

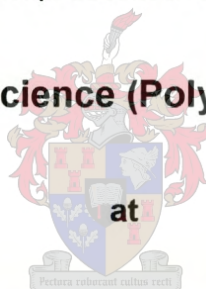
Emulsion Polymerization of Styrene in the Presence of Reversible Addition- Fragmentation Chain Transfer Agents

by

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DECLARATION

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

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ABSTRACT

This work involves the study of the effects of Reversible Addition-Fragmentation Chain Transfer (RAFT) agents on the emulsion polymerization of styrene. The feasibility of RAFT as a method for obtaining controlled radical polymerizations in emulsion systems is also investigated. Both seeded and *ab initio* systems were studied with three RAFT agents of varying structure.

Inhibition and retardation effects on addition of various amounts of the RAFT agents to the emulsion systems were observed and the trends noticed. The effect of the RAFT agents on the average number of radicals per latex particle was calculated from reaction rates. The effect of the RAFT agent on the molecular weight and the molecular weight distribution was monitored by gel permeation chromatography.

Exit of free radicals from the latex particles proves to be a major feature in the studied RAFT emulsion systems. Fragmentation of the RAFT agent in the latex particles, gives rise to free radical species that can exit from the particle and enter other particles where they can either terminate instantaneously or propagate. The exit and termination processes presumably result in both the inhibition and retardation of the emulsion polymerizations. A linear increase in M_n with conversion is observed, however the low concentration of RAFT agent in the latex particles is responsible for the obtained number average molecular weights being much higher than predicted. The low concentrations of RAFT agents in the latex particles is also responsible for the broad molecular weight distributions that are obtained.

Reaction conditions for RAFT experiments should to be chosen so that the effects of exit processes are minimized and that the RAFT agent is primarily situated in the latex particles. These conditions must be met if the RAFT process is to be successful as a method of controlled radical polymerization in emulsions.

OPSOMMING

Hierdie navorsing behels die studie van die effek van 'n bygevoegde addisie-fragmentasie kettingsoordragsreagent (RAFT¹) op die emulsie polimerisasie van stireen. Die uitvoerbaarheid van RAFT as 'n metode om gekontroleerde radikale polimerisasies in emulsiesisteme te verkry is ook ondersoek. Eksperimente met drie RAFT-kettingoordragsreagente van gevarieerde strukture is uitgevoer in beide *seeded* en *ab initio* sisteme.

Die effek van die RAFT-reagent op die inhibisie en vertraging van die emulsie polimerisasie is waargeneem en die invloed van RAFT op die gemiddelde aantal radikale per partikel is bepaal. Die ontwikkeling van die molekulêre massa en die molekulêre massadistribusie is waargeneem deur middel van gel permeasie- kromatografiese tegnieke.

Die ontsnapping van vrye radikale vanuit die partikels was 'n belangrike faktor in RAFT-emulsiesisteme wat ondersoek is. Hierdie radikale is gegeneer deur die fragmentasie van die oorspronklike RAFT-reagent. Fragmentasie van die RAFT-reagent in die lateks partikels lei tot die vorming van vrye radikale spesies wat uit een partikel kan ontsnap en ander partikels kan binnedring waar dit onmiddellik kan termineer of propageer. Die ontsnappings- en terminasieprosesse van vrye radikale lei oënskynlik tot die inhibering en vertraging van die emulsie polimerisasie.

'n Lineêre verhoging in die gemiddelde molekulêre massa tydens konversie is waargeneem, alhoewel die M_n -waardes baie hoër was as wat verwag is. Die verskil kan toegeskryf word aan die klein hoeveelhede van die RAFT-reagent wat in die partikels teenwoordig is. Hierdie lae RAFT-konsentrasies is ook verantwoordelik vir die breë molekulêre massa distribusie wat waargeneem is.

Vir die RAFT-proses om suksesvol te wees in gekontroleerde radikale polimerisasies in emulsies, moet reaksie kondisies so gekies word dat die ontsnapping van vrye radikale tot 'n minimum beperk word en die RAFT-reagent hoofsaaklik in die lateks partikels teenwoordig is.

¹ RAFT = Reversible Addition-Fragmentation Chain Transfer

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LIST OF ABBREVIATIONS

ACPA	4,4-azobis(cyanovaleric acid)
AIBN	azobis(isobutyronitrile)
ATRP	Atom Transfer Radical Polymerization
BMA	butyl methacrylate
CHDF	Capillary Hydrodynamic Fractionation
CRP	Controlled Radical Polymerization
CTA	Chain Transfer Agent
Cumyl RAFT	Cumyl dithiobenzoate
DRI	Double Refractive Index
EMA RAFT	2-(ethoxycarbonyl) prop-2-yl dithiobenzoate
ESR	Electron Spin Resonance Spectroscopy
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
KPS	Potassium persulfate
MMA	methyl methacrylate
MWD	Molecular Weight Distribution
NMR	Nuclear Magnetic Resonance
PBMA RAFT	Polybutyl methacrylate dithiobenzoate
PCS	Photon Correlation Spectroscopy
PDI	Polydispersity Index
PMMA	poly(methyl methacrylate)

PS	polystyrene
RAFT	Reversible Addition-Fragmentation Chain Transfer
SEC	Size Exclusion Chromatography
SDS	Sodium Dodecyl Sulphate
TEMPO	2,2,6,6-tetramethylpiperidine-1oxyl
THF	Tetrahydrofuran
VOC	volatile organic solvents

LIST OF SYMBOLS

C_p	monomer concentration within the latex particles
C_p^{sat}	monomer concentration within the latex particles in presence of monomer droplets
C_W	concentration of monomer in water phase
d_i	diffusion coefficient of a chain whose degree of polymerization is i
d_M	density of monomer
d_p	density of polymer
D_{mon}	diffusion coefficient of monomeric free radicals
D_W	diffusion coefficient of monomeric free radical in the water phase
k_d	first-order rate coefficient for initiator decomposition
k_{dM}	first-order rate coefficient for desorption of monomeric free radical from particle into aqueous phase
k_e	second-order rate coefficient for irreversible entry of a free radical into a particle
k_p	generic propagation rate coefficient
$k_{tr,M}$	second-order rate coefficient for transfer to monomer
$k_{tr,RAFT}$	second-order rate coefficient for transfer to RAFT agent
M	molecular weight of the polymer
M_n	number average molecular weight
M_w	weight-average molecular weight
m_M^0	initial mass of monomer per total volume (discrete plus continuous phase) in the reaction vessel

m_p^0	initial mass of polymer per total volume (discrete plus continuous phase) in the reaction vessel
M_0	molecular weight of monomer
\bar{n}	average number of free radicals per latex particle
n_M^0	initial number of moles of monomer present in latex particles per unit volume of aqueous phase
N_A	Avogadro constant
N_c	number of latex particles per unit volume of aqueous phase
$P(es)$	probability of escape
$P(M)$	instantaneous number molecular weight distribution
ρ	pseudo first-order rate coefficient of entry of free radicals into a latex particle
r_u	unswollen radius of latex particle
r_s	swollen radius of latex particle
T_g	glass transition temperature
V_{sM}	partial molar volume of monomer
V_{sp}	partial molar volume of polymer
w_p	weight fraction of polymer
x	fraction conversion from monomer to polymer
$X(M)$	GPC molecular weight distribution

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND TO THE THESIS

The thesis describes a controlled free-radical polymerization process that can be used in various polymerization media, including aqueous medium (emulsion polymerization). Controlled radical polymerization processes aim to maintain the advantages of radical polymerization while trying to eliminate the disadvantages that are normally associated with radical polymerization. The controlled radical polymerization (CRP) process is capable of producing polymers of pre-determined molecular mass with narrow molecular weight distributions (MWD), and can also be used for the synthesis of block-copolymers by the successive addition of different monomers. The newly introduced Reversible Addition Fragmentation Chain Transfer process, known as the RAFT process, is a novel technique which seems very promising for the achievement of controlled radical polymerization in various systems. The importance of emulsion polymerization, radical polymerization and controlled radical polymerization, all of which have bearing on the thesis, are discussed below.

1.1.1 IMPORTANCE OF EMULSION POLYMERIZATION

Emulsion polymerization is an economically important process. Of the current production of polymers approximately 30% is produced by free-radical means, while emulsion polymerization is used for effecting 40-50% of these free radical polymerizations^[1]. Some of the products made by emulsion polymerization are commodity materials such as artificial rubber and latex paints, while other products

are high value-added, such as for diagnostic kits in biomedical applications. Emulsion systems are relatively cheap and robust, with low sensitivity to impurities. The polymerization results in a low viscosity latex of that has a high solids content. There are thus considerable incentives for the understanding of emulsion polymerization processes as well as the ability to control the micro- and macrostructure of polymers for the development of better products.

Gilbert has documented^[1] the advances and developments made in the field of emulsion polymerization concerning kinetics, thermodynamics, mechanisms, system models and the control of micro- and macro structure. The fundamental mechanisms of the polymerization process dictate what the properties of the polymer and latex will be, given particular operating conditions (for example, choice of monomer, temperature, surfactant, transfer agent, feed profile). These properties of the polymer and of the latex govern the properties that are important to the customer, albeit frequently in a complex way.

1.1.2 THE IMPORTANCE OF FREE-RADICAL POLYMERIZATION

From an industrial point of view, a major benefit of radical polymerizations is that they can typically be carried out under relatively undemanding conditions and they exhibit a tolerance of trace impurities, which is in direct contrast to ionic or coordination polymerization. A consequence of this is that high molecular weight polymers can often be produced, without the removal of the stabilizers present in commercial monomers, in the presence of trace amounts of oxygen, or in solvents that have not been thoroughly dried. Unlike other vinyl-polymerization methods, radical polymerization can be used with numerous monomers as it tolerates a wide variety of functional groups and the reactions proceed at convenient reaction temperatures. Perhaps the most remarkable feature of radical polymerizations is that they can conveniently be carried out in aqueous medium and hence the concentrations of organic solvents in polymers are significantly reduced or

eliminated, with the subsequent reduction in volatile organic solvents (VOC) being emitted into the atmosphere.

It is the apparent simplicity of radical polymerization that has led to the technique being widely adopted for both industrial and laboratory scale polymer synthesis.

1.1.3 IMPORTANCE OF CONTROLLED FREE-RADICAL POLYMERIZATION

One of the often cited problems with free-radical polymerization is a perceived lack of control over the process and the range of undefined defect structures and other forms of structural irregularities that may be present in polymers prepared by this mechanism. Much research over the last decade has been directed at providing answers for problems of this nature and findings have been documented by Moad and Solomon^[2]. Living polymerization mechanisms offer polymers of controlled architecture and molecular weight distribution (MWD). In particular, they provide a route to narrow polydisperse homopolymers, high purity block copolymers and end-functional polymers.

Traditional methods of living polymerization are based on ionic, coordination or group transfer mechanisms. In living radical polymerizations (also known as quasi- or pseudo-living radical polymerization) control over the termination process is achieved through the use of reagents that reversibly terminate polymer chains. These reagents serve to reduce the concentration of propagating species and the incidence of radical-radical termination. The RAFT process is a typical example of a controlled polymerization where the concentration of propagating species is not reduced. Controlled radical polymerization (CRP) aims to retain the advantages of traditional free-radical polymerization while minimizing the disadvantages (see Table 1.1).

Table 1.1 Some advantages and disadvantages of traditional free-radical polymerization

Advantages	Disadvantages
Compatibility with wide range of monomers, including functional monomers	Little control over molar mass distribution
Versatile with respect to reaction conditions	Little control over chain topology (e.g. no block copolymers)
Widely applied in industry	No control over tacticity

Controlled radical polymerization is a relatively new field in polymer science and offers much scope for growth and development. The applications of the living radical polymerization are in the synthesis of:

- End functional homopolymers
- Block, gradient and graft copolymers
- Polymers of narrow polydispersity and chemical homogeneity
- Polymers of controlled molecular weight.

The control of the micro- and macro structure of polymers is of industrial importance. The macro properties ("customer" properties) of industrial products are directly related to the polymer and latex properties such as molecular mass, MWD, particle size, particle size distribution, copolymer composition, particle morphology and end-groups^[3].

