization in aqueous media under the current experimental conditions. Figure 5.19 shows a typical conversion-time plot of a controlled methyl methacrylate miniemulsion.

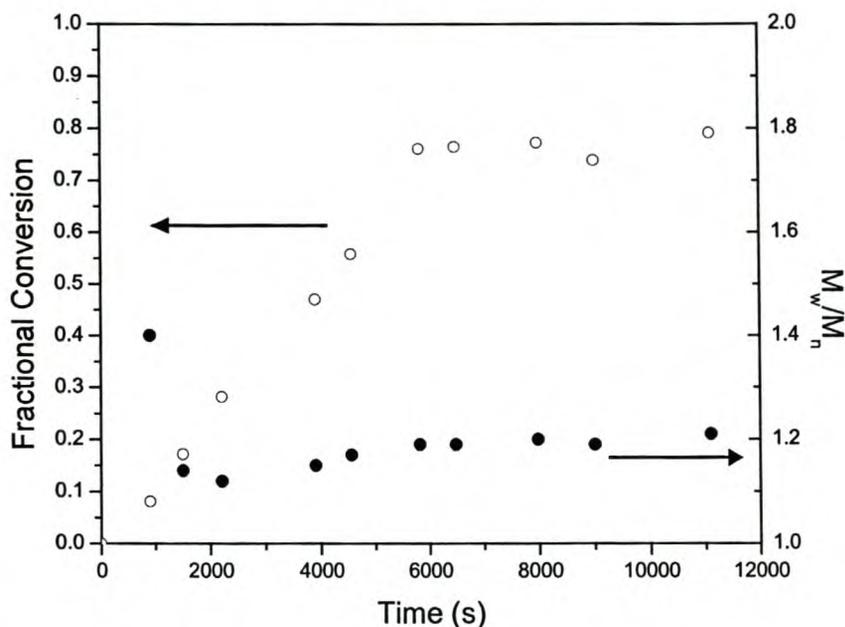


Figure 5.19 Conversion-time data for MMA miniemulsion reaction 12 carried out at 70 °C (see Table 5.2 for composition) showing that conversion did not exceed 80 %.

Conversion data shows that the reactions did not usually reach high conversions (rarely above 80 %), which is not consistent with the higher conversions reached in analogous homogeneous polymerizations. The reasons for the reduced final conversions are still being investigated in our laboratories. It should be noted that once these terminal conversions are reached, the colour in the reactor does not change significantly, nor is it impossible to further extend the polymeric chains through the addition of further radical initiator to the system in cases where the initiator has been fully consumed. The fact that oil soluble initiators do not always provide full conversion in emulsified systems has been documented,³⁴ and this suggests the possibility that the terminal conversions observed in this study were not only due to the presence of a RAFT agent in the system, but potentially due to inherent difficulties associated with the initiation system used. A system that contains an initiator feed might be expected to produce superior conversions, but would not have been suitable

for this study, as it would have substantially complicated rate determinations, due to the variations in radical fluxes in the system that would have been created.

5.12 Dithioacetates and Trithiocarbonates

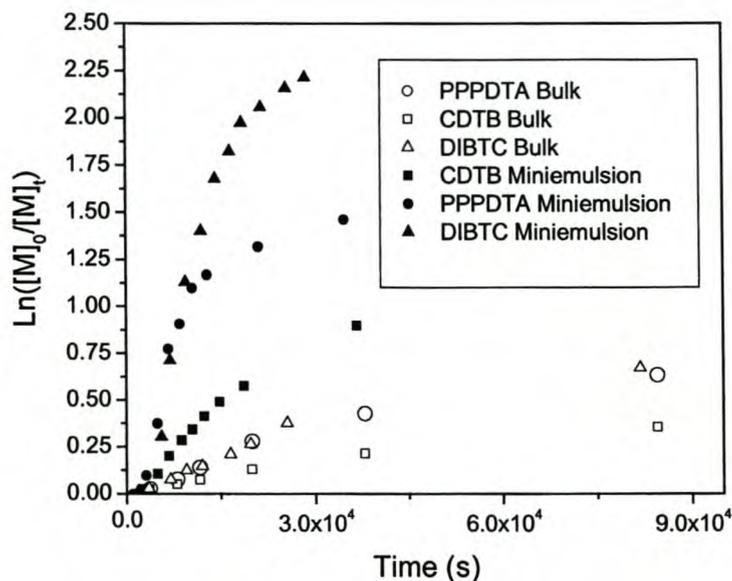


Figure 5.20 First order rate comparison plot of the use of cumyl dithiobenzoate, cumyl phenyl dithioacetate (PPPDTA) and S-dodecyl S'-isobutyric acid (DIBTC) in bulk and miniemulsion.

The use of phenyl dithioacetates and trithiocarbonate RAFT agents leads to a number of different and interesting observations. From figure 5.2, it can be seen that when a bulk comparison in the presence of hexadecane is carried out there is very little evidence of a difference between these two classes of RAFT agent – although there is significant difference between them and the use of a dithiobenzoate. This suggests that both types of RAFT agent provide minimal stabilization of the intermediate radical, and therefore much less retardation in the polymerizations than a comparable dithiobenzoate. It can however be seen that the rate plots are substantially different in the case of the polymerizations of PPPDTA and DIBTC in miniemulsion. The polymerization continues to proceed at high rates at longer reaction times in the case of DIBTC. A difference between the two RAFT agent miniemulsions lies in the formation of secondary particles in the reactions, which is evidenced by the formation of a second distribution of polymer. This phenomenon is discussed in detail in chapter six. The control of molecular weight in the primary distribution of polymer is comparable to that of the dithiobenzoate polymerizations.

5.13 Chain extension

5.13.1 Chain Extension in Bulk

The polystyrene homopolymer from a RAFT miniemulsion, (reaction 16, see Table 5.2: 3.85 mol.dm⁻³ hexadecane, 4.58 × 10⁻³ mol.dm⁻³ AIBN, 0.083 mol.dm⁻³ RAFT agent (2), 25 g.dm⁻³ SDS), was cleaned by drying the sample, dissolving it in THF, removing the insoluble CTAB by filtration, and then concentrating the solution by evaporation of the solvent. The polymer was then precipitated in *n*-pentane and dried under vacuum. The dry polymer (1.0 g, 1.4 × 10⁻⁴ mol, \bar{M}_n 6900, PDI 1.32) was polymerized in bulk using styrene monomer (40 g, 0.38 mol) at 85 °C under nitrogen, with AIBN (0.005 g, 3.0 × 10⁻⁵ mol). Samples were taken throughout the reaction and conversion was determined gravimetrically. To test the living characteristics of the systems, chain extension of polymer produced in RAFT miniemulsion reaction 16 was carried out in bulk for 24 hours. The evolution of the molar mass distribution is shown in Figure 5.21.

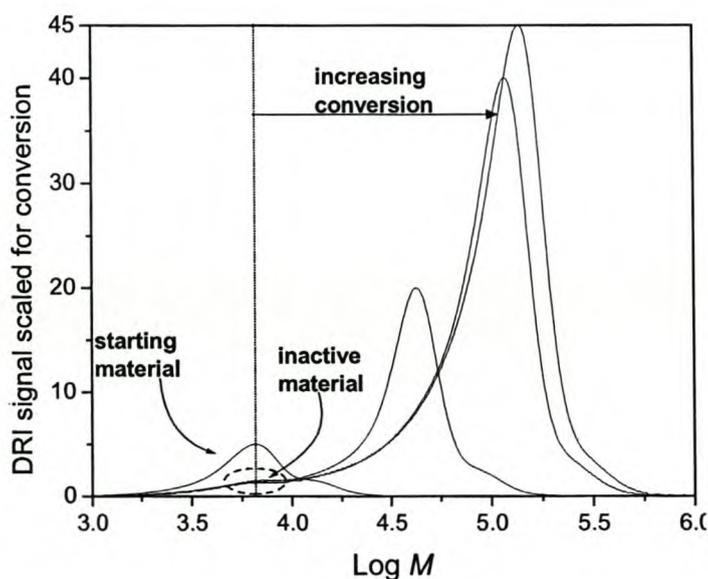


Figure 5.21 Molar mass distributions of the chain extension of styrene miniemulsion macroRAFT agent, using the final polymer from reaction 16 (see Table 5.2). The reaction was carried out by bulk polymerization with styrene (40 g, 0.38 mol) at 85 °C and AIBN (3.0 × 10⁻⁵ mol).

The samples showed living characteristics in that the molar mass of the sample increased with conversion, which shows that a portion of the polymer grown in the initial RAFT miniemulsion underwent reinitiation, to form higher mass polymer (and

had therefore not been irreversibly terminated). A portion of the original polymer did not undergo reinitiation, and the corresponding peak was not completely separated from the growing chains by SEC analysis. The living character of a fraction of the chains was deduced from the chromatograms (see Figure 5.21). Baseline separation problems prevented accurate estimations of \bar{M}_n , and it is clear that a significant fraction of the chains did not reinitiate. The reinitiation of chains from the initial polymer formed in the miniemulsion reaction implied that it was formed by a living process, i.e. that many chains had not been terminated in the miniemulsion polymerization step. The rigorous purification of the polymer prior to chain extension is expected to have a negative effect on the fraction of chains that reinitiate due to the labile nature of the dithiobenzoate functionality.

5.13.2 Chain Extension in Miniemulsion

A 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid-mediated MMA miniemulsion, (0.18 mol.dm⁻³ hexadecane, 15.2 × 10⁻³ mol.dm⁻³ AIBN, 0.045 mol.dm⁻³ RAFT agent (1), 25.3 g.dm⁻³ SDS, reaction 12, see Table 5.2), was polymerized for 24 h and allowed to stir for 48 h at room temperature. The latex was reheated to 70 °C and AIBN (0.025 g, 1.5 × 10⁻⁴ mol) was added, followed by a styrene (10 g, 9.6 × 10⁻² mol) feed over 2 h. The reaction was allowed to continue for 24 h. Samples were taken for SEC analysis and conversion measurement (by gravimetry). Chain extension directly in the miniemulsion system shows that the molar mass of the polymer increased. Figure 5.22 shows the behavior of both blocks, the MMA (Table 5.2, reaction 12, carried out at 70 °C) and the styrene block, with a final SEC PDI of 1.39 and \bar{M}_n of 21500 using polystyrene standards, which corresponded fairly well with the predicted value of 25000, based on monomer conversion.

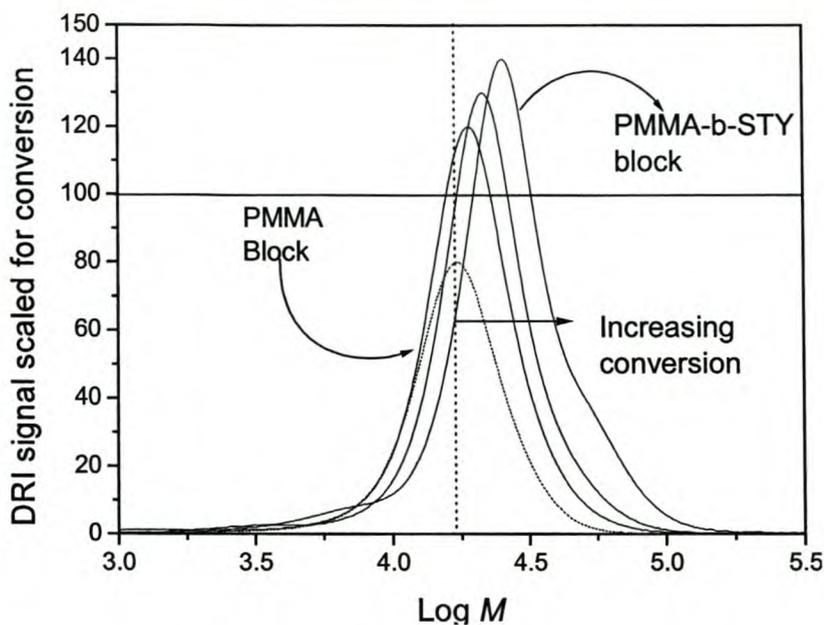


Figure 5.22 Block conversion SEC traces of reaction 12 (see Table 5.2) carried out at 70 °C (0.045 mol.dm⁻³ RAFT, 1.5 × 10⁻⁴ mol.dm⁻³ AIBN), with a styrene feed. The latex was reheated to 70 °C and AIBN (1.5 × 10⁻⁴ mol) and a styrene (10 g, 0.096 mol) feed were added over 2 h. Final $\bar{M}_n = 21500$, PDI = 1.39.

Figure 5.22 shows that polymerization under these conditions was both living and controlled. Broadening of the distribution is evident in the SEC chromatograms, and some shoulder formation to the high M side (the peak is at approximately $2M_p$, which suggests termination via combination), but the peak remained relatively narrow and \bar{M}_n increased with conversion in a linear fashion. It should be taken into account that the fact that the miniemulsion systems in this investigation did not reach 100% conversion means that the reinitiated polymer is expected to contain both MMA and styrene units in the second block, as MMA monomer would still have been present in the latex at the time of the reinitiation and second monomer addition.

5.14 Two dimensional chromatographic analysis

Two dimensional chromatographic analysis of copolymers produced in miniemulsions was carried out, and the results were compared to polymers produced in solution. The two-dimensional separations of the block copolymers were carried out using Liquid Chromatography at Critical Conditions (LC-CC) in the first dimension and Size Exclusion Chromatography (SEC) in the second dimension.

Critical conditions imply that a solvent mixture has been obtained for which there is no molecular weight dependent column interaction for a specific polymer, and all

homopolymers of that polymer will elute simultaneously regardless of chain length. This enables the exact analysis of polymers by their chemical composition distribution. If the eluted polymer is fractionated and analyzed by size exclusion, a two dimensional analysis by composition and size is obtained, providing more definitive analysis of block polymer formation than in the case of simple size exclusion chromatography.