Very few controlled free-radical polymerizations in emulsion have been described in literature.^[4-6] Most experimental work that has been carried out using controlled radical polymerizations has been performed in bulk and solution^[7-11]. There is still much to learn about processes offering control in emulsion systems. Recent discoveries by Rizzardo *et al*^[12] show that certain dithioesters can be used as chain transfer agents in living free-radical polymerizations and that controlled emulsion polymerization using these chain transfer agents is possible. Further investigation

into the control of emulsion polymerization by the use of dithioesters is certainly deemed necessary as we aim to combine the advantages of tailoring polymer microstructure with the convenience of emulsion polymerization.

1.2 OBJECTIVES

The basic objective of this project was to study the RAFT process in both seeded and *ab initio* emulsion systems and to determine the optimal conditions for control of the polymerization process in the emulsion polymerization of styrene with a RAFT agent as the chain transfer agent.

An aim was to gain insight into the mechanisms and kinetics of the RAFT process in an emulsion system by first gaining information on the effects of entry and exit due to the transfer and fragmentation processes, of the different RAFT agents used in this work.

From personal communications and preliminary experiments, it was known that a sticky red layer was formed during emulsion reactions. Work by Rizzardo et al^[12] showed that by reacting all of the RAFT agent in the absence of monomer droplets (Interval III) and then adding monomer slowly, the problem of the red phase separation was overcome.

Seeded experiments were first carried out at 60°C to yield information regarding entry and exit processes. Control experiments were performed in the absence of RAFT agent, and the RAFT agent structure and concentration was varied in the RAFT experiments. To specifically study the effects of the appearance of the conspicuous red layer, the seeded conditions were chosen so as to study the emulsion polymerization changeover directly from Interval II (polymerization in the presence of monomer droplets where the monomer concentration inside the particles is constant) to Interval III (polymerization in the absence of monomer droplets, where the monomer concentration in the latex particles is declining).

Ab initio experiments were then carried out with varying RAFT concentrations to see what the effect of the added RAFT agent was on the process of particle nucleation. The results obtained from the *ab initio* experiments, which were done under typical emulsion reaction conditions, were to be compared and interpreted in the light of the mechanistic information obtained from the seeded experiments.

1.3. THESIS OUTLINE

- Chapter 1:

An introduction to and the importance of the investigation and the investigation into the emulsion polymerization of styrene in the presence of Reversible Addition-Fragmentation Chain Transfer Agents is given.

- Chapter 2:

An historical and literature review of emulsion polymerization, radical polymerization and controlled radical polymerization is presented.

- Chapter 3

The experimental procedures used for the synthesis, purification and characterization of the three RAFT compounds used are described.

- Chapter 4

The procedure followed for the seeded experiments is described , followed by a presentation of the results and a discussion.

- Chapter 5

The procedure followed for the *ab initio* experiments is described, followed by a presentation of the results and a discussion.

- Chapter 6

Discussion and comparison of the seeded and *ab initio* results, and possible future directions for the use of the RAFT process in emulsion systems.

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CHAPTER 2
HISTORICAL AND THEORETICAL

2.1 EMULSION POLYMERIZATION

Emulsion polymerization of unsaturated monomers to produce polymer latexes is a well-established technology, which originated during the First World War. The latexes that are produced are used mainly in paint; paper, textiles, floor wax and adhesive applications. Since the advent of the emulsion system much work has been done on the kinetics and the mechanisms of emulsion polymerization and, due to increasingly stringent government regulations on solvent-borne systems as well as rising energy costs, much more growth in this area can be expected.

Emulsion polymerization follows a free-radical mechanism, which is well documented^[1], and the propagation step can be represented schematically by Figure 2.1:

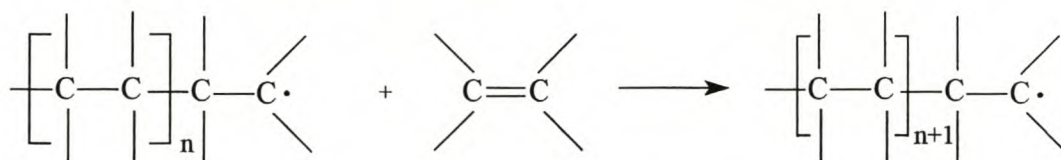


Figure 2.1 Propagation step in free radical polymerization.

The most important ingredients for an emulsion polymerization are water, monomer, initiator, surfactant, chain transfer agents (CTA) and buffers. The role of each of the mentioned ingredients is briefly described below.

Water Reaction medium, which is necessary for both emulsification and heat transfer. Water also serves as the solvent for the surfactant and the initiator.

- Monomer* Vinyl monomers are used as the building blocks in free radical polymerization. The selection of the monomer components in an emulsion polymerization process is determined by the desired properties of the final polymer as the physical properties of the polymer are related to several monomer physical parameters.
- Initiator* Thermal or redox initiators (water soluble) are used to generate the free radicals that will initiate the polymerization reaction in the aqueous phase.
- Surfactant* Imparts colloidal stability to the latex particles, which are the loci of polymerization, by reducing the interfacial tension and by the formation of micelles.
- CTA* Facilitates control of molecular weight and molecular weight distribution.
- Buffer* Prevents hydrolysis of the surfactant by controlling the pH; also sometimes necessary to ensure reasonable initiator efficiency.

The water and the surfactant are charged to the reaction vessel and raised to the desired polymerization temperature while stirring the reactor contents. The monomer(s) are then added and are emulsified by agitation of the reaction medium, which is followed by the addition of the initiator to initiate the polymerization.

The advantages of emulsion polymerization include:

- Heat of the exothermic polymerization reaction is readily absorbed and dissipated by the aqueous phase.
- High average molecular weights are achieved.
- The system is robust and insensitive to impurities.
- Molecular weight can be controlled with CTA's.
- High rates of polymerization are achieved.
- High conversions can be achieved, thereby minimizing residual monomer content.

- The polymer is formed as a latex with a low viscosity, which makes for easier handling.

The drawbacks associated with emulsion polymerization are:

- The large number of additives may impair the quality of the final product.
- Separation of the polymer from the water may be necessary before further processing can take place, thereby increasing production expenses.
- Due to the heterogeneity of the system, the mechanisms are complex, difficult to understand and hence the reaction is difficult to control in terms of the desired end product.

2.1.1 KINETIC EVENTS OCCURRING DURING EMULSION POLYMERIZATION

There are four main free-radical reactions that occur during a free radical polymerization process, they are:

- *Initiation* The series of reactions commencing with generation of primary radicals (from the initiator) and culminating in addition to the carbon-carbon double bond of the monomer so as to form initiating radicals^[1].
- *Propagation* Change in radical position with the addition of new monomer to the growing polymer chain.
- *Termination* Process whereby radicals are destroyed through combination or disproportionation reactions.
- *Chain transfer reactions* Transfer of the free radical from a growing chain to another molecule (CTA, initiator, monomer, polymer, solvent, surfactant). This interruption of the growth of the chain leads to the limiting of molecular mass without affecting the overall rate of polymerization.

The main reactions that occur in and around the latex particles in emulsion polymerization^[2] are illustrated in Figure 2.2:

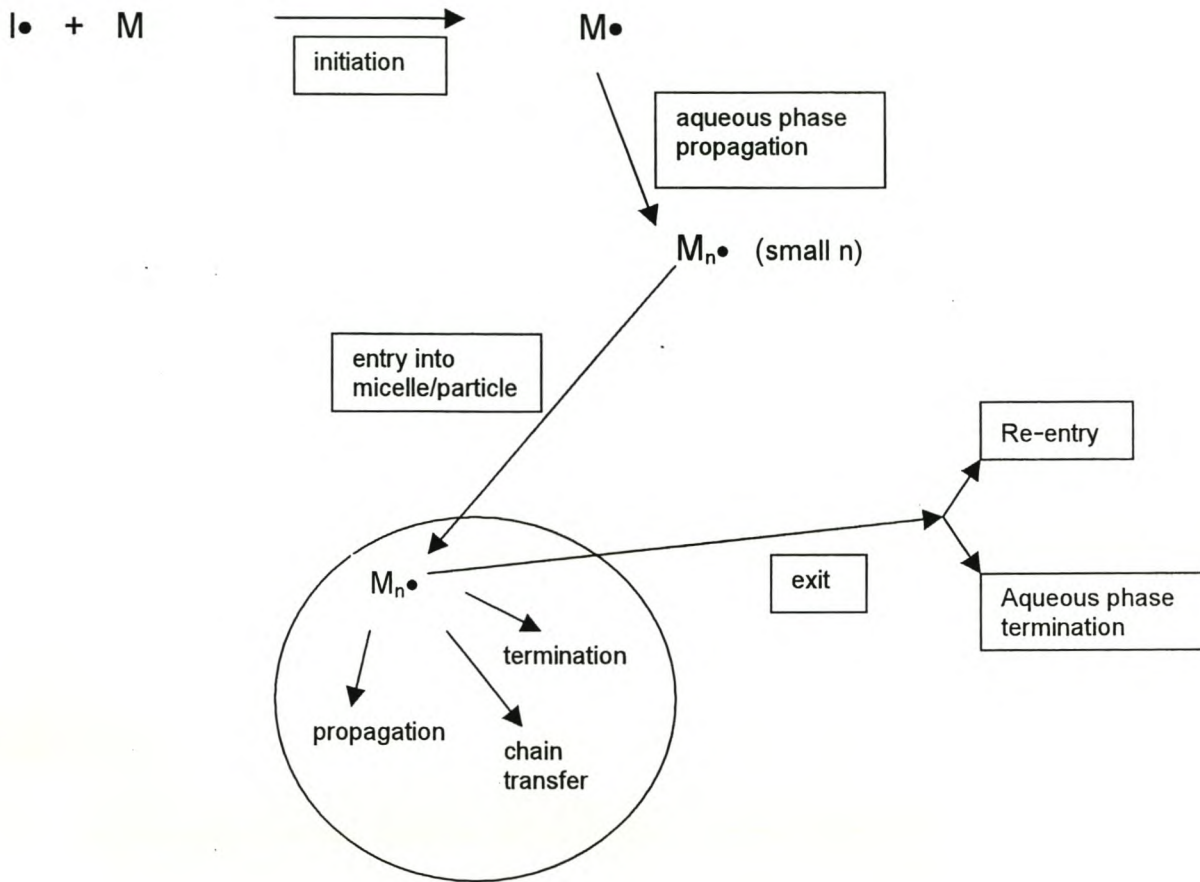


Figure 2.2 Illustration of the free-radical reactions taking place in and around latex particles.

At all times during a free radical polymerization, new free radicals are being created through the process of initiation, existing free radicals are propagating and undergoing termination and chain transfer reactions. The polymerization system will therefore contain dead (non-radical) polymer chains and living (free-radical) polymer chains of any degree of polymerization throughout the course of the polymerization.

The heterogeneous nature of emulsion polymerization adds some complications to the kinetic processes (initiation, propagation and termination) due to the partitioning

of the various ingredients between the different phases. The partitioning of the ingredients between the aqueous phase, the micellar phase, the monomer droplet phase and the particle phase leads to the possibility that the polymerization can take place in all of the different phases in the initial stages of polymerization and then shifts to only the aqueous and the particle phase after the monomer droplets have disappeared. The polymerization is generally predominant in the polymer particles in an emulsion system^[3].

The main issues in dealing with the mechanisms and kinetics of emulsion polymerization involve the understanding of the processes by which latex particles form and grow. This includes the evolution of particle size (and particle number) and size distribution, the development of molar mass and molar mass distribution, the polymerization rate profile during the course of the reaction, and how these are influenced by the basic polymerization parameters. These parameters include the monomer(s), surfactant(s) type and concentrations, initiator type and concentration, type and concentration of chain transfer agent (when applicable), temperature and mode and rate of monomer addition.

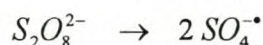
2.1.2 THE DIFFERENT INTERVALS IN EMULSION POLYMERIZATION

Harkins postulated the original qualitative description of emulsion polymerization^[4]. Emulsion polymerization is divided into three intervals, encompassing the particle formation stage, termed Interval I and the particle growth stages, Interval II and III. These Intervals will be described for the emulsion polymerization of styrene with a water soluble initiator^[2].

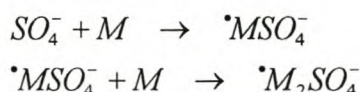
Before polymerization commences there is an induction period, when the primary free radicals arising from initiator decomposition are consumed by residual oxygen or other inhibitor. This period is usually of no direct kinetic interest.

2.1.2.1 Interval I

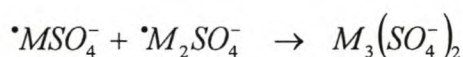
The persulfate initiator, situated entirely in the aqueous phase, decomposes



and the formed sulfate radicals propagate with the rare monomer units encountered in the aqueous phase, to produce oligomeric radicals that are relatively soluble in water:



This oligomeric radical may undergo termination with another radical species, e.g.



Subsequent aqueous phase polymerization of oligomers which escape termination enables them to attain a degree of polymerization at which the species becomes surface active; for styrene this degree of polymerization is about 3. The resulting species now becomes a micelle, either by entering a pre-existing micelle or by forming a micelle by aggregation with surfactant molecules in the aqueous phase.

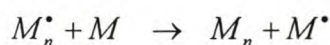
The oligomeric radical is now enclosed in a micelle where the concentration of monomer is much higher than in the aqueous phase and the radical now propagates rapidly to form a long polymer chain. This is now considered to be a young latex particle.

As particle formation is a process (as opposed to an instantaneous event), the distribution of particle sizes at this early stage is broad; the first-born particles are large and the newest ones are small. As these particles grow by propagation, there are eventually enough particles of sufficient size to capture all the propagating radicals, instead of allowing for the formation of new particles. Both the particle number and the polymerization rate increase in Interval I as new particles are formed.

2.1.2.2 Interval II

During Interval II, the particle number remains constant and the monomer droplets act as reservoirs, providing the growing particles with monomer to maintain saturation swelling and support the propagation reaction. The monomer concentration in the particles is of the order of 6 mol dm^{-3} (monomer concentration in a monomer droplet is 10 mol dm^{-3}) and the corresponding weight fraction of the polymer in the latex particles is around 0.35.

The radical within a particle keeps growing by propagation and the monomer that is being consumed by polymerization is replaced by the monomer that diffuses from the monomer droplets. The macroradical can undergo transfer to monomer, resulting in the formation of a monomeric radical:



This monomeric radical can either continue propagating inside the particle, or it may diffuse out of the particle and escape into the aqueous phase. This is known as exit.

A further event that can take place is entry of an aqueous phase radical into an existing particle. This z-mer, although it is surface active, is very mobile and if the entered particle already contains a growing radical, then termination will take place rapidly (instantaneous termination). On the other hand, if the particle does not contain a growing radical, then a new growing chain within the particle results. No particle contains more than one growing chain, and the average number of radicals per particle is equal to or slightly less than $\frac{1}{2}$.

As a result of the entry, transfer and exit processes, the emulsion particles contain a large number of dead chains. The molecular weight of these chains is high (of the order of 10^6).

During Interval II the average size of the particles increases, but the breadth distribution of particle sizes decreases. The polymerization rate in this interval is classically considered to be constant (constant C_p and N_c).

2.1.2.3 Interval III

The beginning of Interval III is signified by the disappearance of monomer droplets, at which point the polymerization rate should decrease as a result of the decreasing monomer concentration in the latex particles. This decreasing monomer concentration results in an increase in the weight fraction of polymer inside the particles, accompanied by an increase in internal viscosity of the particles. As the viscosity increases, the rate of termination decreases (as termination is dependant on the chain lengths of the two diffusing radicals) and the escape of a monomeric radical by diffusion (exit) becomes less likely. The overall result is that now a particle can contain more than one growing radical and there is an increase in the actual polymerization rate.

Depending on the natures of the monomer and polymer and the particle size, a second increase in polymerization rate is sometimes observed in Interval III. This increase is attributed to a decrease in the termination rate between radicals inside the particles due to the increased internal viscosity and is accompanied by an increase in the number of radicals per particle. This phenomenon is known as the Trommsdorff gel effect^[2].

At very high conversion, the system becomes glassy (when using high T_g monomers) and the rate at which a monomer molecule can diffuse to the end of a growing chain becomes rate determining, resulting in a lowering of the rate coefficient for propagation. The rate of polymerization is now very slow due to the decreasing monomer supply and the decreasing propagation coefficient.

The particle size distribution at the end of Interval III is relatively monodisperse, and the average molecular weight is of the order of 10^6 , with a broad distribution of chain lengths.

The reaction rate over the three different Intervals of emulsion polymerization is summarized in Figure 2.3; increases during Interval I, remains constant during Interval II and declines during Interval III.

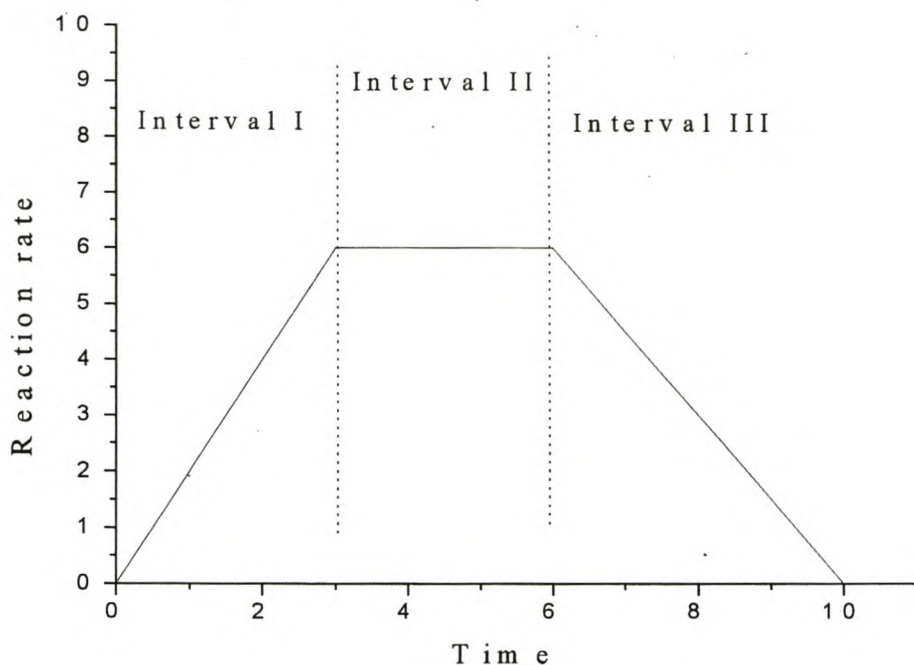


Figure 2.3 Representation of the reaction rates in the different Intervals of emulsion polymerization.

2.1.3 PHASE TRANSFER EVENTS IN EMULSION POLYMERIZATION

Phase transfer is inherent in the heterogeneous, compartmentalized nature of emulsion polymerization. While propagation, transfer and termination are kinetic events, it emanates that the rates of phase transfer events are controlled by both the thermodynamic difference between the phases and the participating kinetic events. Two processes arise from phase transfer, the entry and exit of radicals, to and from the particles.

2.1.3.1 Entry

Entry into a particle involves a preparatory stage during which a free radical which is capable of undergoing entry is formed (i.e. sufficiently hydrophobic), followed by a

step in which an entering species diffuses to the surface of a particle and then irreversibly crosses the particle/water boundary. Prior to successful entry, the radical may undergo termination in the aqueous phase.

2.1.3.2 Exit

Just as free radicals can be captured from the aqueous phase by latex particles, so they may desorb from the particles. Exit reduces the average number of radicals per particle. Small free radicals that result from chain transfer to monomer or transfer agent are the only species which are able to exit, since larger species will be more insoluble in the aqueous phase.

The process of exit is complicated by the concomitant process of re-entry and a number of distinct fates, as illustrated in Figure 2.4, may befall an exited free radical:

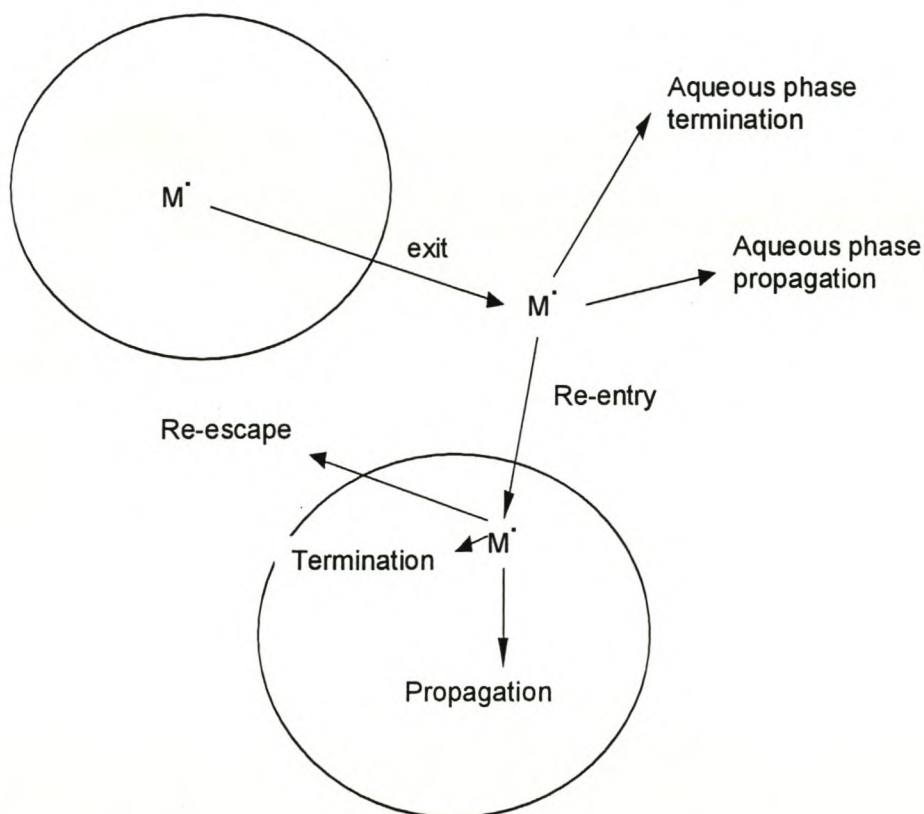


Figure 2.4 The possible fates of exited free radicals.

Different limiting cases can be derived from the different postulated fates of the transferred free radical for a zero-one system^[2]:

Limit 1: Complete aqueous phase termination

In this Limit there is assumed to be no kinetic effect from the desorbed free radicals. The only possible fate of an exited free radical is to undergo either aqueous-phase homotermination with another exited free radical (Limit 1a) or aqueous-phase heterotermination with an aqueous-phase free radical derived from initiator that may otherwise have entered a particle (Limit 1b). If initiator efficiency is very low (with most initiator-derived radicals undergoing aqueous phase termination with themselves) then the loss of a few radicals by heterotermination with an exited free radical results in little change in the overall rate of entry.

Limit 2: Negligible aqueous phase termination

Here it is assumed that the desorbed free radical may re-enter another particle and re-escape, or that it may propagate inside the particle (or instantaneously terminate if there is already a radical present in the entered particle). In this Limit it is assumed that the free radical never undergoes aqueous phase termination. Limits 2a and 2b are obtained by assuming that escape is less probable than propagation for a monomeric radical and *vice versa*, respectively

In Limit 2b, with complete re-escape, the fate of the desorbed radical is always to terminate. Limit 2a with complete re-entry and minimal re-escape, can be viewed as if there were no barriers between the particles and propagation within particles is possible, as is the instantaneous termination with an already existing free radical.

Limit 3: Rapid re-entry and re-escape, intra-particle termination is rate determining

This case exists where the average number of free radicals per particle is low and the termination of short radicals are rate determining. Here it is supposed that the desorbed radical undergoes exit and re-entry and re-escapes rapidly, and that termination is no longer instantaneous. This system behaves like a bulk system and there are no effects of compartmentalization and more than one radical can exist per particle.