5.14.1 Experimental

A modular chromatographic system comprising two chromatographs connected via one electrically driven eight-port injection valve (Valco) and two storage loops were used for the analysis. For the first dimension, a Waters 2690 Alliance separation module was used and a Waters 515 HPLC pump was used for the second dimension. "PSS Win GPC6" software was used to control the operation of the coupled injection valves. Data processing was carried out using "2D_ENG" software. Software packages were obtained from Polymer Standards Service, Mainz, Germany.

Critical conditions for PMMA were methylethylketone-cyclohexane 70.7:29.3, while critical conditions for PS were tetrahydrofuran-acetonitrile 50.8:49.2. Columns were chosen as follows: critical conditions for PMMA: SGE Exsil silica 120 Å, 5µm average particle size, 250×4.6(ID) mm; critical conditions for PS: phenomenex LUNA C18 100 Å, 5µm average particle size, 150×4.6(ID) mm and Macherey-Nagel nucleosil C18 100 Å, 5µm average particle size, 125×4.0 (ID) mm. The columns were conditioned at 30°C. The size exclusion dimension was determined in THF using a PSS SDV linear M, 5µm average particle size, 50×20 (ID) mm. Detection was carried out using an evaporative light scattering detector (ELSD), PL-ELS 1000 from Polymer Labs.

5.14.2 Results

Solution polymers were analyzed to obtain comparison results. The use of a polystyrene dithiobenzoate homopolymer with methyl methacrylate monomer as well as a poly(methyl methacrylate) dithiobenzoate homopolymer with styrene monomer were compared to show the importance of the first block in a RAFT-mediated polymerization. Figure 5.23a shows a poor block formation, while the block formation in the case of a PMMA-dithiobenzoate agent is clearly improved in figure 5.25b. Colour is simply an indication of signal intensity.

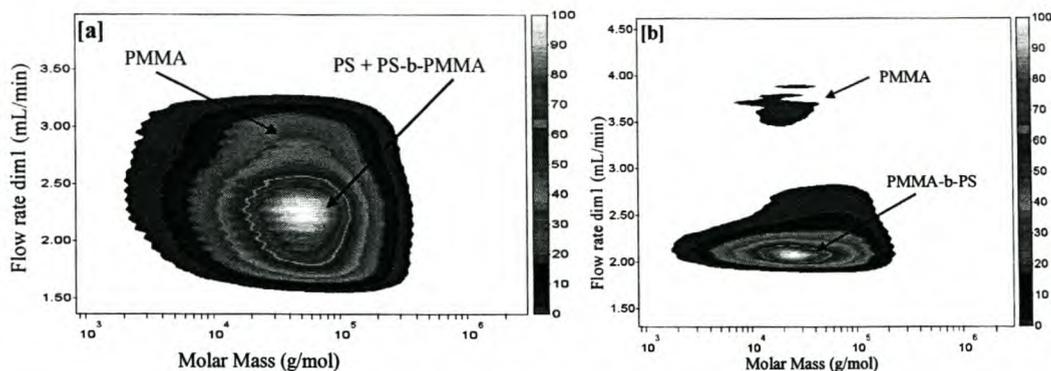


Figure 5.23 [a] Contour plot for homogeneous PS-b-PMMA, critical conditions for PMMA and [b] contour plot for homogeneous PMMA-b-PS, critical conditions for PMMA. The differences in figures 5.23 (a) and (b) can be explained by the fact that the relative ability of a polymer prepared by RAFT-mediated polymerization to be converted into a block polymer is dependent on the relative abilities of the radical leaving groups to compete for the intermediate radical that is formed during the addition fragmentation process. Tertiary radicals which, as we have discussed in chapter four are more stable than secondary radicals, are more likely to fragment from the intermediate radical. Styrene provides a secondary radical species, while methyl methacrylate provides a tertiary radical species. This means that the purity and control of a block copolymer produced from a PMMA polymer using styrene monomer to form a diblock polymer is likely to be better than the styrene-methyl methacrylate copolymer produced using a polystyrene polymer as the first block. Figure 5.24 shows the same polymers used in figure 5.23 analyzed at critical conditions for polystyrene. It can clearly be observed that the amount of homopolymer polystyrene is substantially increased in the case of polystyrene being used as a first block.

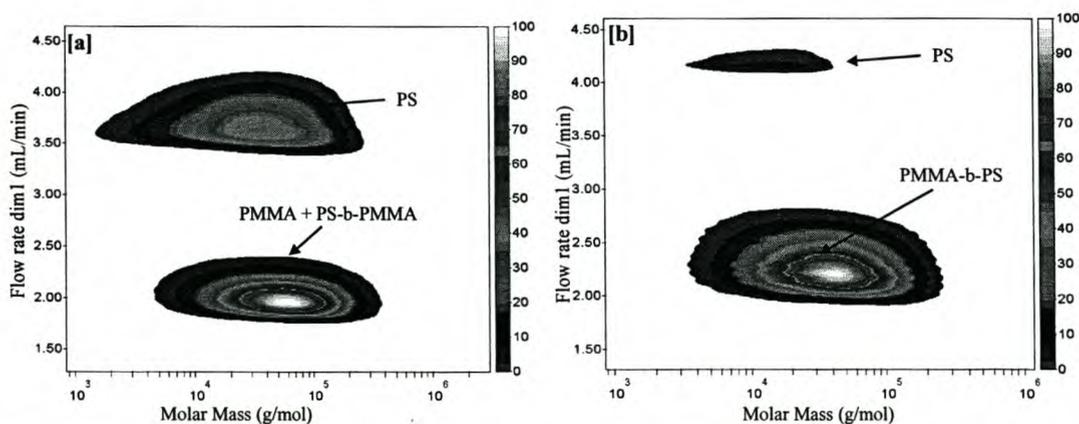


Figure 5.24 [a] Contour plot for homogeneous PS-b-PMMA, critical conditions for PS [b] contour plot for homogenous PMMA-b-PS, critical conditions for PS.

The purity of the block polymer produced by the addition of methyl methacrylate to a polystyrene RAFT polymer could potentially be improved substantially by the use of a feed system to limit the concentration of the methyl methacrylate until all of the chains have successfully exchanged styrene for MMA end-groups. In the case of the solution diblock copolymer produced from a PMMA-dithiobenzoate first block, there is approximately 5% homopolymer PMMA and 10% homopolymer PS in the resultant polymer. This can be improved by reducing initiator concentrations, and minimizing termination.

Two block copolymers were prepared in miniemulsion using different addition methods for the monomer for the second block. Both seed latexes were polystyrene latexes from a single miniemulsion reaction and methyl methacrylate was added for the formation of the block copolymer, AIBN initiator was dissolved in the monomer. A simple “shot” addition of monomer was carried out, and a “feed” addition of monomer was carried out. The polymers produced were then compared via 2-dimensional chromatography. The maximum solids content was increased from 20% to 33% by the addition of monomer. Figure 5.25 shows the contour plots at critical conditions for PMMA, while figure 5.26 shows the contour plots at critical conditions for polystyrene.

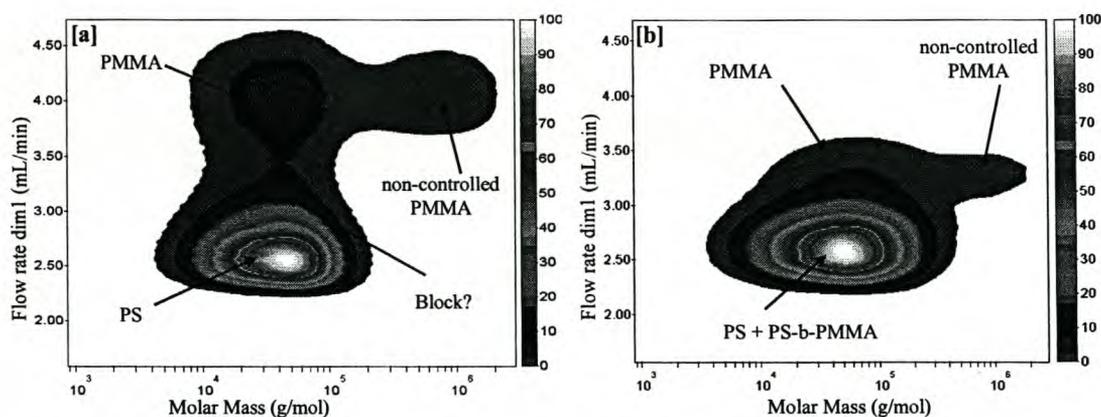


Figure 5.25 [a] Contour plot for FEED PS-b-PMMA prepared in miniemulsion at critical conditions for PMMA, [b] contour plot for SHOT PS-b-PMMA prepared in miniemulsion, analysed at critical conditions for PMMA.

The contour plots of the copolymers in figures 5.25 and 5.26 prepared in miniemulsion differ significantly from those of figures 5.23 and 5.24. In the four contour plots, the main polymer observed is homo-PS (intensity set to 100%). The presence of homo-PMMA was detected as well, giving higher intensity peaks at the critical conditions for PS, due to a better solubility of the polymer in a mixture of

THF/acetonitrile than in MEK/cyclohexane. Uncontrolled high molar mass PMMA was formed under these reaction conditions, presumably largely due to the formation of new latex particles. Some block copolymer was formed, with an intensity of about 20-25% which is best observed in figure 5.26(a), but the best block was obtained with the “shot” addition (SHOT PS-b-PMMA), with an intensity of about 75% (figure 5.26(b)).

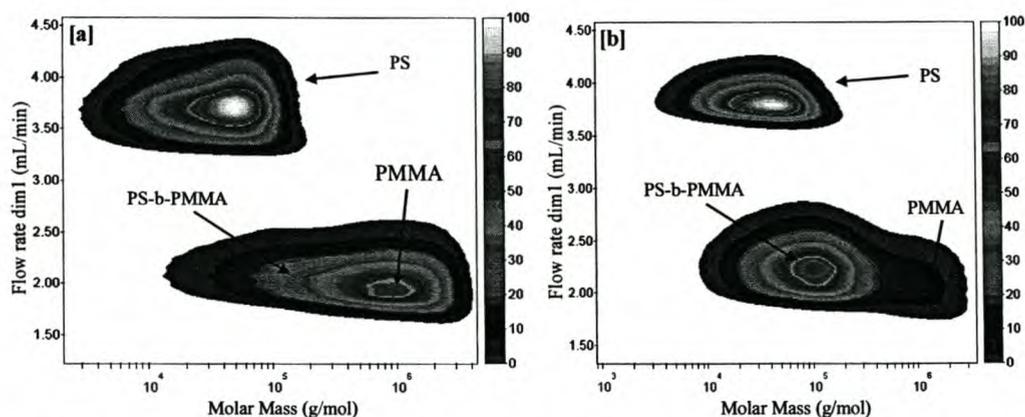


Figure 5.26 [a] contour plot FEED PS-b-PMMA prepared in miniemulsion at critical conditions for PS and [b] contour plot SHOT PS-b-PMMA prepared in miniemulsions at critical conditions for PS.

The feed addition of MMA to a polystyrene seed did not improve the quality of the block copolymer produced. This can be explained by the fact that a feed system in a high surfactant system may lead to an increased percentage of secondary particle formation when compared to a simple shot addition, as the aqueous phase will remain monomer-saturated in the case of a feed system. The shot addition may lead to swelling of the seed, while the feed system does not allow the monomer to swell the seed, leading to a predominance of secondary uncontrolled polymer forming in secondary particles. The likelihood of formation of high molecular weight uncontrolled homo-PMMA in the existing polystyrene particles is small due to the presence of dithiobenzoate endgroups. This can be seen in the comparison of the two different emulsion systems, where the increase in block polymer formed in the case of the shot addition can clearly be observed. The most important deduction that can be made from the results is that polymerization in heterogeneous media significantly influences the block-polymers produced by a RAFT system. The more complex mechanisms that play a role in emulsion systems can to some extent be countered by using different strategies, such as shot versus feed addition of monomer. Removal of

excess surfactant by dialysis is also expected to provide a substantially different copolymer after block formation.

5.15 Conclusions

Stable RAFT-containing miniemulsions could be formed using CTAB and SDS with styrene and MMA. For miniemulsions where the surfactant concentration was greater than roughly 5 wt % with respect to monomer, latex stability was excellent, and the documented phase separation leading to the formation of a red layer²⁴ was not observed. The reasons for this is considered to be one or more of the following: the higher stability that is provided by the dense packing of surfactant chains on particles in miniemulsions at these high surfactant concentrations; the high levels of hexadecane used; and possibly the rapid nucleation on the reaction time scale of the particles in the polymerizations, due to the small particle sizes. One or more of these factors prevented a super-swelling state, as predicted by Luo *et al.*⁶, from occurring. The exit characteristics of the RAFT oligomers in the system are also expected to differ due to the efficient maximum surfactant packing.

Under the conditions used, controlled free radical miniemulsion polymerization reactions were successfully carried out using the RAFT technique, giving polymers of low PDI and reasonably predictable molar mass. The polymer formed in these reactions had living characteristics, as indicated by the subsequent conversion of the initial homopolymer formed in the RAFT miniemulsion polymerization into a block copolymer by further polymerization in bulk and miniemulsion reactions. The colloidal stability of the miniemulsions was excellent.

Dithiobenzoate RAFT agents can be used successfully in miniemulsion without prepolymerization and can provide low PDI, living polymer. Small particles with dense surfactant layers and high costabilizer concentrations provide a route for stable miniemulsion particles in systems that contain destabilizing elements, and might be applicable to other living polymerization techniques. Different types of RAFT agents do however provide different behaviour in different systems. Some of the possible reasons for this behaviour will be addressed in chapter six.

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Chapter 6: Studies on secondary particle formation in miniemulsion systems

Abstract

The application of specific RAFT agents in a predispersed emulsion led to mixed distributions of polymer as well as particles in the final latex. The application of deconvolution, double detector Size Exclusion Chromatography (SEC) techniques and Capillary Hydrodynamic Fractionation (CHDF) show that different RAFT agents and monomers change the nucleation behaviour of conventional emulsion particles in predispersed media.

The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' (I found it!) but 'That's funny ...'

Isaac Asimov

6.1 Introduction

Particle nucleation in heterogeneous systems is a highly complex field that still generates a substantial amount of discussion.¹ In chapter two a number of mechanisms by which a particle might form in an emulsified system were discussed, these include the HUFT (Hansen, Ugelstad, Fitch, and Tsai) theory, which allows for droplet, micellar and homogeneous nucleation. In this chapter, the effect of a RAFT agent on the particle nucleation mechanism in a preformed emulsion will be discussed. As discussed in chapter five, miniemulsion systems should have a bare minimum of micellar aggregates,² and the small droplets should possess the overwhelming surface area in the system, which should lead to a reasonably efficient droplet nucleation. Unfortunately that is not always necessarily the complete truth.³⁻⁵ In a conventional free radical miniemulsion it is very difficult to distinguish between particles that are formed by different mechanisms when the droplets are small.

In a RAFT system however, in which the aqueous phase transport of the RAFT agent is expected to be low, it may be possible to distinguish between particles in which RAFT agents are present and particles that have no mediating species. Aqueous phase transport of RAFT species has been shown to be quite limited.⁶ This would suggest that particles that do not contain RAFT-mediating species would probably be formed after predispersion.^{7,8} If we examine SEC traces it should be quite straightforward to determine the presence of RAFT endgroups in specific distributions of polymer in a system. This can be done by using dual detectors for SEC, i.e. refractive index (RI) and ultraviolet (UV) at 320 nm.⁹ The substantiation of the process would then be carried out by particle size analysis to determine whether the hypothesis of secondary particle formation can be justified.

6.2 Approach

From preliminary experimental data, it was known that dodecyl isobutyric acid trithiocarbonate (DIBTC) provides significant secondary polymer distributions. The second distribution of polymer polymerizes in a manner that shows no control or living character. A hypothesis to explain the behaviour was that polymerization takes place in two different types of particles of which in one there are no RAFT-mediating species present. This type of behaviour has been reported in ATRP and RAFT

systems.^{10,11} The RAFT agent DIBTC was compared with other RAFT agents, to show the effects of leaving groups, retardation and water solubility. The presence of a RAFT agent gives rise to two phenomena related to the formation of secondary distributions of polymer that need to be considered. These are the initialization behaviour and the retardation behaviour as discussed in chapter four. To simplify the determination of where particles are formed it was decided to make use of aqueous phase only radicals to influence the total aqueous phase radical concentration. The polymer analysis was carried out by distinguishing between polymer chains in which there is RAFT agent present and chains that have been formed by an uncontrolled mechanism. This can be done by examining the SEC traces of the polymer produced in the latex, and observing the differences in the two distributions of polymer that occur by peak deconvolution.

6.3 Phenyl Dithioacetates

The possibility of preparing two different RAFT agents with similar initialization and retardation behaviour, while having opposing water and oil solubilities, is a synthetic challenge that is not easily addressed at this point. For that reason, considering that the bulk behaviour is quite similar as shown in chapter four, it was decided to carry out the polymerizations using PPPDTA and DIBTC, which have oil and water soluble leaving groups respectively. Figure 6.1 shows SEC traces of a PPPDTA mediated miniemulsion. The preparation of the emulsion is discussed in section 6.7.1.1.

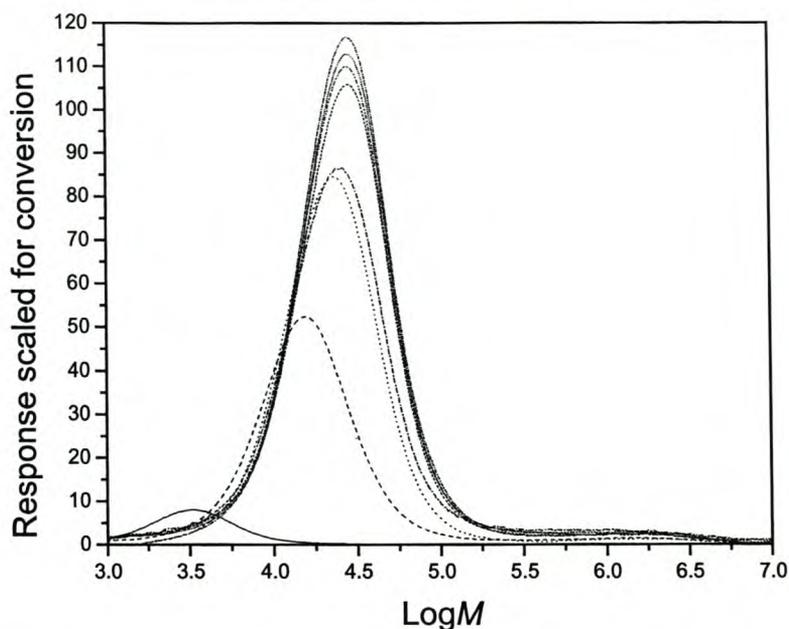


Figure 6.1 A styrene miniemulsion polymerization mediated by 2-phenyl propyl phenyl dithiocetate (PPPDTA) using AIBN as an initiator and SDS as surfactant.

The use of an oil soluble RAFT agent which has been successfully used in the acetone transport mediated polymerization of a seeded RAFT latex¹² provides interesting results. The oil soluble leaving group, in conjunction with low retardation, leads to the mild development of a secondary polymer distribution. The RAFT agent, which differs from cumyl dithiobenzoate only in its retardation behaviour, suggests that the ability to develop a higher intermediate radical concentration assists in limiting the development of a second polymer distribution. This would be possible if the intermediate radical is not capable of particle exit, i.e. it exceeds solubility limits in the aqueous phase.

6.4 Trithiocarbonates

As mentioned in 6.2, the development of a secondary polymer distribution in the presence of DIBTC had been documented in preliminary experimental studies. To demonstrate the point, figure 6.2 shows the SEC distributions of a DIBTC miniemulsion. Experimental details are given in 6.9, and ratios are similar to those used in chapter five.

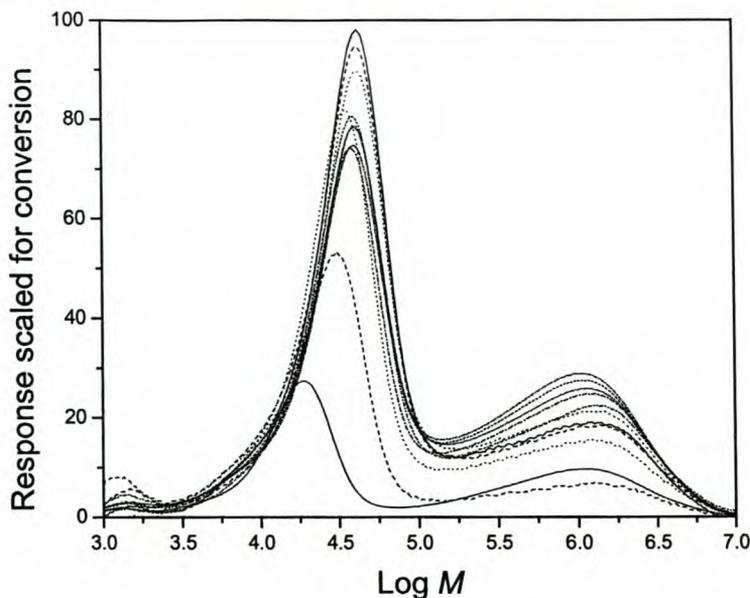


Figure 6.2 A miniemulsion polymerization of styrene mediated by a trithiocarbonate RAFT agent (DIBTC) using AIBN as initiator and SDS as surfactant.

The use of a RAFT agent that contains a water-soluble leaving group and a water insoluble supporting group, leads to a significant uncontrolled distribution, which can plausibly be explained by aqueous phase particle formation. There are a number of factors that may play a role in the formation of secondary particles in the aqueous phase. Firstly, the initialization period of the reaction was determined in solution and is extremely short, which implies very rapid propagation of the leaving group radical. Secondly, the use of a water-soluble leaving group should facilitate homogenous nucleation in the aqueous phase.

6.5 Particle nucleation

It is important to be able to differentiate between (R) leaving group dependent behaviour and the less retarded polymerization or (Z) group behaviour. As all components are distributed homogeneously during sonication, the formation of a second distribution of particles would imply that these particles were formed after miniemulsion preparation. As the surfactant concentration used in these systems is very high, there is potentially surfactant available to assist in homogeneous nucleation of particles in the aqueous phase, or even potentially micellar nucleation (although as was discussed in chapter five, it is unlikely).

In a conventional emulsion (or miniemulsion for that matter), the radicals reach a length by propagation in the aqueous phase at which they are surface active (*z*-mer). If

the radical continues to propagate rather than enter a droplet or particle, they will reach a critical length (j_{crit}), such that they will form particles in the aqueous phase by homogenous or micellar nucleation. This process was discussed in chapter two. The amount of oil phase initiation is normally quite small for small particles, and is typically discounted. As we have seen in chapter five, this may very well not be the case in the RAFT mediated miniemulsion systems (at least in cases in which dithiobenzoates are used as mediating agents in the presence of AIBN).

In the reactions discussed in this chapter, oil soluble initiators were used. Regardless of the fact that AIBN should allow less secondary particle nucleation when compared to KPS whose ionic character aids in nucleation,¹³ coagulative particle formation of aqueous phase chains seems to be the best explanation for the formation of a second distribution of particles. When we consider the fact that the isobutyric acid leaving group should show hydrophilic character as a leaving group, then it is conceivable that the leaving group can be attributed a substantial part of the blame for the size of the secondary polymer distribution. To create secondary particles, aqueous phase radicals are required. In a RAFT-mediated polymerization, it is important to consider not only the initiator derived radical, but also the RAFT leaving group derived radical's water solubility. These radicals will also provide different j_{crit} values due to the endgroup's ability to help support particle formation. In a RAFT-mediated polymerization, the radicals that are most significant during the first steps of polymerization are derived from the R group of the RAFT agent in a homogenous system, as we have seen in chapter four. If the RAFT process is efficient in the oil phase, as seen in the preliminary NMR experiments presented in chapter five, then the leaving group of the RAFT agent is the most significant radical in the case of heterogeneous miniemulsions as well. The nature of these radicals should affect aqueous phase solubility and radical exit from particles.

Particle nucleation in the aqueous phase – if we start from the consideration that there are no or very few micelles present – is generally caused by the aggregation of a critical number of oligomers. The higher the value of j_{crit} , the lower the critical aggregation value m_c . These values have been well characterized for aqueous phase soluble initiators such as KPS, and values of 6 and 800 respectively have been reported for styrene emulsions initiated by KPS.¹⁴ If rate retardation plays an important role in restricting the number of chains that achieve lengths suitable for homogenous nucleation in the aqueous phase, then the implication is that radical exit

is retarded in RAFT miniemulsions in which RAFT agents provide retardation. The surfactant concentration and particle size is constant, which implies that there is no increased physical barrier to exit. The only plausible explanation is that there are fewer radicals that are capable of exiting the particles.

It seems apparent that the behaviour in these systems is somewhat different to that of conventional systems. This becomes clearer when we compare the systems in this chapter to the study conducted by Luo *et al.*¹⁵ Their study showed that in conventional butyl acrylate miniemulsions, of particle size below 100 nanometers, the primary nucleation by AIBN occurs from the aqueous phase, and very little oil-phase initiation could be detected. The radicals derived from AIBN in the aqueous phase can occur via one of two mechanisms, namely desorption from particles, or from that small fraction of AIBN that is partitioned in the aqueous phase. If nucleation occurs in the same fashion in conventional and RAFT-mediated systems, we then have two cases to consider. Firstly, in the case that radicals are derived from AIBN in the aqueous phase, the RAFT agent, being distributed predominantly in the droplets, should be unable to influence the radicals in the aqueous phase that are derived from the aqueous partitioning of AIBN. (Although radicals from particle exit events would still be affected)

The polymerization rate of an uncontrolled secondary particle distribution would then be largely independent of the RAFT agent used in the system and polymerization of the particles without RAFT agent present would occur at rates that would lead to larger particles due to diffusion of monomer to the rapidly polymerizing particles. Slower polymerization rates observed in retarding RAFT agent miniemulsions should lead to more secondary particle formation or there should be at least equal amounts of secondary particle formation regardless of RAFT agent type. The experimental evidence presented in this chapter contradicts this argument.

6.6 Effects on radical desorption

RAFT agents could play a substantial role in desorption of radicals from particles. This is due to the extremely high rate at which radical addition to dithioesters occurs when compared to propagation of monomers. This rate is potentially high enough that diffusion controlled processes such as termination and desorption could be affected. Retardation in RAFT was discussed previously in this dissertation. There are two

suggested causes of additional propagating radical “loss”, namely slow fragmentation and intermediate termination. Both reasons will decrease the number of propagating radicals that are able to leave particles.

If the desorption or exit of radicals from particles is a significant role player in RAFT-mediated miniemulsions, it is necessary that the portion of radicals that survive in the particles be increased in the case of systems that are more retarded. Zero-one type conditions would suggest that this is not possible, but pseudo bulk, or pseudo zero-one conditions in which there are only single propagating radicals in the particles, but high concentrations of intermediate radicals are present, would allow this type of behaviour. It should be kept in mind that the average size of an intermediate radical as well as its termination products should easily exceed j_{crit} especially in a system with an oil soluble initiator. Less retarded RAFT polymerizations will typically have a lower total number of radicals per particle due to the lower intermediate radical concentrations that occur in these systems. The possibility then exists that the average number of propagating radicals within the particles (\bar{n}), is decreased and more radicals will be available for aqueous phase propagation, as they do not exceed aqueous phase solubility limits. If the RAFT agent was not able to affect desorption then we should see radical desorption at the same rate in all types of RAFT reactions and the secondary particle formation should be precisely the inverse of what has been observed in practice (or at least independent of type of RAFT agent).