2.2 “LIVING” RADICAL POLYMERIZATION

There is increasing academic and industrial interest in the synthesis of polymers by methods that enable one to control the physical properties of the formed polymer. Living radical polymerizations offer important applications because they avoid the major limitations of conventional free radical polymerization. These limitations are due to the polymer formation in mutual termination reactions of the transient propagating radicals and include the poor control of MWD, of end group functionalities and of chain architecture^[5]. Living polymerizations provide an excellent degree of control for the synthesis of polymers with predictable, well-defined structures. Living polymerizations can be used to synthesize polymers (homopolymers, random copolymers or block copolymers) that have narrow molecular weight distributions, where the length and the composition of monomer sequences can be controlled. Controlled radical polymerization leads to the formation of polymers with reactive end groups, where the degree of polymerization increases linearly with conversion and is determined by the ratio of monomer to initiator concentration. The polydispersity index (PDI) decreases with conversion and can approach a value of 1 (ideal monodisperse case) and the formed polymer chains can be extended to yield block copolymers and other architectures.

The characteristics of a living polymerization are discussed by Quirk and Lee^[6] who give the following experimentally observable criteria:

1. Polymerization proceeds until all of the monomer has been consumed. Further addition of monomer results in continued polymerization.
2. The number average molecular weight is a linear function of conversion.
3. The number of polymer molecules (and active centers) is a constant that is independent of conversion.
4. The molecular weight can be controlled by the stoichiometry of the reaction.
5. Narrow molecular weight polymers are produced.
6. Block copolymers can be prepared by sequential monomer addition.

7. Chain end-functionalized polymers can be prepared in quantitative yield.

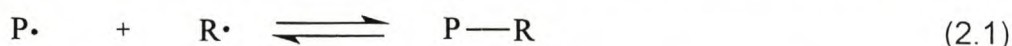
Living polymerization is classically defined as a chain reaction during which no chain termination or chain transfer occurs, with the consequence that all polymer molecules in the system are capable of growth as long as there is monomer present. If chain transfer and terminating agents are present then the polymerization system loses its living character and the formation of narrow MWD polymers does not result^[7]. It has however been shown that if the chain transfer process is reversible then the polymerization can still possess most of the characteristics of a living polymerization. Perhaps a better definition of a living polymer system is one in which the capacity for growth remains constant^[8], where termination and transfer are negligible compared to propagation.

Living carbocationic polymerization (where the active centre is a carbonium ion) has successfully been used to produce polymers with $MWD < 1.2$. The rate of transfer between the species in the reaction medium is faster than the rate of propagation, resulting in the low MWD, and the propagating species is end-capped by an anion.

2.3 CHAIN TRANSFER AGENTS

There are three current approaches towards achieving controlled radical polymerization:

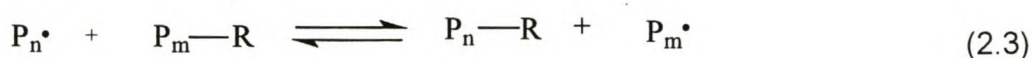
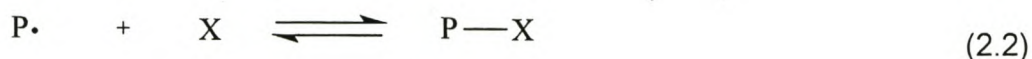
1. Reversible deactivation with a stable radical (the persistent radical effect^[5])



where $P\cdot$ is a polymeric radical and $R\cdot$ is a small, stable radical

- Nitroxide mediated CRP
- Atom transfer radical polymerization

2. Reversible deactivation with a non-radical species



3. Reversible degenerative chain transfer

- alkyl iodated mediated CRP
- reversible addition fragmentation chain transfer

2.3.1 NITROXIDE MEDIATED CONTROLLED RADICAL POLYMERIZATION

A conventional free radical initiator is used in the presence of a nitroxide stable free radical. The nitroxide radical rapidly combines with a carbon-centered radical to form an alkoxyamine in a reversible reaction, as shown in Figure 2.5.

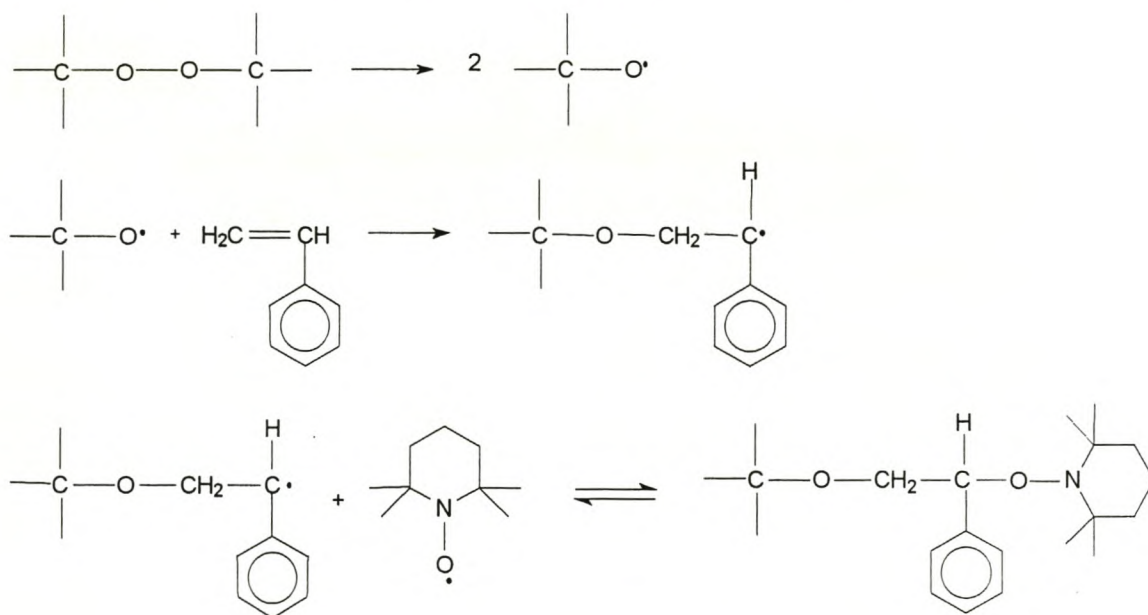


Figure 2.5 Formation of an alkoxyamine.

Alkoxyamines are thermally labile and cleavage of the C-O bond of the alkoxyamine results in an alkyl radical and the nitroxide radical. The alkyl radical initiates

polymerization while the nitroxide radical can recombine with any radical, without initiating propagation^[8]. Propagation proceeds via free diffusion of the active chain, with termination being inevitable.

A common example of nitroxides as chain transfer agents is the use of alkoxyamine 1-tert-butoxy-2-phenyl-2-(1-oxy-2,2,6,6-tetramethylpiperidinyl)ethane to give TEMPO (2,2,6,6-tetramethylpiperidine-1oxyl)^[10]. When TEMPO is used as the nitroxide, polymerization is restricted to styrene and derivatives, where polydispersities between 1.2 and 1.4 have been achieved. The temperature range for the reaction is 110-140°C and the reaction is well controlled for molecular masses < 50 000. The molecular masses can be predetermined by the ratio of reacted monomer to the initial concentration of TEMPO or its adducts^[11]. The transfer of the nitroxide unit from the end of one block to another has been monitored by ¹H NMR spectroscopy^[12], confirming that the nitroxide-mediated polymerization process occurs by a reversible chain capping mechanism.

The nitroxide system provides excellent control for the polymerization of styrene but is not as efficient with the acrylics, methacrylics and acidic monomers. Another drawback of the nitroxide system is the high reaction temperature that is required, which leads to problems with the colloidal stability in emulsions and eventually coagulation.

2.3.2 ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

In ATRP reactions the catalyst contains a transition metal species with suitable ligands and a simple alkyl halide is used as an initiator. ATRP was first introduced by Sawamoto *et al.*^[13] and Matyjaszewski *et al.*^[14] who used a catalytic complex containing ruthenium and copper, respectively. The mechanism for the reversible activation and deactivation of a Cu(I)-complex as the CTA in ATRP is shown below and involves the reversible termination of polymerization by ligand transfer to the metal complex.



The alkyl radical can either polymerize or be deactivated. A traditional free-radical initiator such as AIBN can also be used in the presence of a Cu(II) complex and the polymerization is then termed reversible ATRP and the mechanism for initiation is shown in Figure 2.6.

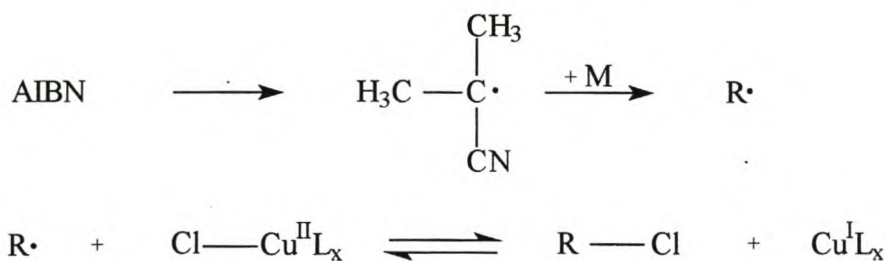


Figure 2.6 Mechanism of initiation of reversible ATRP.

A negligible amount of irreversible termination and transfer reactions occurs during the ATRP of alkenes and polydispersities of less than 1.2 have been obtained. The process is quite versatile and has been used successfully with styrene and acrylic monomers although its propagation mechanism has not been unambiguously elucidated.

Both the nitroxide mediated and ATRP processes rely on the persistent radical effect^[5], in which control is dictated by the ratio of the persistent species (nitroxide or metal) over active species (polymeric radical). If this ratio decreases during polymerization then bimolecular termination will occur, with the resulting formation of dead polymer. In emulsion polymerization the persistent species may exit the particles, depending on both the partition and diffusion coefficients in the oil and water phases, and terminate with small radicals in the aqueous phase. This could perhaps be overcome by the use of highly insoluble compounds, but there are other problems associated with both nitroxide mediated and ATRP processes^[15].

With nitroxide-mediated polymerizations requiring high reaction temperatures ($\approx 120^{\circ}\text{C}$), which are well above the temperatures used in conventional emulsions ($60\text{--}80^{\circ}\text{C}$), problems with colloidal stability are experienced and coagulation results. Shying away from ATRP in emulsion polymerizations is largely an environmental issue, as the elimination of heavy metals is becoming a critical issue in industry.

2.3.3 REVERSIBLE DEGENERATIVE TRANSFER WITH ALKYL IODIDES

This thermodynamically neutral (degenerative) reaction involves the transfer of an atom or group from a covalent, dormant species present in the large excess to the classic initiator-producing free radicals. The overall polymerization scheme comprises all typical elementary reactions, such as initiation, propagation and termination, but is supplemented by degenerative transfer. The degenerative transfer step in the radical polymerization of alkenes in the presence of a transfer agent as proposed by Matyjeskewski^[16], is shown in Figure 2.7.

The alkyl iodides do not generate radicals spontaneously, they participate exclusively in bimolecular exchange where a growing radical reacts with the alkyl iodide ($\text{R}'\text{-X}$) to form a dormant species by transferal of the iodine atom. The new radical R' reacts with a monomer molecule to become a propagating polymer chain, which then in turn transfers an iodine group from another dormant chain. This transfer is thermodynamically neutral (degenerative).

The total number of chains formed in the system is equal to the sum of the chains generated by initiator and those formed from the transfer agent. If exchange is fast in comparison to propagation, all R' moieties will become initial end groups in the polymer chains. When the transfer agent is in large excess over the initiator, the proportion of the chains irreversibly terminated should be very low as the maximum amount of irreversibly terminated chains cannot exceed the initiator concentration and thus nearly all chains will be terminated with the iodine group which can be activated.

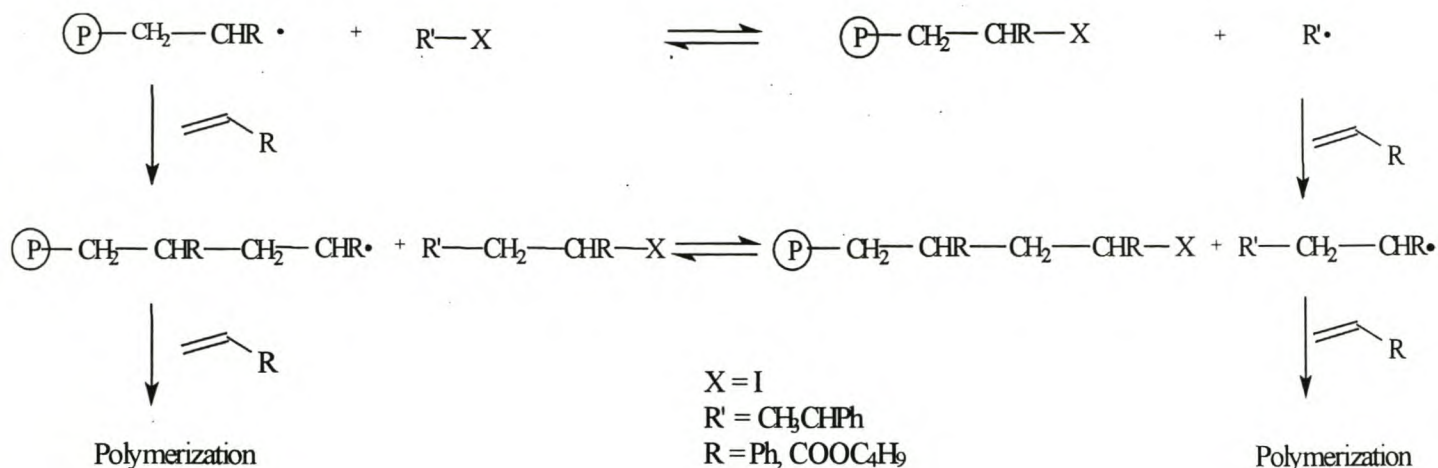


Figure 2.7 The degenerative transfer step in the polymerization of alkenes in the presence of an alkyl halide transfer agent. (Matyjaszewski^[16])

2.3.4 REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER POLYMERIZATION (RAFT)

A versatile and robust process based on reversible addition-fragmentation chain transfer has recently been developed in the CSIRO Molecular Science laboratories by Rizzardo *et al.*^[17] The RAFT process involves free-radical polymerization of an unsaturated monomer in the presence of a (thiocarbonyl)sulfanyl compound of general structure $\text{S}=\text{C}(\text{Z})-\text{SR}$. The experimental conditions employed are similar to those used for conventional free-radical polymerization.

The mechanism of RAFT polymerization involves a reversible addition-fragmentation sequence in which the transfer of the $\text{S}=\text{C}(\text{Z})\text{S}$ moiety between active and dormant chains serves to maintain the living character of the polymerization^[18], as illustrated in Figure 2.8. In Figure 2.8, J and R are species that can initiate free-radical polymerization. They may be polymer chains (i.e. $-\text{[CH}_2\text{CXY]}_n-$) or they may be derived from radicals formed from the dithio compound or the initiator.

Evidence for the RAFT mechanism is provided through end group analysis by NMR and UV/visible spectroscopy^[17-18] and the intermediate radicals proposed have been observed directly by ESR.^[20] The active functionality of the transfer agent is retained and thus the transfer is degenerate and provides a sound basis for the synthesis of well-defined polymers with narrow molecular weights.

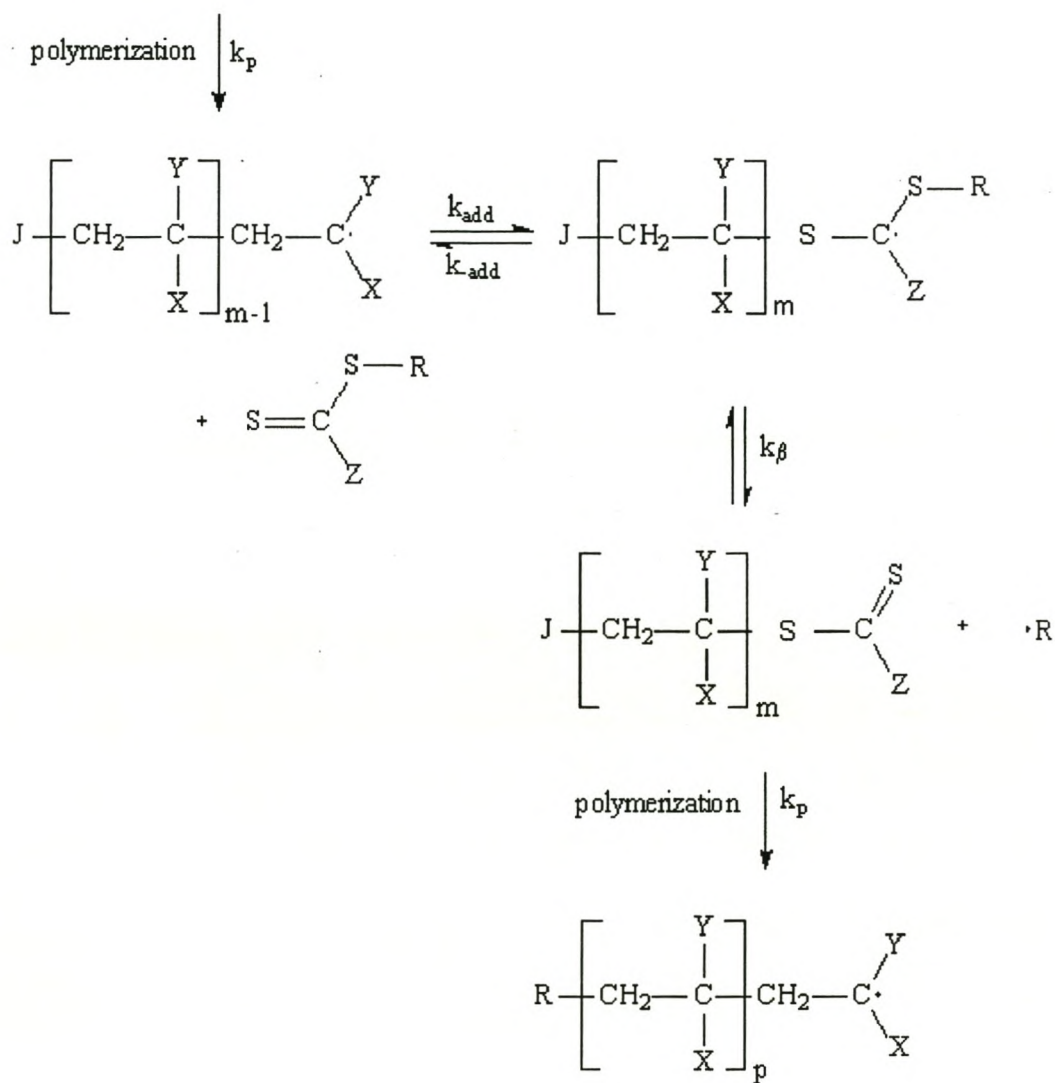


Figure 2.8 Mechanism of transfer of the S=C(Z)S moiety between active and dormant chains in the RAFT process.

Living character, in this addition-fragmentation process, is achieved by utilizing a chain transfer agent with a large transfer constant which ensures that a dynamic equilibrium is established between active (radical) and dormant chains. The choice of Z and R (see Figure 2.8) in the dithio reagent is crucial to the success of the RAFT process. To ensure a high transfer constant, Z should activate (or at least not deactivate) the C=S double bond towards radical addition. Suitable Z groups include aryl and alkyl. When the Z group is a dialkylamino or alkoxy group the RAFT compound has a low transfer constant and is therefore relatively inefficient in achieving a low polydispersity. The R group should be a good free radical leaving group (e.g. cumyl, cyanoisopropyl) and, as an expelled radical, R \cdot should be effective in reinitiating free radical polymerization.

The living character of RAFT is indicated by^[17]:

- Narrow polydispersity (often < 1.2, sometimes < 1.1)^[18]
- A linear molecular weight conversion profile
- The molecular weight is predictable from the ratio of monomer to the dithioester consumed
- The retention of the active thiocarbonylthio end group [S=C(Z)S] in the polymeric product
- Pure block copolymers and higher molecular weight polymers are produced by further monomer addition^[18]
- Polymers of complex architecture (e.g., star polymers) can be produced^[19].

Other important attributes of the RAFT polymerization are^[17]:

- Its compatibility with a very wide range of monomers, including those containing functionalities such as carboxylic acid, acid salt, hydroxy, and tertiary amino
- The process is tolerant of functionality in the dithio compound and the initiator
- The experimental conditions are those used for conventional free-radical polymerization

- It can be performed in bulk, solution, emulsion or suspension.

The persistent moiety is always attached to the chain-end of the polymer (see Figure 2.8) and thus will not exit during polymerization. In principle, the rate of polymerization should be comparable to the rate of polymerization without RAFT agent. However, the initiator concentration has to be low in comparison to the RAFT agent concentration so that narrow MWDs can be obtained in bulk or solution.

Most experiments published so far by Rizzardo *et al.*,^[17-20] were carried out in either solvent or in the case of bulk at high temperatures (styrene thermal initiation). Little has been published on RAFT emulsion polymerization to date. Only starved feed emulsion polymerization has been reported, where the RAFT agent is added with a small amount of monomer to the emulsion and a monomer feed to the reactor is begun once initiation has occurred^[18]. It is thought that these conditions are selected so as to start the emulsion polymerization in Interval III and force the rather water insoluble RAFT agent into the micelles/particles before the occurrence of any monomer droplets.

2.4 EFFECT OF TRANSFER AGENTS ON EMULSION POLYMERIZATION

Traditionally, transfer does not affect the overall rate of polymerization^[2]. However, if the rate constant for re-initiation is smaller than the propagation rate coefficient then the polymerization will be retarded^[1], and the likelihood that the transfer agent derived radical will undergo side reactions is increased. In the case of addition-fragmentation chain transfer, slow fragmentation of the transfer agent could also result in retardation.

Transfer reactions are of major kinetic importance and are often dominant in the controlling of molecular weight in emulsion polymerizations. In addition, the transfer reaction also controls the distribution of small free radicals, which can play a major part in shaping the overall rate of polymerization. If small species created by chain

transfer reactions are much more likely to experience termination than large species, then the overall rate of termination will be increased by transfer. Chain transfer in these heterogeneous systems could promote interphase migration of free radical species and thereby increase the rate of exit.

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CHAPTER 3

SYNTHESIS AND CHARACTERISATION OF RAFT AGENTS

3.1 SYNTHESIS OF THE DITHIOESTERS

Three RAFT agents were selected for this project to see the effect of RAFT agent structure on the emulsion polymerizations. The different dithioester compounds utilized as chain transfer agents in this project were synthesised, purified and kindly supplied by Hans de Brouwer, Technical University of Eindhoven, The Netherlands. A schematic representation of the synthesis methods used are given for the three RAFT agents in Figures 3.1, 3.2 and 3.3.

3.1.1 CUMYL RAFT

Cumyl dithiobenzoate, also referred to as Cumyl RAFT in this work, was synthesized according to the method described in a German patent^[1] (for synthesis of the dithiobenzoate intermediate) and Rizzardo *et al*^[2] (for the conversion of the dithioacid to Cumyl dithiobenzoate). The synthesis is represented schematically in Figure 3.1.