One of the interesting facts that leads from the discussion above is that the aqueous phase radical scavenger used by Luo *et al*¹⁵ would have different effects on differing RAFT agent miniemulsions. Specifically, that the effect of its use on the rates of polymerization should be less visible in the use of a dithiobenzoate when compared to a dithioacetate or trithiocarbonate.

6.7 Aqueous phase radical traps

The effect of aqueous phase radical traps on the rate of polymerization have been studied and compared to control experiments. Both ionic and non-ionic surfactant systems have been used to attempt to gain a deeper understanding of the mechanisms that play a role in the formation of the second polymer distribution.

6.7.1 Ionic surfactants

The use of ionic surfactants with aqueous phase radical traps has a number of inherent limitations. The change in ionic strength may interfere with the surfactant, which is dependent on electrostatic stabilization, according to Derjaguin, Landau, Verwey and Overbeck (DLVO) theory.¹⁶

6.7.1.1 Experimental

The experiments in this section were conducted in the same fashion as the emulsions prepared in chapter five. The reactions were run at 75 °C. RAFT agents were prepared as discussed in chapter three.

Table 6.1: Components for reactions

Component	Mass (g)	Mol
Styrene	19.92	0.1915
Hexadecane	0.896	
H ₂ O	81.2	
SDS	2.1	
AIBN	0.022	1.34×10^{-4}
RAFT (1) or (2)	0.249	8.89×10^{-4} or 6.84×10^{-4}

(1) PPPDTA (2) DIBTC

The following aqueous phase radical traps were added to the two experiments and duplicates were carried out without traps. Fremy's salt (1) 0.08g, 2.98×10^{-4} mol and NaNO₂ (2) 0.02g, 2.89×10^{-4} mol.

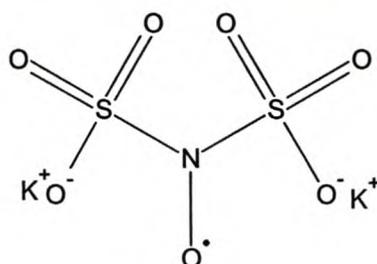


Figure 6.3 Fremy's salt-(Potassium nitrosodisulfonate) (KSO₃)₂NO

6.7.1.2 Results

Figure 6.4 show SEC traces of PPPDTA in the presence of the aqueous phase radical inhibitor Fremy's salt.¹⁷

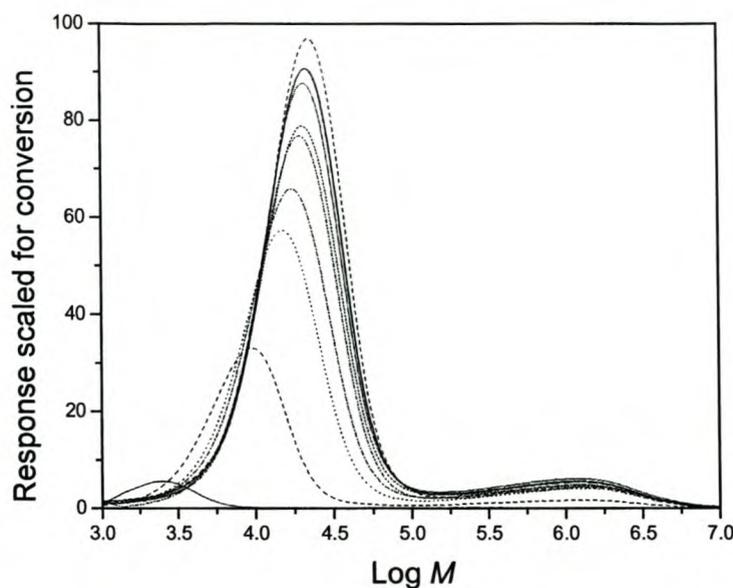


Figure 6.4 A Phenyl dithiocetate (PPDDTA) mediated miniemulsion reaction containing an aqueous phase radical inhibitor ($(\text{KSO}_3)_2\text{NO}$), using the ionic surfactant SDS.

The SEC results demonstrate an increased appearance of a second polymer distribution in the presence of the Frey's salt. The total number of radicals that exit the living polymerization loci during the course of the reaction and do not re-enter is thus increased in the presence of the aqueous phase radical trap. In an ionically stabilized emulsion system, this may be due to a number of different factors including interference with the ionic bilayer that supports the latex particle in the aqueous media as well as the mode of particle nucleation. In chapter five, it was suggested that RAFT-mediated polymerizations may have a high degree of droplet initiation. Regardless of the cause, the addition of an extra ionic species leads to an increase in aqueous phase particle formation (and therefore polymer). When normalizing to the controlled peak it is difficult to determine a trend in whether the second distribution is increasing in proportion to the controlled distribution in the system. Figure 6.5 shows the comparison first order kinetic plots of the reaction in 6.4 and the reaction in the presence of Frey's salt.

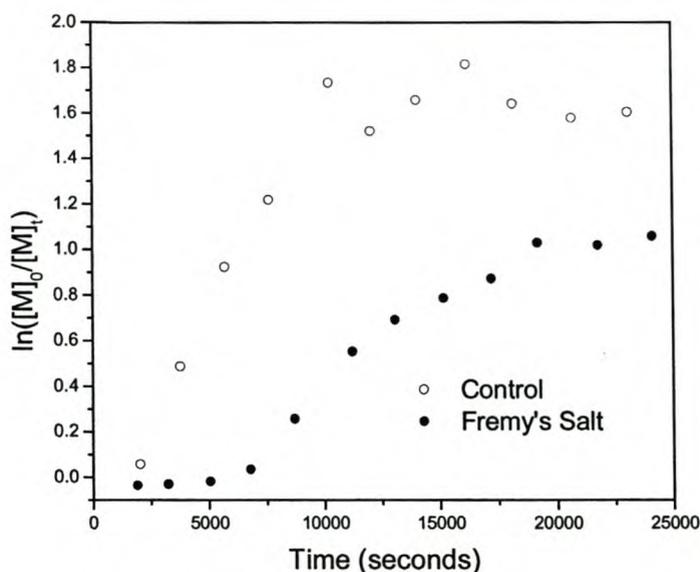


Figure 6.5 Rate plots for polymerization of styrene mediated by PPPDTA in miniemulsion with and without Frey's salt in reactions using the ionic surfactant SDS.

Figure 6.6 shows the SEC distributions of a DIBTC miniemulsion which contains NaNO_2 .¹⁵

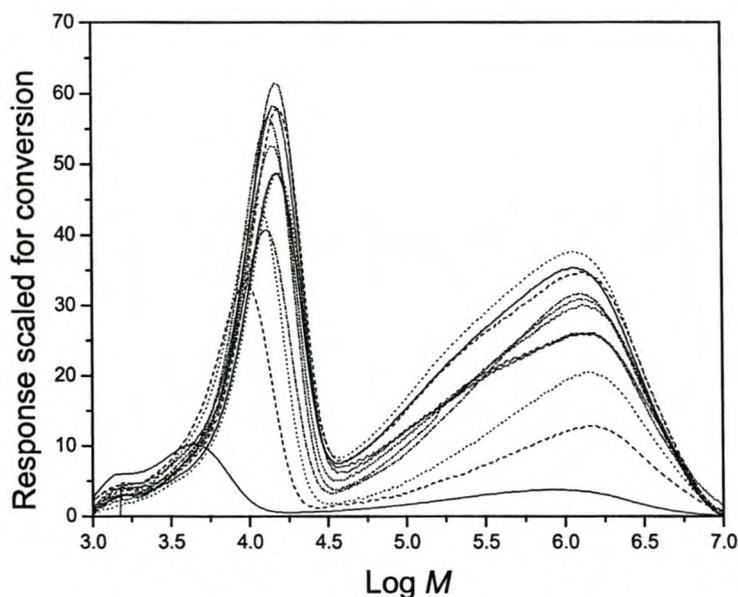


Figure 6.6 A trithiocarbonate (DIBTC) mediated miniemulsion polymerization of styrene using SDS as a surfactant containing an aqueous phase radical inhibitor (NaNO_2).

The results obtained in the presence of sodium nitrite show that the addition of an ionic aqueous phase radical trap leads to the increase of aqueous phase particle formation. It is possible that the radical trap plays a contributing role in this particle formation, either by becoming a hydrophilic head on a chain end or by destabilizing

existing particles to allow significant radical exit to occur. The reasons for this behaviour are still under investigation within our research group.

The first order kinetic plot shows that the DIBTC mediated experiment with NaNO_2 was slower and had a longer “inhibition” period, but reached a similar terminal conversion (around 80%).

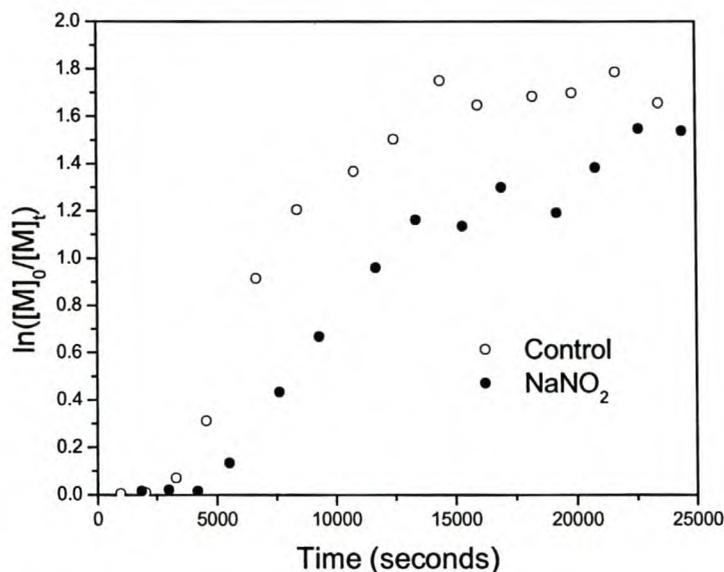


Figure 6.7 Rate plots for polymerizations of styrene mediated by DIBTC in miniemulsion with and without sodium nitrite using SDS as a surfactant and initiated by AIBN.

From the rate plots in figures 6.5 and 6.7 it is possible to judge the efficiency of the respective radical traps in inhibiting polymerization in the respective systems. The effect of the trap is clear in both reactions an extended inhibition period occurs prior to conversion becoming significant in the polymerization. It can be observed that the Fremy's salt is more efficient in the inhibition of polymerization in its respective system. This suggests that the influence of aqueous phase radicals is still very significant in the polymerization of particles in RAFT-mediated miniemulsions. If, as suggested by the data in chapter five, the RAFT-mediated particles show significant oil-phase initiation, then it would be plausible to suggest that the presence of the aqueous phase radical trap should affect the development of the relative sizes of the two polymer distributions in the polymerization. Secondary particles would not have predissolved initiator and would be unlikely to show significant oil-phase initiation. This would suggest that the secondary distribution would initially be a smaller proportion of the polymer in the reactions carried out in the presence of an aqueous

phase radical trap. This is not borne out by the experimental results in the presence of ionic surfactants.

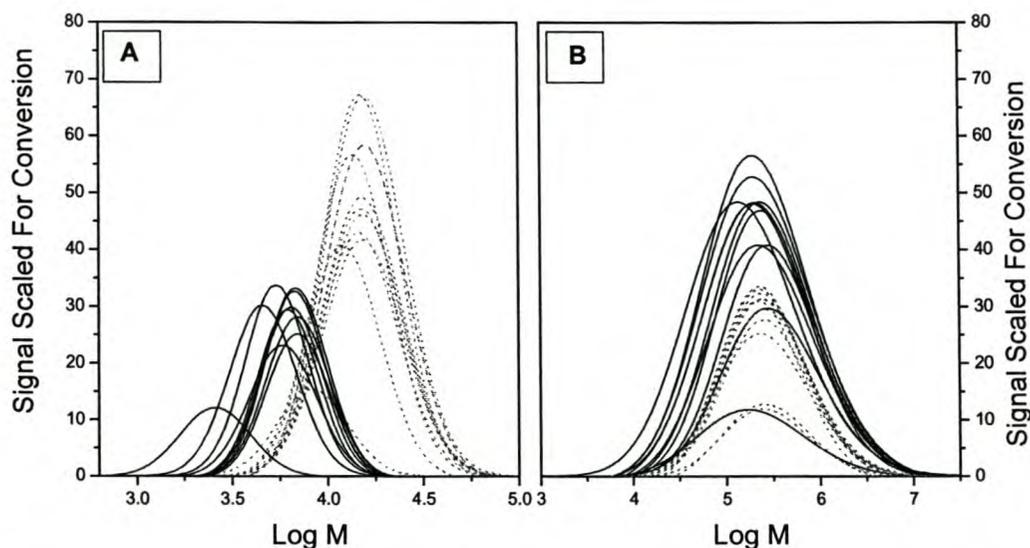


Figure 6.8 Comparison of the distributions produced in the presence and absence of sodium nitrite in the DIBTC mediated polymerization of styrene. (A) Shows the controlled distributions and (B) shows the uncontrolled distributions. Dotted lines indicate the reaction without the sodium nitrite and solid lines indicate the reaction with sodium nitrite. Peaks were deconvoluted using Origin7PRO®.