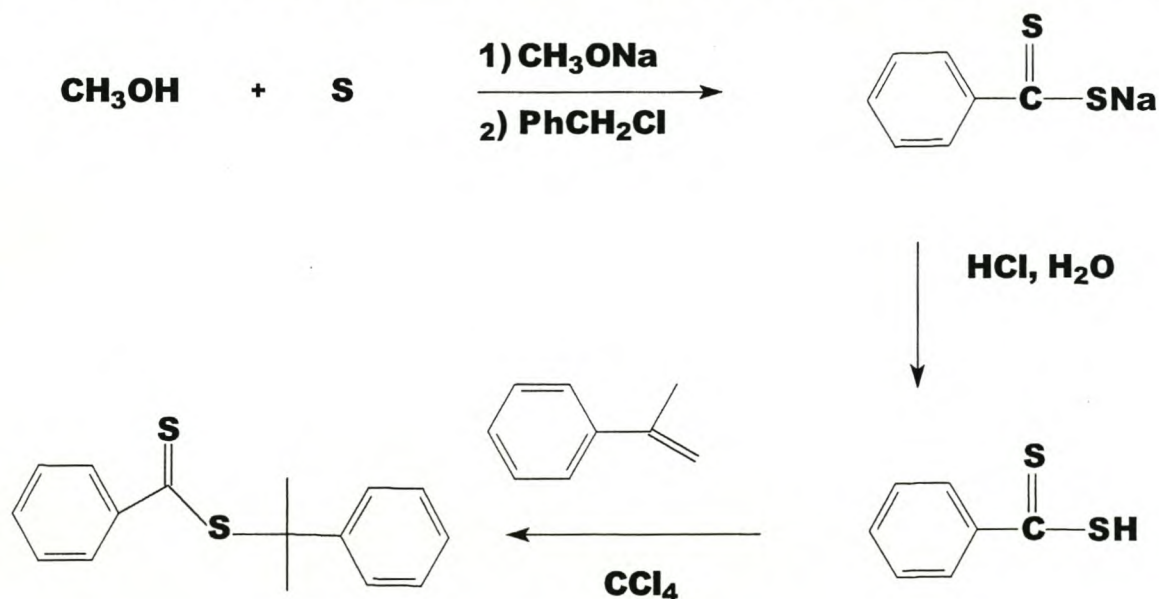


Figure 3.1 Schematic representation of the synthesis of Cumyl dithiobenzoate.

Column chromatography with aluminium oxide (activity II-III) as the stationary phase and a mixture of heptane and pentane (1:1) as the eluent was used for purification. Another possibility would be to use fractional distillation for the purification process. ^1H NMR spectroscopy was used to check the purity of the RAFT agent (the NMR spectra is given in the Addendum and was checked with the chemical shifts given in the Rizzardo *et al* patent^[2]). It should be stated that the Cumyl RAFT compound is not entirely stable and is negatively affected by UV light.

3.1.2 EMA RAFT

The RAFT agent 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate, hereafter referred to as EMA was prepared according to the method used by Rizzardo *et al*^[2] after which it was purified by column chromatography with silica gel as the stationary phase and a heptane, pentane mixture (1:1) with 10% diethyl ether as the eluent. The purity of the compound was verified with ^1H NMR spectroscopy (the NMR spectra is given in the Addendum and was checked against the chemical shifts given in the Rizzardo *et al* patent^[2]). A schematic representation of the synthesis is given in Figure 3.2.

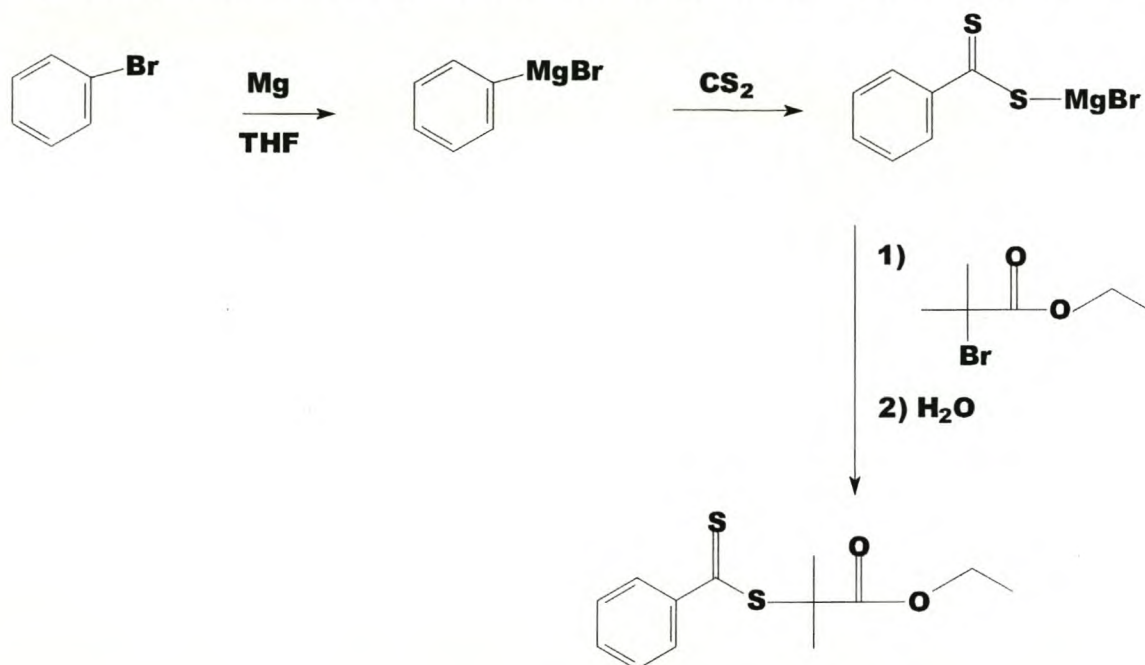


Figure 3.2 Schematic representation of the synthesis of 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate.

3.1.3 PBMA RAFT

The synthesis of the oligomeric PBMA RAFT species was carried out by synthesis of the dithiobenzoic acid dimer, followed by polymerization of butyl methacrylate using AIBN as the initiator, to an average chain length of 3. The synthesis is schematically represented in Figure 3.3. Due to the difficulties in purification of the viscous oligomeric CTA slight impurities remained in the compound after extraction, these impurities were observed by NMR spectroscopy. It can also be seen from the NMR spectra that it is a crude mixture of oligomers with RAFT groups connected to them.

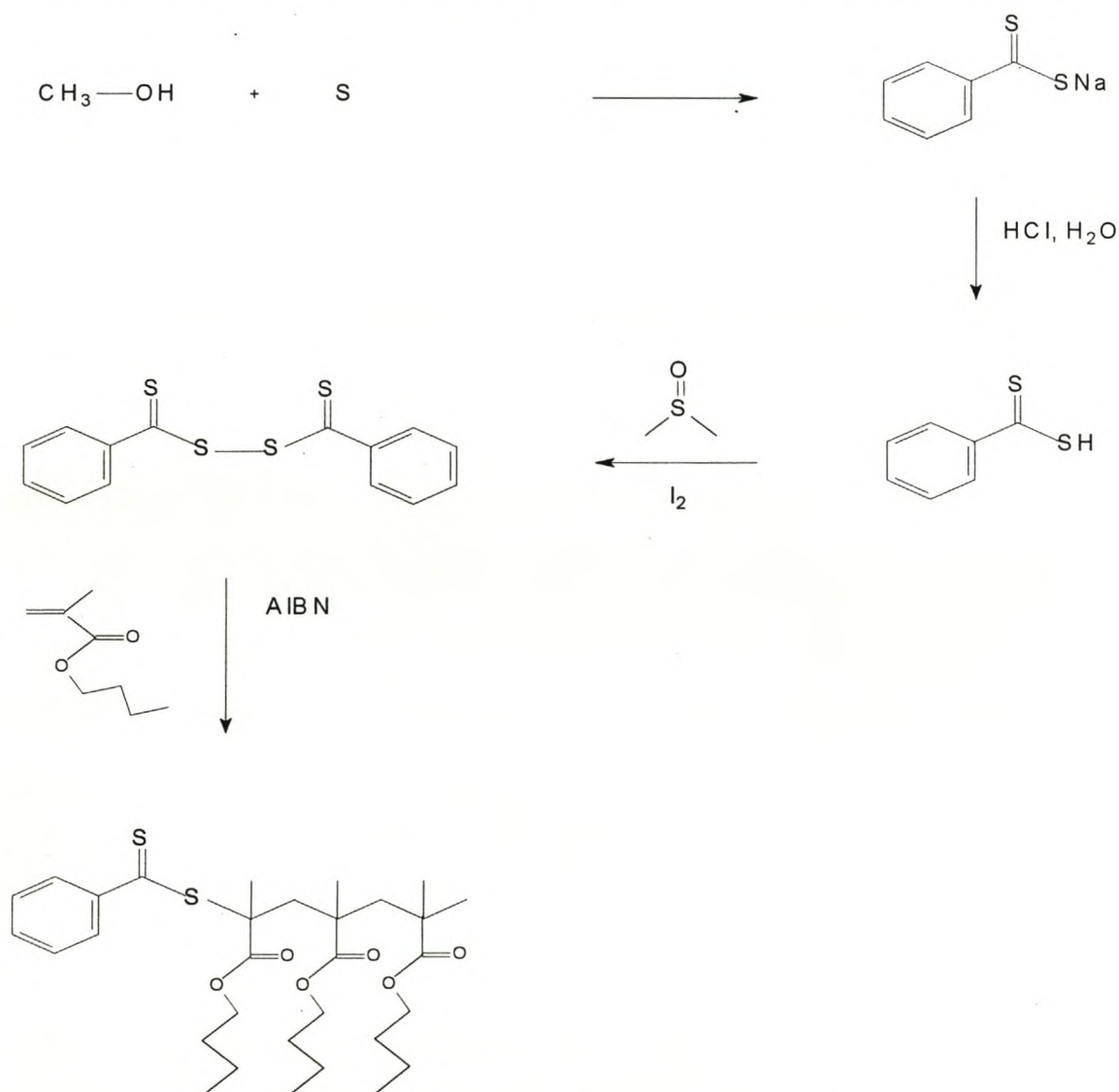


Figure 3.3 Schematic representation of the synthesis of PBMA RAFT with average chain length of 3.

3.2 CHARACTERIZATION OF THE DITHIOESTER COMPOUNDS

3.2.1 DETERMINATION OF THE WATER SOLUBILITY OF THE DITHIOESTER COMPOUNDS

The aqueous phase solubility of the RAFT agents is important in emulsion polymerizations as the RAFT agents have to be transported from the monomer droplets through the aqueous phase and into the latex particles.

UV-Vis calibration curves for the three dithioester compounds was set up by measuring the individual UV absorptions at 300 nm and at 325 nm through a range of concentrations with methanol as solvent on the UV-Visible Chemstation HP 8453. Calibration curves for the three dithioesters at a wavelength of 325 nm are given in Figures 3.4 through to 3.6.

It must be stressed that as the PBMA RAFT was not entirely free from impurities, these impurities could exert an effect on the UV absorption and therefore serve to influence the UV calibration curve. Values obtained from use of the PBMA RAFT calibration curve must therefore be viewed with caution.

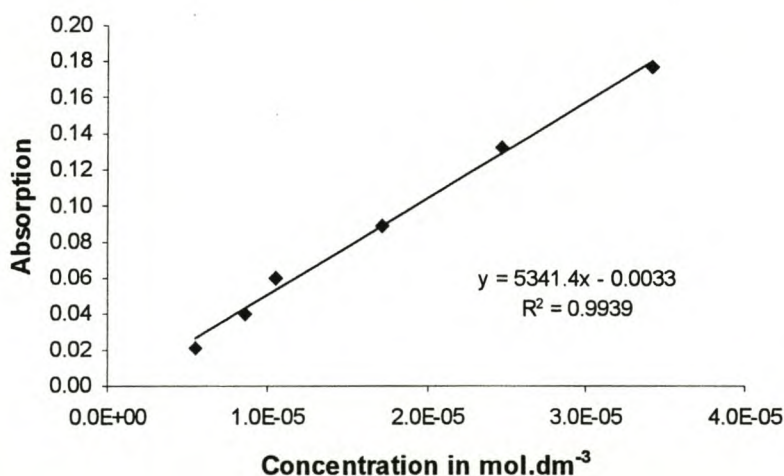


Figure 3.4 UV calibration curve for the Cumyl RAFT agent in methanol at a wavelength of 325 nm.