It should of course be noted that the larger size of the second distribution also plays a significant role in baseline identification for the separation of peaks. The controlled peak has a lower \overline{M}_n by necessity due to the increased consumption of monomer by the uncontrolled distribution. The comparisons in figure 6.8 are based on deconvoluted spectra. The assumptions of Gaussian distributions and bimodality have been made in the systems to generate the deconvolutions. There is some deviation in the distribution shape in the deconvolution of the higher molecular weight peaks. This is quite possibly due to the molecular weight cut off of the GPC column set and could therefore be an instrument artifact rather than a poor mathematical assumption. The difference in polydispersities can be observed more clearly if we examine the deconvoluted peaks. There is also an apparent increase in the area percentage of the uncontrolled polymer distribution with time in the presence of sodium nitrite, suggesting a difference in polymerization rates within the two distributions of particles. It is interesting to note that the controlled distribution appears to have a narrower polydispersity in the case that an aqueous phase radical trap is used. The variance shows narrower peaks in the case of the sodium nitrite containing reaction.

This behaviour is possible if the polymerization in the aqueous phase occurs via a conventional polymerization mechanism. Oligomers entering particles from the aqueous phase would have a conventional length distribution instead of the very strict initialization behaviour that would occur in the particle. This would lead to a broader distribution in the polymerizations in which no aqueous phase radical trap is initially present.

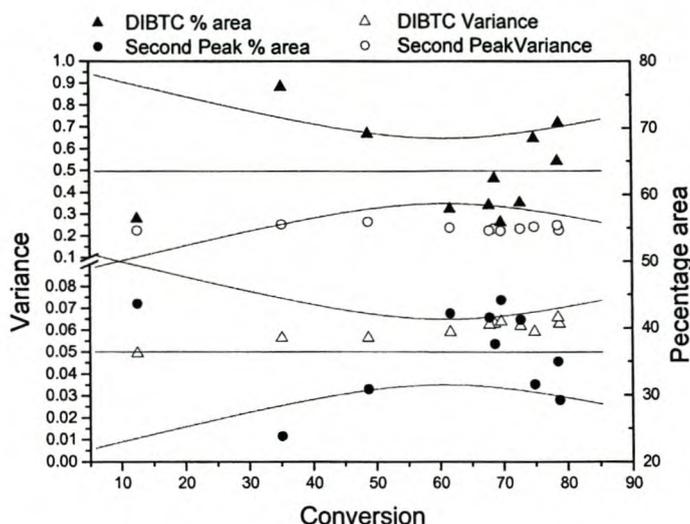


Figure 6.9 Deconvolution and comparison of peaks at similar total system conversion in a DIBTC mediated polymerization that did not contain an aqueous phase radical trap, showing linear fits of relative percentage areas as well as 95% confidence intervals.

When the chromatograms are normalized to the controlled peak height, it becomes noticeable that the proportion of the polymer in the system contained in the uncontrolled peak is increasing throughout the reaction regardless of the presence of the trap, but comparisons of figures 6.8 and 6.9 suggest a larger increase in the presence of the radical trap, as expected.

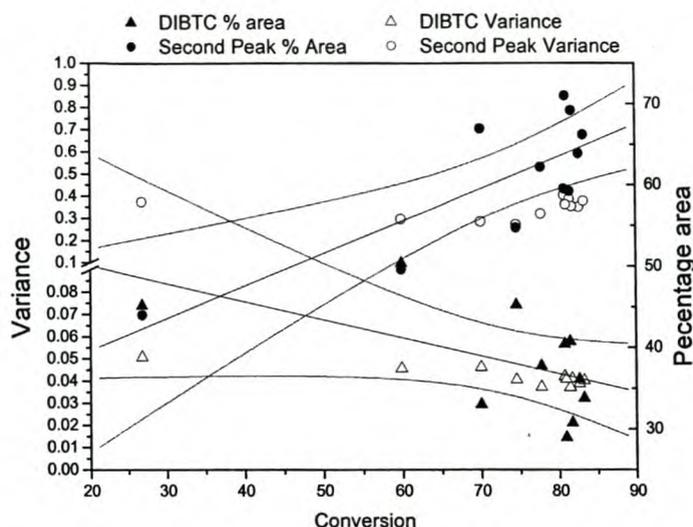


Figure 6.10 Deconvolution and comparison of peaks at similar total system conversion of a DIBTC mediated miniemulsion polymerization in the presence of NaNO_2 , showing linear fits of relative percentage areas as well as 95% confidence intervals.

There are two possible explanations for the general increase, firstly that the rate of polymerization is higher within the uncontrolled particles, which is a plausible explanation due to the mild retardation that will be caused by the presence of the RAFT agent. The distribution growth behaviour has been shown to be dependent on the RAFT agent concentration, and if the concentration of the RAFT agent in the system affects this behaviour, then the retardation is the most likely explanation. It is also possible that more particles are being formed throughout the polymerization, resulting in a higher surface area in the case of the uncontrolled distribution. This would result in a distribution of small particles that rapidly increase in size in the system. This is possible if the presence of the radical trap has affected particle stability or increased amphiphilic character of polymer chains thereby increasing the probability of aqueous phase particle formation.

6.7.2 Non ionic surfactants

Non ionic surfactants provide stabilization predominantly via steric stabilization. This minimizes the effect of added electrolytes on an emulsion polymerization. The particle size generated by nonionic surfactants is quite different from that of ionic surfactants at similar weight percentages,¹⁰ although the CMC values may be relatively low. Non ionic surfactants have been used successfully in RAFT-mediated miniemulsion polymerizations.¹⁰

6.7.2.1 Experimental

The size difference that is typically obtained when nonionic and ionically stabilized latexes are prepared makes direct comparisons between the results in 6.7.1.2 and non-ionic latexes complex. Size plays an important role in oil-phase initiation as well as droplet stabilization.^{15,18} For this reason it was decided to use butyl acrylate as a monomer to allow a more direct comparison to the work of Luo *et al.*¹⁵ General recipe conditions were 1g of Igepal®CO-990, 0.433 g hexadecane, 40 g DDI water and 10 g monomer. Experiments were conducted in the same fashion as in chapter five, and the RAFT agent, DIBTC, was prepared in the same fashion as in chapter three. AIBN was used as initiator.

Table 6.2: Composition of non-ionic surfactant reactions.

Number	DIBTC (mol)	Initiator (mol)	Aqueous radical trap	Radical trap mass (g)	mol
1	4.97×10^{-4}	6.21×10^{-5}	Fremy's salt	3.26×10^{-2}	1.21×10^{-4}
2	4.99×10^{-4}	6.46×10^{-5}	NaNO ₂	8.6×10^{-3}	1.24×10^{-4}
3	5.07×10^{-4}	6.40×10^{-5}	--	--	--

SEC analyses of the polymer samples were carried out using both RI and UV detectors with the UV detector at 320nm.⁹ At 320 nm the RAFT agent is the only reaction component that displays a UV signal and it is thus possible to distinguish between polymer chains that have RAFT endgroups, the polymeric surfactant, and uncontrolled distributions of polymer.

6.7.2.2 Results

The molecular weight distributions of reaction 1, table 6.2, are shown in figure 6.11. The presence of an uncontrolled distribution can be observed when comparisons are made between the RI and UV signals obtained. It should be taken into account that the UV detector is only capable of showing a single chromophore per chain and as a result, the distributions observed using RI and UV detectors are not directly comparable. It is however possible to make deductions as to which distributions contain chromophores that are UV sensitive at the wavelength of detection.

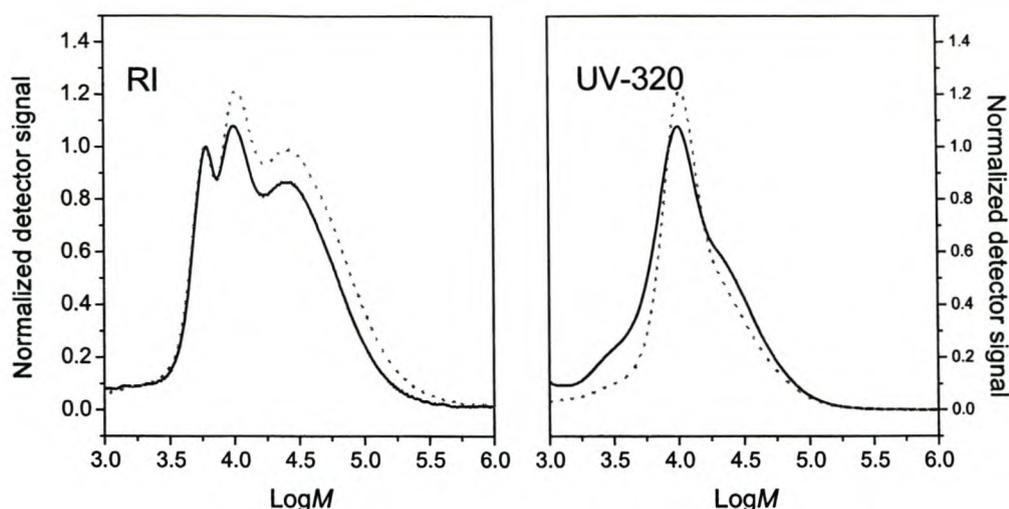


Figure 6.11 DIBTC mediated polymerization of butyl acrylate in the presence of a nonionic surfactant IGEPAL CO 990 and initiated by AIBN. The two curves correspond to increasing conversion in the reaction.

The signals are normalized to surfactant concentration in the case of the RI detector and the difference in RI peak heights was used as a scaling factor in the UV signal chromatographs, the lower molecular weight distribution in the RI corresponds with the non-ionic surfactant in the system. The peak derived from the RAFT agent functional polymer, seen in the UV plot, shows distinctive shoulders in the lower conversion sample. The lower molecular weight fraction corresponds to oligomeric RAFT fractions, which would have a significant UV signal, while the higher molecular weight fraction suggests that some particles are nucleated more rapidly in the system, although the shoulder becomes less significant at higher conversion.

In figure 6.12 the molecular weight distributions of reaction 2 table 6.2 are shown. The marked decrease of the second distribution (high molecular weight fraction) can be deduced from the chromatogram.

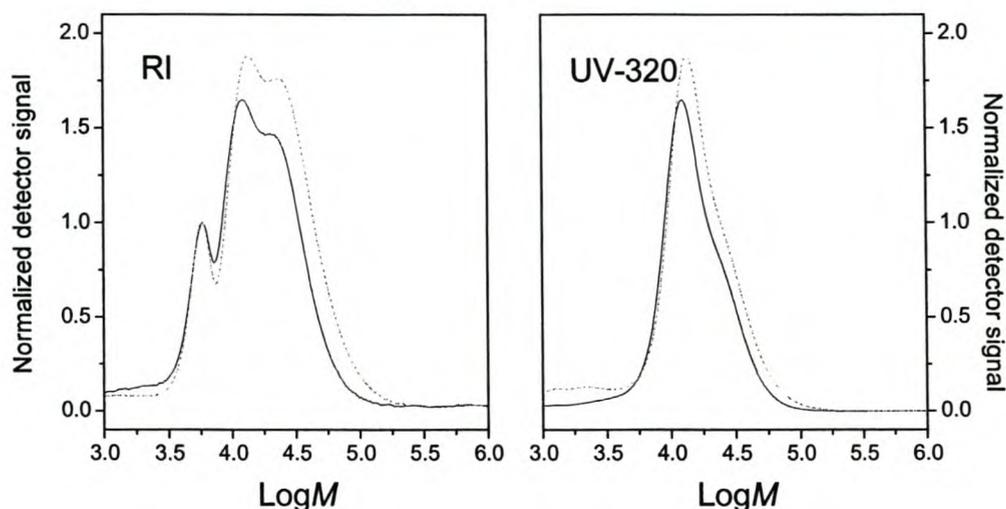


Figure 6.12 DIBTC mediated polymerization of butyl acrylate in the presence of Fremy's salt and a non ionic surfactant IGELPAL CO 990 initiated by AIBN. The two curves correspond to increasing conversion and are normalized to the surfactant peak.

In figure 6.13, the molecular weight distributions of reaction 3 table 6.2 are shown. It is clear that the use of sodium nitrite in the polymerization prevented the formation of an uncontrolled distribution of polymer.

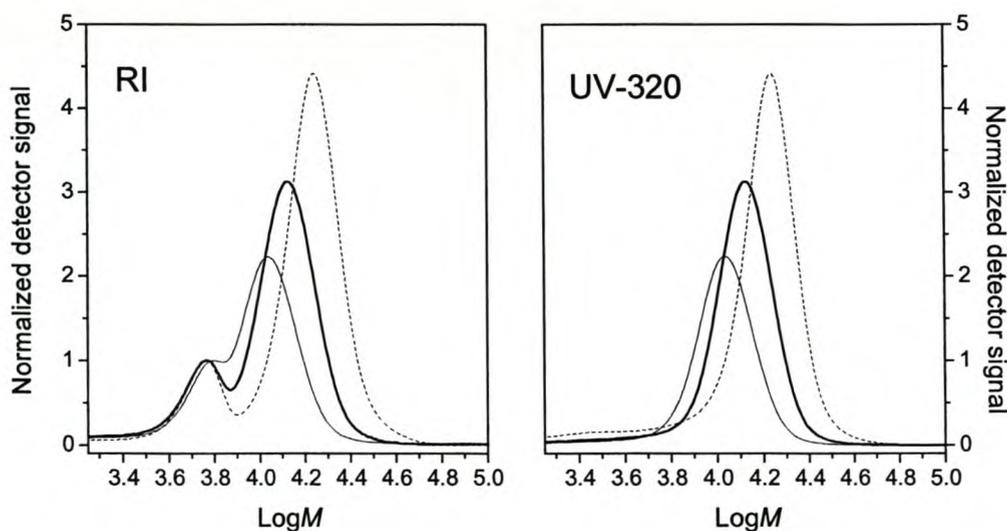


Figure 6.13 DIBTC mediated polymerization of butyl acrylate in the presence of sodium nitrite and a non ionic surfactant IGELPAL CO990 initiated by AIBN. The curves are normalized to the non ionic surfactant and correspond to increasing conversion.