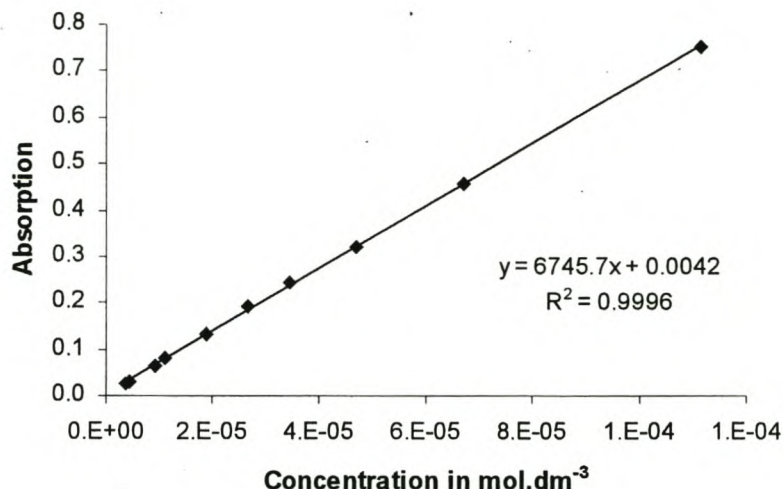


Figure 3.5 UV calibration curve for the EMA RAFT agent in methanol at a wavelength of 325 nm.

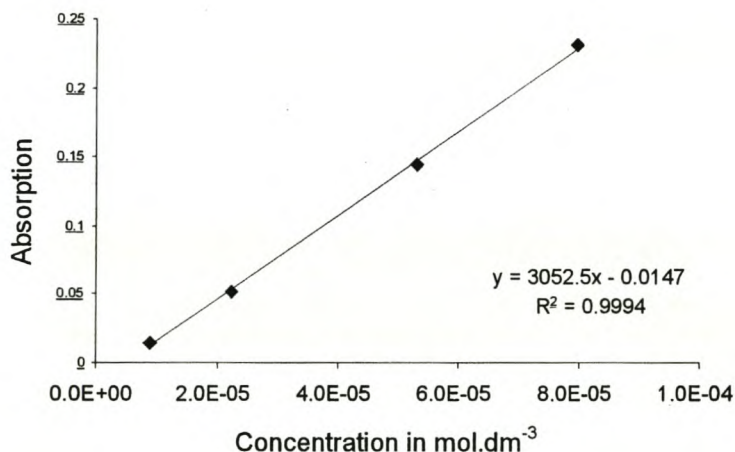


Figure 3.6 UV calibration curve for the PBMA RAFT agent in methanol at a wavelength of 325 nm.

A saturated aqueous solution of the dithioester was heated to 90°C with agitation in the glass apparatus pictured in Figure 3.7. Mixing was continued for an hour, after which agitation was ceased and the dithioester compound is allowed to equilibrate between the oil layer and the aqueous phase for an hour. A sample of the saturated aqueous solution was drawn through the sample arm and transferred directly to a cuvette placed in the temperature controlled UV-Vis cell. Absorption measurements

were then taken at 10°C intervals, starting at 90°C and decreasing down to 10°C, allowing time for equilibration at the specific temperature between absorption measurements.

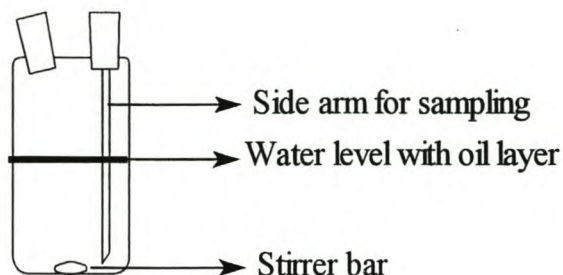


Figure 3.7 Glass apparatus used for sampling of the saturated aqueous solutions of the dithio-compounds.

The water solubility of the Cumyl RAFT agent was determined to be $1.127 \times 10^{-5} \text{ mol dm}^{-3}$ at 90°C. Below 90°C the aqueous phase solubility of the Cumyl RAFT agent diminishes to below $5 \times 10^{-6} \text{ mol dm}^{-3}$ (the detection constraint of the UV-Vis spectrophotometer for the specified dithioester compound). There is therefore no available profile for the aqueous phase solubility of the Cumyl RAFT agent through a range of temperatures and the aqueous phase solubility of the Cumyl RAFT at 60°C can at best be approximated as less than $5 \times 10^{-6} \text{ mol dm}^{-3}$.

The water solubility of the EMA RAFT agent was determined to be $8.44 \times 10^{-5} \text{ mol dm}^{-3}$ at 60°C, and a profile of the aqueous phase solubility through the temperature range 10°C to 90°C is given in Figure 3.8.

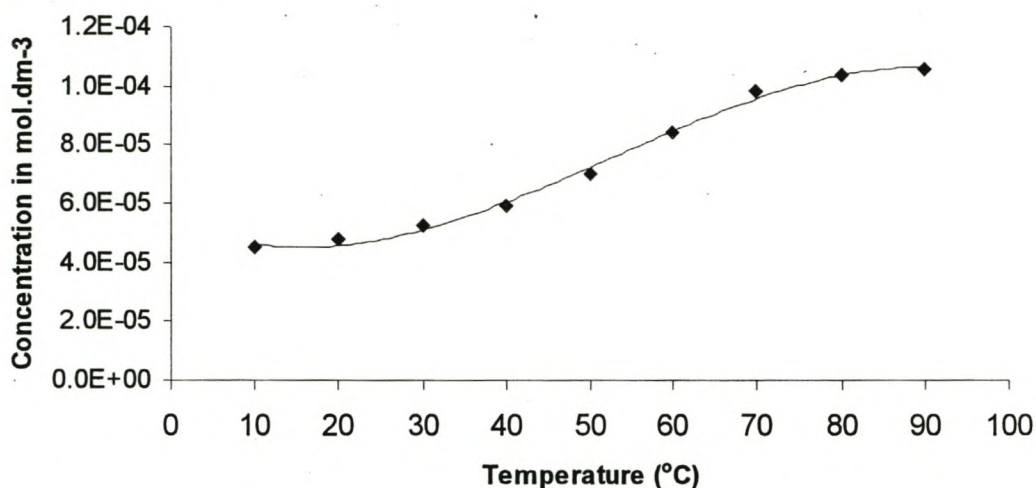


Figure 3.8 Water solubility of EMA RAFT agent as a function of temperature.

The water solubility of the PBMA RAFT compound was determined to be 3.0×10^{-4} mol dm⁻³ at 60°C. A profile of the aqueous phase solubility of the PBMA RAFT compound through a range of temperatures is given in Figure 3.9. (A note of reminder that because of impurities probably present in the compound, which could lead to misinterpretation of UV data, the water solubility parameter must be viewed with caution.)

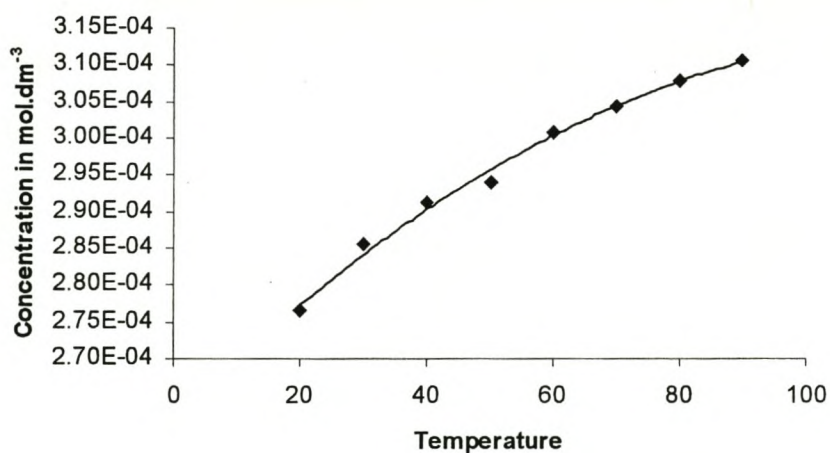


Figure 3.9 Water solubility of the PBMA RAFT agent as a function of temperature.

3.3 FRAGMENTATION PRODUCTS OF THE RAFT COMPOUNDS

The structure of the RAFT compound is very important in the chain transfer process. Variation of the RAFT agent structure results in a change in the transfer constant value and also in the chain end group and the fragmented product, R' . The process by which the chain transfer to RAFT agent occurs, followed by fragmentation, is depicted in Figure 3.10.

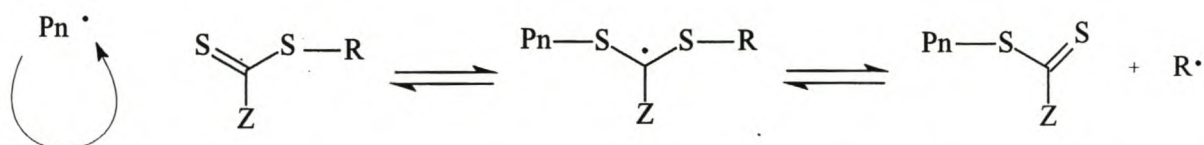


Figure 3.10 Schematic chain transfer to RAFT agent and fragmentation of the intermediate.

The Z group in Figure 3.10 is a phenyl group for the Cumyl, EMA and PBMA RAFT agents. The R group is different for the individual RAFT agents, which results in a different fragmented radical R' on initial transfer to RAFT agent. The leaving radical for the Cumyl, EMA and PBMA RAFT agents, on initial transfer to RAFT agent, is depicted in Figures 3.11, 3.12 and 3.13.

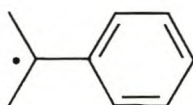


Figure 3.11 Leaving radical, R' for chain transfer to the Cumyl RAFT agent.

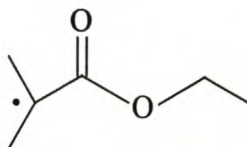


Figure 3.12 Leaving radical, R' for chain transfer to the EMA RAFT agent.

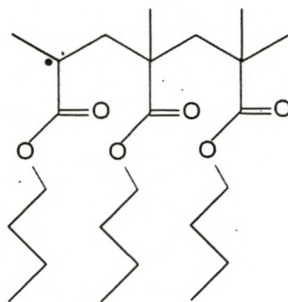


Figure 3.13 Leaving radical, R' for chain transfer to the PBMA RAFT agent.

On comparison of the three different leaving radicals, it is evident that the different structures of the leaving radicals should dictate the different aqueous phase solubilities of the fragmented species as well as the aqueous phase solubilities of the original RAFT agents. The aqueous solubility of the RAFT agent leaving radical should decrease in the order EMA, Cumyl, and then PBMA. The aqueous phase solubility of the leaving radical can be anticipated to exert an effect on the process of exit in emulsion polymerizations.

3.4 BIBLIOGRAPHY

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CHAPTER 4

SEEDED STUDIES

4.1 BACKGROUND

Mechanistic analysis of an emulsion polymerization system is complicated by the three intervals of polymerization, namely particle nucleation (Interval I), particle growth after cessation of particle formation (Interval II) and particle growth after the disappearance of monomer droplets (Interval III). Each interval of the polymerization involves different phases and are as such often characterized by different dominant kinetic events. It would be advantageous if these intervals of emulsion polymerization could be studied in separate experiments, to simplify the interpretation of data.^[1]

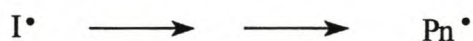
Particle formation is poorly understood and as such it is preferable that Interval I be by-passed in experiments seeking to elucidate information regarding particle growth. The particle formation step is avoided by using preformed polymer particles in seeded experiments, which starts the polymerization in Interval II or Interval III depending on the concentration of monomer present in the system. As the number of latex particles per unit volume of the aqueous phase, N_c , is constant and known and the variation of the monomer concentration within the latex particles, C_p , with conversion is well understood throughout these stages, such seeded experiments are suitable for kinetic analysis.

In a seeded experiment, a seed latex, formed from an *ab initio* run, is subjected to dialysis or ultrafiltration to remove excess surfactant and soluble initiator decomposition products and the resulting clean latex is then polymerized further by the addition of monomer, surfactant and initiator.