The efficiency of the aqueous phase radical trap is related to the period in which particles are nucleated. If the controlled particles are rapidly nucleated in substantial numbers then aqueous phase particle formation is unlikely to be significant, as few monomer droplets will remain that are able to supply aqueous phase monomer for particle growth. If however, the nucleation process is inefficient the probability of secondary particle formation is increased as a significant number of droplets remain available and aqueous phase monomer is freely available. Long nucleation periods are more probable in cases of predominantly aqueous phase nucleation in the presence of aqueous phase radical traps. In figure 6.13, it is noticeable that the UV distributions do not show evidence of high or low molecular weight shoulders, which suggests that the shape of the UV distributions in figures 6.11 and 6.12 is related to aqueous phase radicals. The implication is that some coagulation and interaction with high molecular weight polymer is occurring as well as some slow nucleation of RAFT containing particles, allowing a broader distribution of UV active polymer. The use of the aqueous phase radical trap appears to “smooth” the nucleation process and prevent the formation of uncontrolled particles. Coagulation will now have less of an effect on molecular weight distributions.

In figure 6.14, the first-order kinetic plots for the three reactions in table 6.2 are shown. All of the reactions reach conversions greater than 90% but it is noticeable that reaction 2, which has no second distribution of polymer, has a large inhibition period.

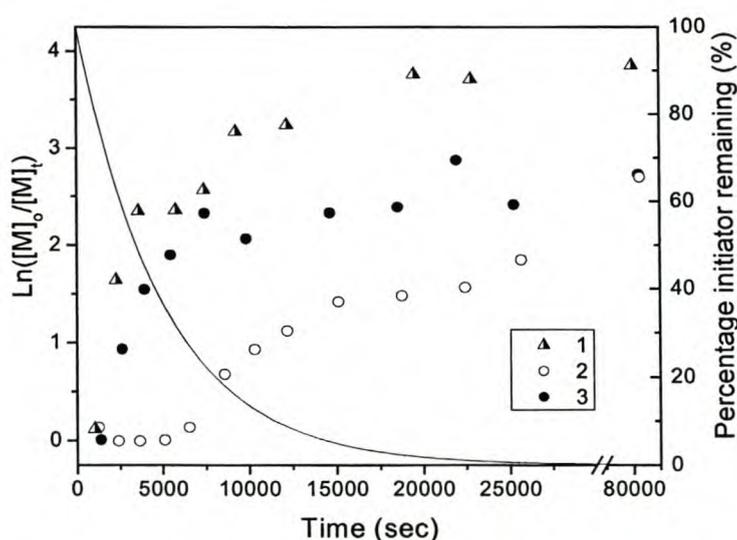


Figure 6.14 First order kinetic plots of DIBTC mediated miniemulsions of butyl acrylate in the presence of a non ionic surfactant, IGEPAL CO 990. Reactions 1 (Fremy’s salt), 2 (Sodium nitrite) and 3 (no aqueous phase radical trap) shown in Table 6.2.

As we have seen in chapter five, the inhibition period in reactions is very misleading, as significant reactions can be occurring without a noticeable change in monomer concentration. The long inhibition period appears to be a requirement to allow the controlled particles to nucleate successfully and render the aqueous phase particle formation insignificant. This is quite similar to results in chapter five.

The results shown in figures 6.11-6.14 show that sodium nitrite was the most efficient aqueous phase radical trap in the reaction series. The use of a radical trap eliminated the secondary distribution of polymer from the molecular weight distributions. The results are not directly comparable with the results in 6.7.1, due to the different particle sizes and aqueous phase surfactant concentrations as well as monomer type. In other reactions, which will be reported at a later date, it has been observed that the concentration of surfactant plays a significant role in butyl acrylate secondary polymer distributions, but is not as important in the case of styrene polymerizations. Whether the issue is thus aqueous phase surfactant concentration or particle size is difficult to discern at this point, as the two are related.

Other effects that have been observed include initiator effects and effects on the dominant termination mechanism in the uncontrolled polymer distributions. The concentration of RAFT agent is also significant, but RAFT agent dependent. This suggests that the leaving group radical plays a very significant role in the formation of secondary distributions. However, the results are preliminary and investigations are ongoing.

6.9 Particle size

The development of the molecular weight distribution should not be seen in isolation. It is important to examine the particle size distribution to determine whether there is a significant difference in size between particles that contain different distributions of polymer, i.e. controlled and uncontrolled and more importantly double distributions. Latexes with multimodal particle size distributions are increasing in popularity due to the higher solids contents that are possible in these systems.^{14,19} The possibility of producing mixed latexes which contain both high molecular weight polymer for matrix strength and lower molecular weight polymer for film forming properties²⁰ combined with a variation in particle sizes is potentially hugely applicable in coatings applications. If multiple particles size distributions were present in the systems, the

hypothesis that the high molecular weight fraction of polymer that is observed in the systems is contained in particles that do not contain RAFT agent and which were formed after sonication could potentially be more fully substantiated. The following determinations were carried out on the MATEC Capillary Hydrodynamic Fractionation apparatus at TU/e. In figure 6.15, a typical particle size distribution of a CTAB, styrene, dithiobenzoate latex, as prepared in chapter five, is shown.

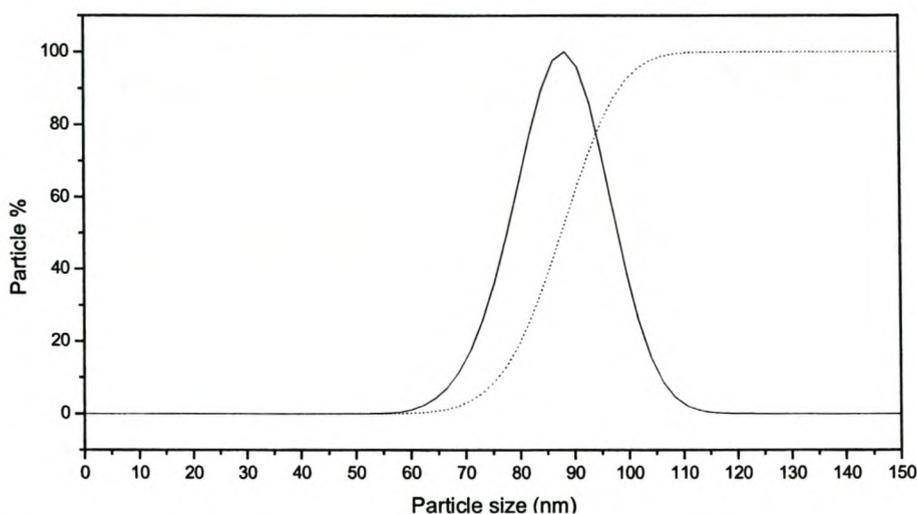


Figure 6.15 Weight-based particle size distribution data of a typical AIBN/CTAB/styrene/CVADTB miniemulsion.

Although the distribution is quite broad, there is no indication of multiple distributions of particles sizes in this latex. The average particle size shows good correlation to the light scattering determinations in chapter five as well as to TEM analysis.

In figure 6.16 the particle size distribution of a DIBTC mediated latex is presented and it can clearly be observed that double distributions of particles are quite significant in polymerized systems that show double molecular weight distributions.

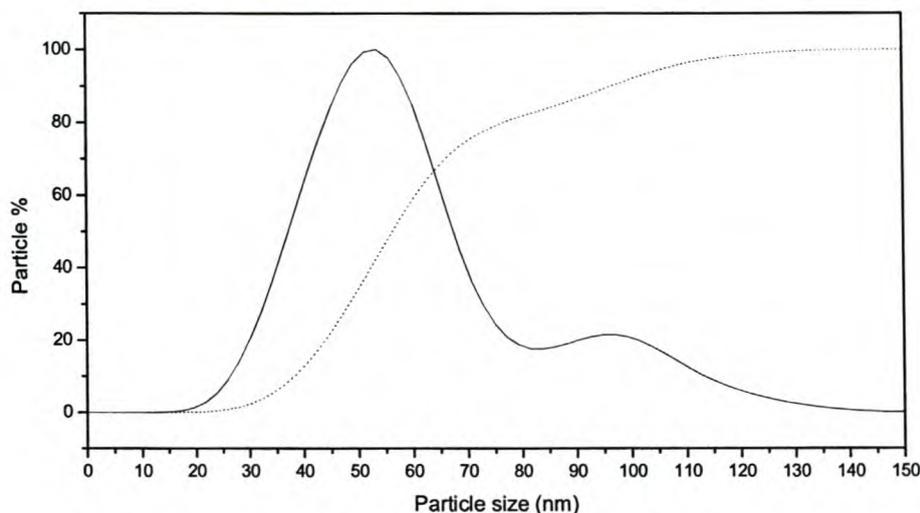


Figure 6.16 Weight overlaid data of a typical AIBN/SDS/DIBTC/styrene miniemulsion.

The interesting point to note here is that the smaller distribution appears at a higher particle size. This distribution is however potentially due to secondary particle formation. The reason that the larger particle distribution may be secondary is due to the higher rate of polymerization within a conventional emulsion particle, in comparison to a RAFT-mediated particle. This could easily lead to the formation of larger secondary particles than primary particles, if the primary particle size distribution is reasonably small. It should also be kept in mind that the secondary particles grow at the expense of the primary particles, causing the primary particles to shrink with time rather than grow and for that reason it is unlikely that the larger particle size particles would be related to the initial droplets. The droplet size in the reactions should be quite similar, as the conditions and surfactant concentrations were similar to those in chapter five.

Figure 6.17 presents some typical secondary distributions through a number of experiments. This type of behaviour is typical in the cases in which DIBTC or PPPDTA were used as RAFT agents. The distributions have been deconvoluted as gaussian peaks using Origin7Pro®. The correlation between the fit and the raw data is greater than 99.5%. The relative peak sizes have also been added to the plots to provide an indication of the relative percentage of particles in the weight overlaid data.

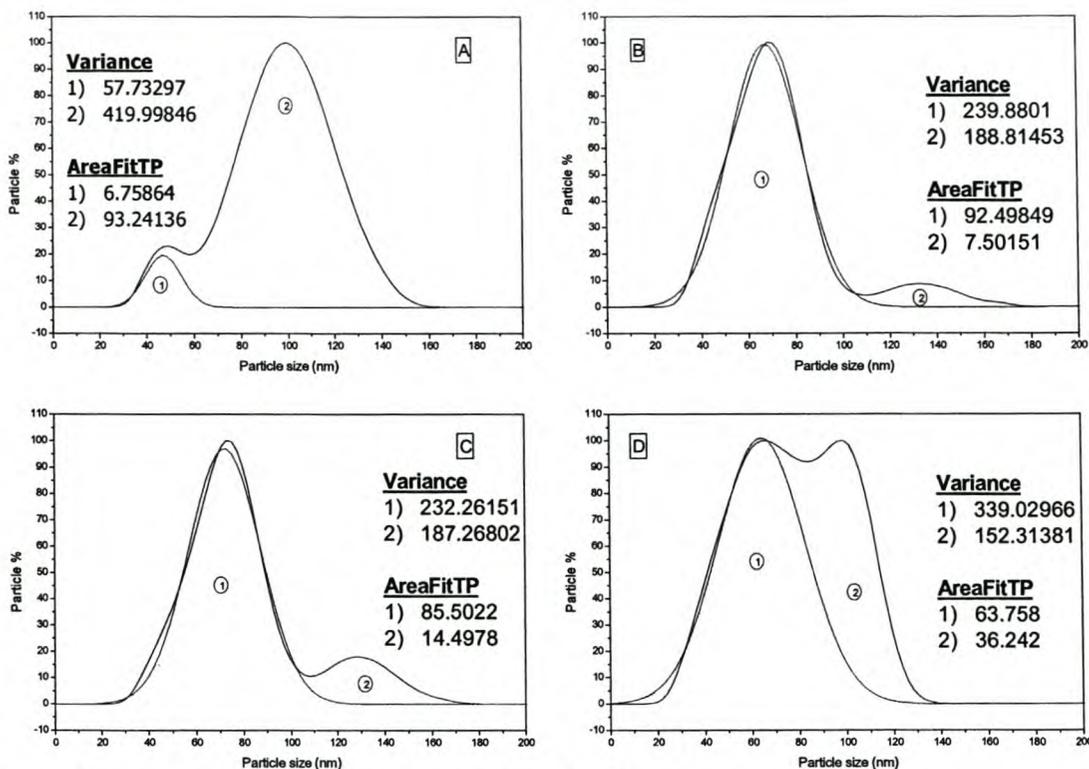


Figure 6.17 Secondary distributions with varying RAFT agent concentrations.

An increase in the concentration of the RAFT agent appears to lead to an increase in the relative size of the secondary particle distribution (though this behaviour seems to be leaving group dependent). Latex systems prepared with RAFT agents that do not provide significant secondary nucleation, create particles approximately 60-80 nm in size. It appears that the secondary distribution of polymer in the latexes has a larger particle size than the primary distribution, which can be explained if the rate of polymerization is higher in the uncontrolled particles (and the primary particles are quite small). In the case of the largest distribution of secondary particles in figure 6.17a, the primary particle size has been reduced to below 50 nm through the diffusion gradient of monomer. In cases where there appear to have been less secondary particles formed, the uncontrolled particles appear to be larger in size, which indicates that the nucleation behaviour is different, but the diffusion gradient is likely to be similar. Although the progression in figure 6.17 is not from a specific experimental series, it serves to illustrate the problems that occur in the analysis of these systems. To be able to successfully discriminate between the distributions, and with a high degree of certainty assign distributions to specific molecular weight distributions as determined by SEC, a hyphenated technique such as CHDF-SEC

would be required. The development of such a technique is of course a study on its own and may form part of extensions of this work.

6.10 Conclusion

In conclusion, it should be stated that the results described here are merely scratching the surface of the information that is potentially available. The application and analysis of latexes containing different particle sizes, types of polymer and molecular weight distributions is only starting, although a significant focus for this type of system is high solids latexes that have excellent film forming abilities. Mixed particle size distributions appear to be more successful in maintaining stability in high solid content materials and the short chains produced by the RAFT process may be very significant in the improvement of film forming without the significant decrease in mechanical strength of the film, which would occur if all the chains in the latex system were short.

It was shown that aqueous-phase radical traps are capable of eliminating uncontrolled polymer distributions (presumably by decreasing aqueous phase particle formation). However, this behaviour only occurred in cases where non-ionic surfactants were used. In cases where ionic surfactants were used, the secondary distribution of polymer increased in size.

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Chapter Seven. Protoseeded Emulsion

Chapter 7: Protoseeded Emulsion

Abstract

The application of N-isopropyl acrylamide in an emulsion process is presented. The use of short NIPAM blocks to stabilize an emulsion at temperatures above the Lower Critical Solubility Temperature of NIPAM provides a route to protoseed latex. The addition of styrene is shown to approximate a pseudo interval II emulsion.

US patent application NO. 60/449,516

7.1 Introduction

In chapter two, the reasons for the use of free radical polymerization in *ab initio* emulsion systems were discussed. It is worth repeating that emulsion polymerization is commercially of critical importance due to the environmentally friendliness of the process as well as the inherent industrial advantages of high molecular weights and fast reaction times. The heat capacity of water also helps in controlling the exotherm and thus allow for a safer polymerization.

Free radical polymerization unfortunately leads to high polydispersity polymers that are formed in the reactors, due to the large number of side reactions that can take place. Advanced polymer architectures are out of reach and true block copolymers are not accessible. From the early 1990's vast amounts of capital and man-hours have been used to develop techniques to expand radical polymerization into a tool that can be used to produce product-specific predictable polymers under the same conditions that are used for conventional polymerizations (see chapter two). We discussed some of the limitations of RAFT in heterogeneous media in chapter two.

Predispersed emulsion polymerization (mini-emulsions) is the most widely used aqueous dispersed polymerization technique in RAFT literature. They suffer from a number of disadvantages, including the need to include non-polymeric species, which may have environmental drawbacks. Specific RAFT agents, i.e. xanthates^{1,2} and dibenzyl trithiocarbonate³ have been shown to have some effectivity, but as they are considered poor control agents, they have limited the improvements in emulsion to the ability to produce block polymers and limit molecular weights (in and of itself no small feat). The use of traditional emulsion techniques with the help of a "magic ingredient" to produce advanced materials has however so far remained out of reach – but has remained tantalizingly close, and RAFT continues to be the best candidate.

The critical problem appears to be the fact that the development of the molecular weight distribution with time is an essential element in an emulsion polymerization. The almost instantaneous development of high molecular weight polymer in emulsion particles seems to be the most important factor in obtaining a stable latex. Unfortunately, this is quite unlikely with the present state of the art in a system that provides controlled polymerization, and for that reason other alternatives to emulsion stabilization need to be developed.

Miniemulsion systems have proven superior to *ab initio* systems, due to the simplification of the polymerization to a pseudo interval III emulsion in which no transport of species is required. This approach was discussed in chapter five. Some problems have still occurred due to limiting conversions, etc. This is largely due to short initiator half-life times in the systems and an initiator feed allows higher conversions to be reached – although the mechanism of RAFT often means that higher conversions allow less control of polydispersity due to viscosity and long chain interaction problems. Predispersion is also a costly technique and would require new industrial plants or extensive modification of existing facilities. A truly *ab initio* emulsion system has not as yet been achieved using an effective RAFT mechanism – unless xanthate agents are used,^{2,4-6} which do not result in low polydispersity index polymers, due to their chain transfer characteristics.

Gilbert *et al*⁷ have shown that a starved feed system, with acrylic acid oligomeric amphoteric RAFT agents, can be used to produce controlled latexes. Starved-feed however remains a technique that requires intimate knowledge of the system to use successfully and operates in interval III of a classical emulsion mechanism as discussed in chapter two. Polymerization of NIPAM, which begins in a homogenous solution, and with increasing conversion becomes heterogeneous in aqueous systems, has been investigated in organic solvents using RAFT,^{8,9} but not in aqueous media.

7.2 Conformational changes in NIPAM

In the final part of this dissertation, a specific monomer will be introduced that plays a significant role in the work presented in this chapter. N-isopropyl acrylamide (NIPAM) belongs to a class of monomers that have a number of interesting properties.

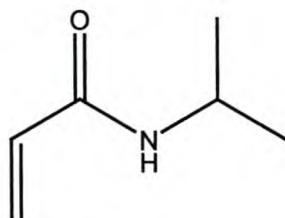


Figure 7.1 The monomer NIPAM (N-isopropyl acrylamide)

The polymers of these monomers exhibit what is known as a Lower Critical Solubility Temperature (LCST) in aqueous media.¹⁰ What this means is that by

applying heat to a homogeneous aqueous solution of the polymer, a coil-to-globule transition occurs, which renders the polymer insoluble in water. This transition is the result of the intramolecular association of the amide functionalities, leading to a tightly coiled polymer chain with no polar groups available for water association for solubilization.¹¹ In aqueous media, the transition is then directly followed by the intermolecular aggregation of the water-insoluble chains.

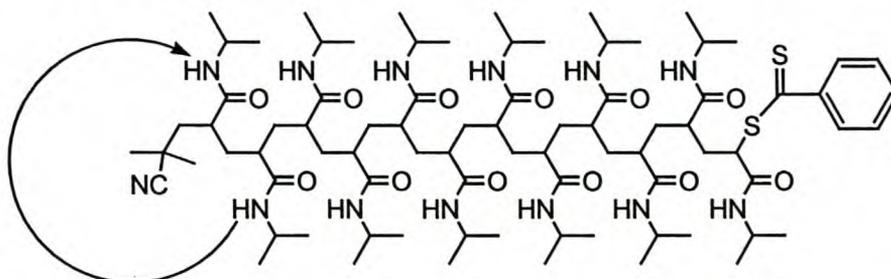


Figure 7.2 A sample RAFT endcapped poly(NIPAM) showing the potential interaction sites for intramolecular association.

In the case of NIPAM, the transition occurs at 32 °C, which is a very useful temperature for a number of biological processes. This has stimulated the scientific community to use these monomers as reversible reservoirs for the storage of molecules and drug release capsules. The temperature¹² can be influenced by a number of factors including pH,¹³ presence of surfactant and chain length.^{14,15} NIPAM has frequently been polymerized in emulsion systems and has also been used in RAFT mediated homogeneous polymerizations.^{8,16} The applications in emulsion are related to the change in solubility with polymerization. NIPAM exhibits very rapid polymerization due to a high k_p which has been determined by pulsed laser polymerization (PLP).¹⁷ In this chapter, we will address the application of this monomer to emulsion, polymerization mediated by the RAFT process and show that LCST polymers can provide a new route to particle formation in emulsion.

The LSCT (lower critical solution temperature) properties of NIPAM show molecular weight as well as concentration dependencies, which can be exploited to produce the desired system. Surfactant free polymerization is also possible, as short NIPAM blocks provide stabilization to emulsified systems at ambient as well as raised temperatures. This is due to the molecular weight dependence of the coil-to-globule transition. NIPAM is commonly used in emulsion to obtain fine crosslinked latexes in concert with a difunctional monomer such as divinyl benzene or ethylene glycol dimethacrylate.¹⁸⁻²⁰

7.3 Hypothesis

The use of DIBTC in an environment where exit is not a significant problem, and in which the possibilities for secondary nucleation are minimal, should provide none of the disadvantages of its use in miniemulsion, as seen in chapter six, while still providing the advantage of minimal rate retardation. The method used in this study to achieve these conditions was the use of poly-NIPAM as a proto-seed to allow a surfactant-free latex system to be polymerized without the use of predispersion. P-NIPAM shows a lower critical solubility temperature (LCST) at 32 °C. By polymerizing NIPAM in the presence of DIBTC in solution at 75 °C, proto-seed latex should be formed by the precipitation of the polymer as it reaches longer chain lengths. If a second monomer were added to the proto-seed in a dropwise fashion, swelling should occur. This swollen proto-seed could then be diluted to the required solids content while polymerization proceeds. This approach would provide an interval II emulsion, as particle formation would be complete, but monomer droplets would be present to act as monomer reservoirs.

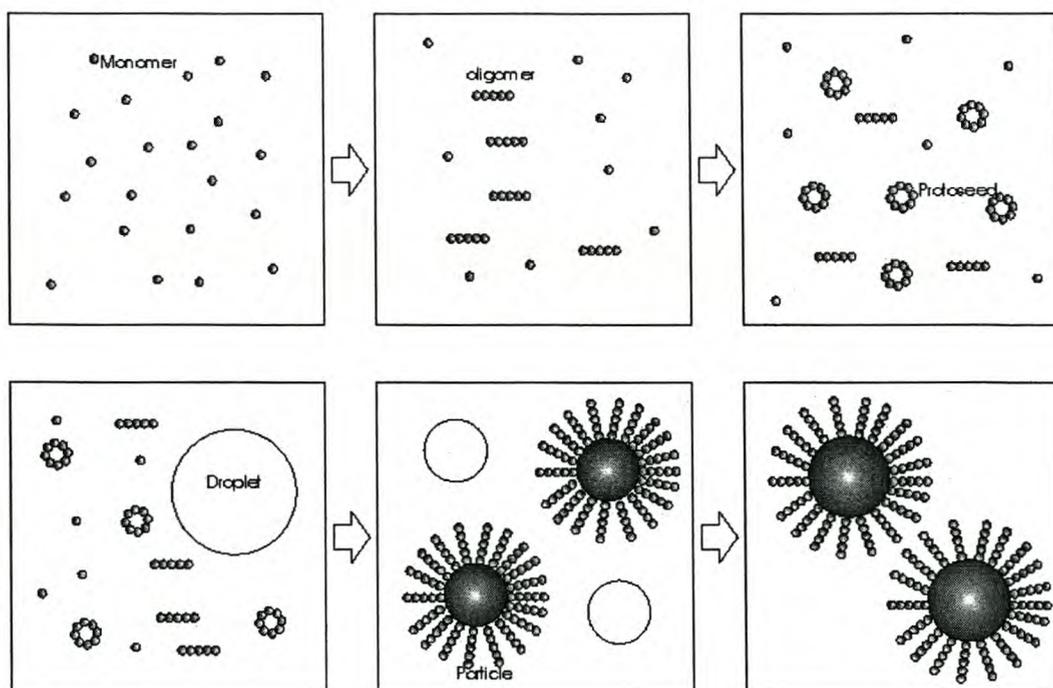


Figure 7.3 The mechanism by which the NIPAM aggregates in solution to form protoseeds, which are then swollen by the addition of monomer droplets to the system. Water-soluble monomer is polymerized resulting in an oligomer, which is short enough that it does not undergo conformation change. As the polymer extends in length it begins to undergo intramolecular association and forms a protoseed. The addition of a second monomer at this point leads to monomer droplets in the system and the monomer can

then swell the protoseeds. The aggregation of the NIPAM cannot continue to the point that the polymer precipitates due to chain extension with the second monomer and a “hairy latex particle is formed. The latex then behaves as a conventional interval II emulsion.

7.4 Experimental and results

7.4.1 Chemicals

NaOH (Associated Chemical Enterprises 97%), azo-bis(4-cyanovaleric acid) (Aldrich 75%), NIPAM (Aldrich 97%), and sodium dodecyl sulfate 90%(Aldrich) were used as purchased. DIBTC was synthesized according to the procedure of Lai *et al.*,²¹ as reported in chapter three, purity was estimated to be 99%+ by NMR. Styrene (Protea Chemicals 99.5%) was washed with a 0.3M KOH solution and freshly distilled prior to use.

7.4.2 General procedure

NIPAM monomer (10-20% of total solids) is added to water to provide a 30% by weight solution in the presence of a RAFT agent and a small amount of NaOH (equimolar amount relative to the RAFT and initiator concentration combined). Initiation was carried out using a carboxylate functional azo initiator. The polymerization temperature used was 75 °C, while mixed by a mechanical stirrer at 100 rpm. After 20 minutes at polymerization temperature, the mixture was heterogeneous, and a styrene addition was begun (~ 5-10 minutes for addition depending on the amount added). Once styrene addition was ~50% complete a water addition was begun to allow the system to have the required total solids content (20-30%). The additions were carried out over a few minutes to ensure that the temperature of the reactor was not decreased too far due to the large increase in contents. Sampling was carried out for analysis, and volatile monomer conversion was determined gravimetrically – total reaction time was typically 3-5 hours.

7.4.3 Precipitation?

Table 7.1: Components for reaction 7.4.3

Reactor charge:	
NaOH	60 mg
4,4'-Azobis(4-cyanovaleric acid)(75%)	22 mg
DIBTC	100 mg
NIPAM	5.03 g
DDI water	15 g
Feed 1:	
Styrene monomer	19.23 g
Feed 2:	
DDI water	54 g

The reactor was charged with the primary charge and heated from room temperature to 75°C. The temperature at the start of the heating cycle was 22°C. The temperature at 5 minutes was 54°C. The total time required for the reaction to reach reaction temperature was 8 minutes. 25 minutes after the reactor oil bath was allowed to begin heating, the styrene charge was added dropwise. After 5 minutes, the water charge was begun, also dropwise through a second addition funnel. Sampling commenced after all ingredients were present in the reactor, and the reaction was allowed to stir at reaction temperature overnight. (After 4 hours the latex appeared stable and higher conversion was envisaged). The reactor was filled with fluffy powder polymer the next morning, which was easily removed from the reactor and dried to obtain powdered polystyrene with a faint yellow tinge from the RAFT agent. There was no indication that the RAFT agent had in any way phase-separated in the system and SEC provided evidence that the polymerization had proceeded in a controlled fashion. The behaviour was somewhat similar to a precipitation polymerization.

7.4.4 Rheology modifiers?

Table 7.2: Components for reaction 7.4.4

Reactor charge:	
NaOH	57 mg
4,4'-Azobis(4-cyanovaleric acid)(75%)	26 mg
DIBTC	113 mg
NIPAM	5.09 g
DDI water	20 g
Acrylic acid (Sodium Salt)	1 g
Feed 1:	
Styrene	24 g
Feed 2:	
DDI water	50 g
Feed 3:	
DDI water	50g

Styrene addition was begun at 26 minutes after the oil bath heating commenced and took 13 minutes. Water addition began 29 minutes after oil bath heating commenced, and took 7 minutes. Latex viscosity increased substantially after 4 hours, and a water addition was carried out over 23 minutes (Feed 3). Viscosity remained high (no samples could be removed by needle), and at 7 hours, the reactor was removed from the oil bath. The latex showed no physical signs of RAFT phase-separation, but viscosity was high. No signs of coagulation were observed, and the latex remained smooth and consistent. The solubility of the latex in THF was poor due to the presence of the sodium salt, but the long-term stability and water retention of the “whipped cream” latex product was excellent.

7.4.5 Secondary particles

Table 7.3: Components for reaction 7.4.5

Reactor charge:	
NaOH	50 mg
4,4'-Azobis(4-cyanovaleric acid)(75%)	20 mg
DIBTC	100 mg
NIPAM	5.00 g
DDI water	15 g
Feed 1:	
Styrene monomer	20 g
Feed 2:	
DDI water	65 g
Sodium dodecyl sulfate	0.4g

The reactor was placed under a nitrogen atmosphere and in an oil-bath, which was then set to reach 75 °C, and heating was initiated. After 5 minutes (temperature 50 °C), the mixture was heterogeneous but still stirrable, and a shot addition of styrene was added to the system, followed immediately by a shot addition of deionised water containing sodium dodecyl sulfate. Samples were taken periodically for analysis. The addition of surfactant to the latex resulted in new particles being formed in the system and a lack of controlled behaviour in the system. The reasons for the formation of secondary distributions as well the general behaviour of the systems are quite different to the polymerizations discussed in chapter six as the surfactant concentration appears to be more significant here than the RAFT agent type. The major difference is the efficiency of the ionic surfactants when compared to pNIPAM oligomers at raised temperatures.

7.4.6 Stable latex

Table 7.4: Components for reaction 7.4.6

Reactor charge:	
NaOH	53 mg
4,4'-Azobis(4-cyanovaleric acid)(75%)	17.8 mg
DIBTC	108 mg
NIPAM	5.00 g
DDI water	15 g
Feed 1:	
Styrene monomer	15.15 g
Feed 2:	
DDI water	65 g

The reaction was carried out in the same fashion as reaction 7.4.3 and 7.4.4 but after 3 hours was removed from the oil bath, as a fine precipitating polymer could be observed. The latex was filtered through a fine mesh, and a particulate precipitate was recovered. The latex product was stable on cooling. The characteristics of the latex and the polymer that was removed by filtration were very similar by SEC. The product produced was a stable controlled emulsion latex with excellent room temperature stability.

7.5 Discussion and conclusions

The use of trithiocarbonate RAFT agents (DIBTC), which contain stabilizing carboxylate leaving groups, under raised pH, provided stable latexes. The use of dithiobenzoate RAFT agents was ineffective, due to their instability at raised pH. SEC results of the polymers produced show controlled behaviour. The nature of the process requires reactivation of the chains, which inherently shows the living character of the polymer. Figure 7.4 presents the size exclusion chromatograms of the successful reaction process, as discussed experimentally in 7.4.6.

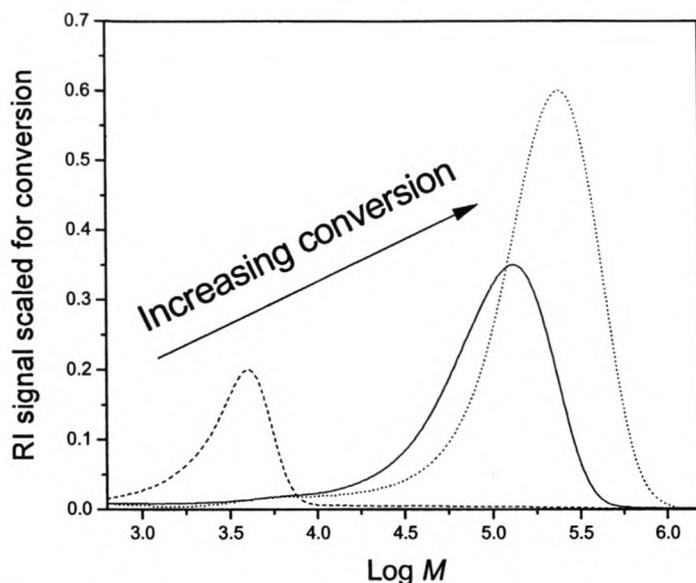


Figure 7.4 SEC traces of the development of molecular weight with time in the proto-seed NIPAM/styrene emulsion polymerization showing the increasing molecular weight with conversion.

There is a clear increase in molecular weight with conversion. There is some broadening of the distribution as well as some tailing. The PDI of polymer product is approximately 1.6, which is similar to corresponding published systems.⁷ Figure 7.5 shows the conversion-time behaviour of the system once all components are present.

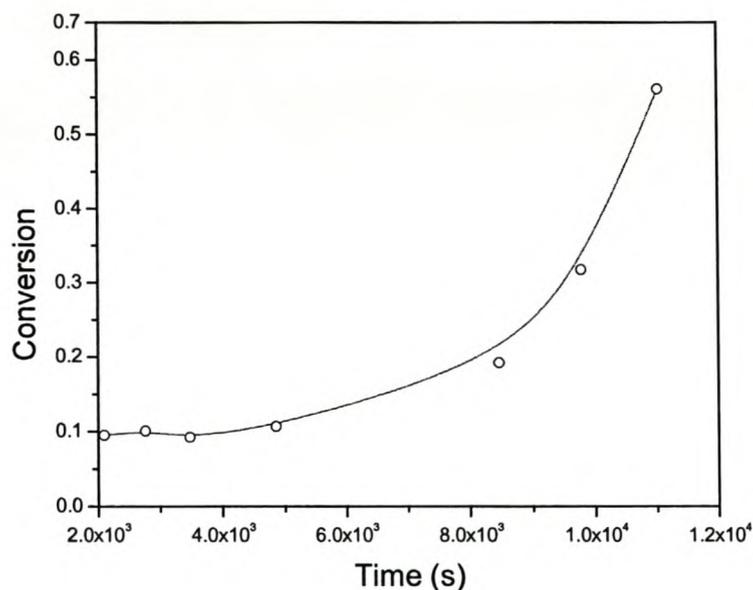


Figure 7.5 The conversion-time behaviour of the styrene in the system showing the inhibition of polymerization after the addition of monomer droplets to the system. The B-Spline fit is added as a guide for the eye.

It seems probable that the system is monomer flooded, as conversion onset is delayed. The system shows some instability at conversions >80%. Room temperature stability is excellent if cooled before 80% conversion, or if filtered at higher conversions. The precipitate is in the form of a fine coagulum that can be easily removed by filtration. If the reaction is allowed to reach full conversion, the reactor contains particulate polymer which, when dried, yields a fine powder. This powder shows a SEC distribution that is controlled and not far removed from that formed in the latex. The RAFT agent colour, which in the case of trithiocarbonates is very slight, but still observable, means that the powder has a pale yellow colouring if observed under good lighting. Figure 7.6 presents a typical CHDF chromatogram.

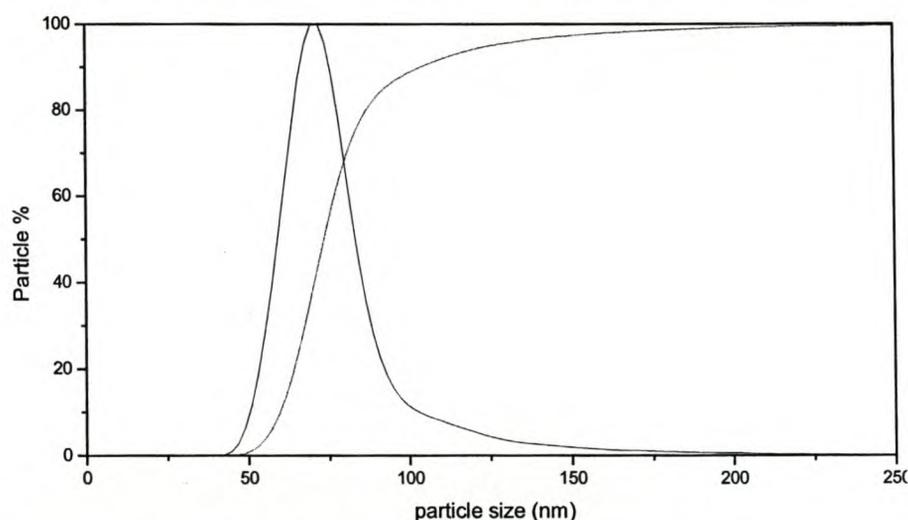


Figure 7.6 Typical CHDF of the latexes produced.

CHDF analysis of the latex particle size shows that particles are around 70 nm in size. Tailing was observed towards the larger particle side – but this would be expected in the system, due to the approach used to add monomer to the system as well as the timing requirements for temperature decrease, which could both lead to coagulation in the reactor.

The use of a proto-seed to ensure the RAFT agent's presence in the polymerization loci of an emulsion system has been successfully achieved by using the temperature dependence of solubility of N-isopropyl acrylamide in water. The work carried out at this stage is preliminary. The following points support the hypothesis:

1. *If water is added as the first addition, then the oligoNIPAM is redissolved.*
2. *If the NIPAM concentration is too low, then no particle formation takes place.*
3. *If the NIPAM block is not grown to the point of heterogeneity, then phase separation occurs in the same fashion as for a conventional RAFT mediated emulsion. After a period of time, an oligomeric RAFT-rich phase separates in the vortex.*

Proof of principle has been obtained, but problems remain as far as high conversion stability are concerned. The system's specificity towards certain monomers or RAFT agents still needs to be investigated. If the SEC results achieved are compared directly to those achieved by Ferguson *et al.*⁷ then it can be observed that the distributions obtained are quite similar. Some broadening occurs at higher conversions, and low molecular weight tailing is quite clear throughout the reaction. There are some significant theoretical reasons why this should occur in a RAFT-mediated emulsion; these include the generation of new short chains by initiator decomposition as well as the efficiency of radical termination within particles. Work on the system is ongoing, and a number of routes have been suggested as possible approaches to ensuring high conversion latex stability. These include "chasing" the monomer remaining at temperatures below the LCST of NIPAM, using a redox couple as an initiating system. The use of monomers such as NIPAM provides a potentially interesting route to proto-seeded emulsions in systems where droplet polymerization is a potential problem. There are currently some constraints involved, but this approach shows early promise.

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Conclusion and Recommendations

Conclusions to the study

The understanding of the RAFT process in homogeneous and heterogeneous media has been improved by the work presented here.

In Chapter four, the application of NMR in mechanistic studies of the RAFT process was discussed. Initialization was defined as a concept, and examples were provided to show that some inhibition phenomena can be related to initialization. It was shown that the early steps in a RAFT-mediated polymerization are extremely selective, and that individual monomer additions could be monitored in the reactions. The increased understanding of the RAFT mechanism, especially involving initialization, provides a number of interesting new insights into synthetic approaches to polymeric and oligomeric materials.

In chapter five, the development of a stable robust miniemulsion system for RAFT-mediated polymerization was presented, that allowed the formation of block copolymers with conventional ionic surfactants. The effects of surfactant concentration on particle size were discussed and, it was demonstrated that particle size could easily be tuned without destabilizing a RAFT-mediated latex.

In chapter six, an analysis of particle nucleation phenomena was shown, and some suggestions for working in high surfactant systems were given. The most important factors were correct dispersion, and the nature of the RAFT agent used. It was shown that CHDF and SEC provide complementary information, and double detector techniques allow us insight into the processes occurring in particle formation in emulsion.

In chapter seven, a new approach to *ab initio* emulsion polymerization from N-isopropylacrylamide was presented. It was shown that it was possible to use RAFT in an interval II emulsion based on a protoseeded emulsion approach. A water soluble

monomer that provides an oligomer with decreasing water solubility upon increasing its chain length, allowed a single step seeded polymerization in interval II.

The development of successful RAFT-mediated predispersed media as well as *ab initio* emulsion techniques open the door for the development of structured latex particles. The examination of plausible nucleation pathways to explain the polymer and particle distributions in heterogeneous aqueous media show routes to complex latexes containing both living and conventional (FRP) distributions of polymer.

The understanding of the RAFT process, which is after all barely 6 years old, still presents a number of interesting challenges. The work presented in this dissertation should be a meaningful contribution.

Suggestions for future investigation

Miniemulsion and emulsion polymerization in general still need significant investigation before living radical polymerization in these media is commercially viable. The potential of the living radical techniques is however tremendous, and a completely new range of materials are within reach for materials scientists. Some of the most important aspects that still require attention include particle nucleation mechanisms in living radical emulsion techniques, terminal conversions in RAFT systems, and high conversion effects on the RAFT equilibrium. The importance of living radical emulsion techniques in the development of conventional free radical emulsion principle and theories should also not be underestimated. It has been clearly illustrated that the full understanding of all of the issues that surround the formation of a polymerized latex still require substantial investigation. Hypenated CHDF-SEC, although presenting a developmental challenge is in all likelihood the tool of choice to further analyze the mixed latex products. The use of NMR techniques for emulsion polymerization also needs to be investigated further. *In situ* NMR may offer a route towards increased understanding of particle formation and chain growth processes.

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--The End--