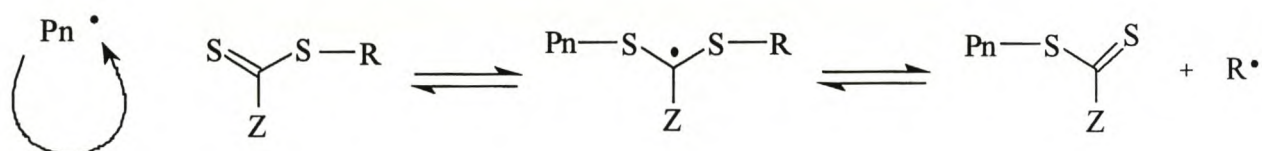
Despite confining attention to Intervals II and III where the complexities of nucleation are not included, the interpretation of experimental data is made difficult by the large number of kinetic processes involved in seeded emulsion polymerizations. These comprise the various aqueous phase events leading to radical entry into a particle, the various intra-particles fates of a radical (transfer, which can lead to exit, and termination, which generally depends on the lengths of the two radicals involved), propagation of a growing radical inside and outside a particle, and the various possible fates of an exited radical.

The mechanism of RAFT is depicted in Figure 4.1, illustrating the different addition fragmentation reactions that can occur, including chain equilibrium reactions. These chain transfer reactions add to the different mechanistic possibilities already present in a seeded emulsion system, resulting in an even more intricate system.

Initiation



Chain transfer



Reinitiation



Chain equilibrium

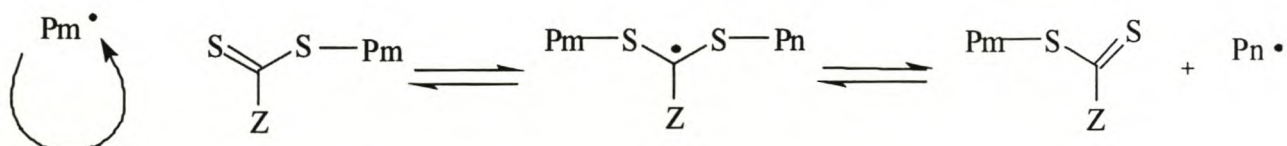


Figure 4.1 The RAFT mechanism.

4.2 PREPARATION AND CHARACTERIZATION OF THE SEED

A PMMA seed latex was prepared for seeded studies. Styrene was used as monomer so that a distinction could be made between the polystyrene and PMMA with the double detection system (UV and DRI) attached to the GPC.

To get as monodisperse a seed latex as possible, a high initiator concentration was employed and the latex was prepared at an elevated temperature. The high initiator concentration ensures a high flux of free radicals, resulting in particle formation finishing relatively early when the particles are sufficient in size and/or number to capture all newly formed aqueous phase free radicals before they can form new particles. This effect is enhanced by use of higher temperatures as the particles also grow faster, thereby reducing the time for formation of enough particles that are sufficient in size to capture aqueous phase radicals. If no new particles are being formed, a system becomes more monodisperse over time. Such a system where particle formation is finished earlier will be more monodisperse at 100% conversion than a system where particle formation is prominent till late into conversion.^[1]

The particle size and number of the seed latex were so 'chosen' as to keep the system under zero-one conditions ^[2] and to avoid secondary particle nucleation^[3].

4.2.1 SEED RECIPE

The recipe for the preparation of the seed latex was as follows:

- 821.0 g Deionized water
- 14.11 g Aerosol MA 80 (surfactant)
- 1.074 g NaHCO₃ (buffer)
- 130.0 g Methyl methacrylate
- 3.631 g KPS (initiator)

The surfactant, buffer and most of the water was charged to a 1.3 Liter stainless steel reactor with baffles and the reactor contents were allowed to reach 90°C. The reactor contents were then degassed by bubbling Argon through the mixture at 90°C for 1 hour with stirring. MMA monomer (from which the inhibitor had been removed, by passing it through an inhibitor removal column) was then added to the reactor and 5 minutes was allowed for emulsification to take place. Initiator that had been dissolved in the remaining water and heated up to the reaction temperature was then added to the reactor, after which the reactor was sealed under Argon at 1 Bar. The reaction was allowed to proceed for 3 hours.

The resulting latex was dialysed for two weeks, with twice daily changes of deionized water to remove some of the residual surfactant, monomer and initiator so that anomalies are not found in the kinetics, and secondary nucleation is avoided. If all residual surfactant is removed (which can be determined by conductivity measurements) the seeded experiments would be prone to high levels of coagulation, which would strongly influence the emulsion polymerisation kinetics. The dialysed latex was then characterised.

4.2.2 CHARACTERISATION OF THE PMMA SEED

The solids content of the seed after dialysis was 5.8 %.

The number average diameter of the PMMA seed was determined to be 43.8 nm by Capillary Hydrodynamic Fractionation techniques (CHDF 2000 2.73, Matec Applied Sciences) and 39.4 nm with light scattering techniques (Malvern 4700 light scatterer with PCS for Windows).

The number concentration (N_c) of the PMMA seed was calculated to be 1.12×10^{18} with Equation 4.1 where r_u is the unswollen particle radius and m_p^o is the initial mass of polymer per unit volume of the aqueous phase.

$$N_c = \frac{m_p^o}{\frac{4}{3}\pi r_u^3 d_p} \quad (4.1)$$

The PMMA seed was diluted in the seeded studies to give an N_c of 4.37×10^{17} , which is above the critical particle number needed to avoid secondary nucleation^[1].

4.3 EXPERIMENTAL

4.3.1 DETERMINATION OF C_p^{sat}

The monomer concentration within the latex particles in the presence of monomer droplets, C_p^{sat} , of styrene in the seed was determined by creaming experiments (where the latex is swollen with monomer and then the excess monomer is allowed to 'cream') according to the method used by Ballard *et al.*^[4]

Swelling of the preformed seed was allowed to take place overnight at 60°C in the glass apparatus pictured in Figure 4.2. After agitation was ceased, the excess monomer was allowed to cream for two hours, after which pre-heated water was slowly and carefully added to the reactor through the septum so that the creamed monomer was forced into the capillary. The height of the monomer layer was read off and the volume of creamed monomer is determined from the dimensions of the capillary. Mass balance equations were then used to determine the saturation constant, C_p^{sat} , of styrene in the PMMA seed.

The saturation constant was also determined for the three cases where the Cumyl, EMA RAFT and the PBMA RAFT agents were dissolved in the styrene monomer prior to the swelling of the PMMA seed. Subsequent to overnight swelling of the seed followed by a two hour equilibration period (all at 60°C), the volume of creamed monomer was determined and a sample of the creamed monomer layer was drawn. The concentration of the RAFT agent in the creamed monomer layer was then determined by UV absorption (in methanol) at a wavelength of 325 nm, which is above the styrene absorption range.

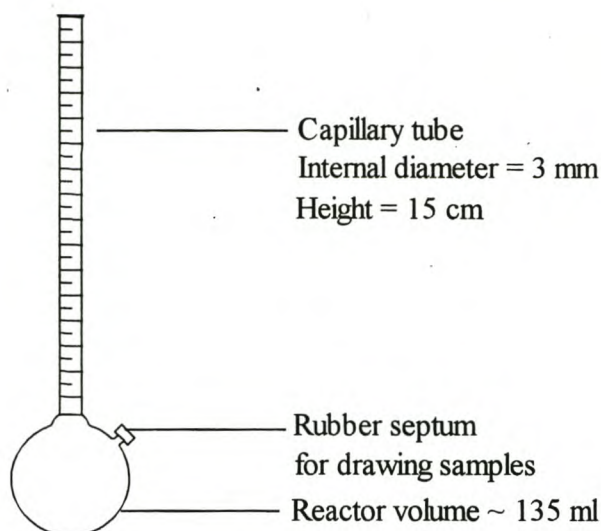


Figure 4.2 Glass apparatus (dilatometer) used for the creaming experiments.

4.3.2 PROCEDURE ADOPTED FOR SEEDED EXPERIMENTS

Seeded experiments were carried out at 60°C to determine the effects of RAFT agents on entry and exit, due to the transfer, addition and fragmentation processes of the three RAFT agents used in this work.

From personal communications and preliminary experiments it was known that a red layer (phase separation) was formed during emulsion reactions containing RAFT agent. Rizzardo *et al*^[6] showed that by reacting all the RAFT in Interval III and then slowly adding monomer, the problem of the red layer was overcome. Therefore, to study the effects of the peculiar appearance of the red layer in the emulsion, the conditions for the seeded experiments were chosen to begin polymerization in Interval II and then to move into Interval III at low conversions.

The conversion at which the system changes from Interval II to Interval III can be determined from Equation 4.2 (which is also used to determine the monomer

concentration inside a particle during Interval III) by substituting the C_p^{sat} value into the equation and solving for x .

$$C_p = (1-x) \frac{m_M^0 / M_0}{m_M^0 V_{sM} + m_p^0 V_{sP} + x m_M^0 (V_{sP} - V_{sM})} \quad (4.2)$$

where C_p is the monomer concentration within the latex particles, m_M^0 is the initial mass of monomer per total volume, M_0 is the molecular weight of the monomer and the partial specific volumes of monomer and polymer, V_{sM} and V_{sP} , are defined respectively as

$$V_{sM} = \frac{1}{d_M} \quad (4.3)$$

and

$$V_{sP} = \frac{1}{d_p} \quad (4.4)$$

The amount of monomer added to the seed was selected so that the changeover from Interval II to Interval III occurred below 10% conversion.

The procedure adopted for the seeded experiments was as follows:

50 ml of the PMMA seed latex was measured into the dilatometer reactor (refer to Figure 4.1) and 75 ml of deionized water was added to the reactor to achieve a solids content of approximately 2.8% and a particle number, N_c , of $4.37 \text{ E}+17$. Argon was then bubbled through the stirred latex at 60°C for 30 minutes. A small portion of SDS (0.032g) was then added to prevent coagulation during the reaction (but not enough to allow for secondary nucleation).

The tert-butyl catechol inhibitor present in styrene was removed from the monomer by passing it through an appropriate inhibitor removal column. The dithioester was then dissolved in the styrene monomer and the mixture degassed by three consecutive freeze-evacuation-thaw cycles. The monomer and RAFT agent were

then added to the dilatometer reactor and swelling was allowed to proceed overnight at 60°C.

Potassium persulfate was selected as the initiator as it has been used in literature to obtain kinetic information^[1] and consequently many properties, such as decomposition rate, entry and exit parameters in zero-one emulsion systems are known for the initiator and can thus be used for comparison with our results.

The persulfate initiator was dissolved in deionized water, heated up to the reaction temperature and then added to the reactor through the septum. The volume of water used was chosen carefully so that the reaction mixture would be forced up slightly into the dilatometer bore.

The start of the reaction was observed by monitoring the height of the reaction mixture in the capillary tube. After the preheated, dissolved initiator was added to the system, a volume expansion (and corresponding height increase in the capillary) was initially observed. This volume expansion is due to thermal equilibration. Thermal equilibration is followed by a short period where the remaining inhibitors were removed (induction period). The start of the polymerization reaction was marked by an increase in latex density, which was observable by the decrease in latex height in the capillary tube.

KPS was used as initiator at two different concentrations (differing by an order of magnitude). Styrene was used as monomer at an approximately constant starting concentration (0.3 mol dm^{-3}) and the reaction temperature for all the reactions was 60°C. The dithioester concentration was varied between a high and a low value. Control experiments, where no RAFT agent was added, were also performed. Table 4.1 and Table 4.2 give a summary of the different initiator and RAFT concentrations used and the various combinations.

Table 4.1 Concentration limits for KPS initiator and the RAFT agents used in the seeded experiments

	Concentration in mol dm ⁻³
High [Initiator]	1×10^{-3}
Low [Initiator]	1×10^{-4}
Very High [Initiator]	5×10^{-3}
High [RAFT agent]	5×10^{-4}
Low [RAFT agent]	1×10^{-4}

Table 4.2 Summary of the concentrations used in the seeded experiments

Exp	[KPS]	[EMA RAFT]	[Cumyl RAFT]	[PBMA RAFT]
1	HIGH		HIGH	
2	HIGH		LOW	
3	LOW		HIGH	
4	LOW		LOW	
5	HIGH	HIGH		
6	HIGH	LOW		
7	Very HIGH	HIGH		
8	LOW	LOW		
9	HIGH			HIGH
10	HIGH			LOW
11	LOW			HIGH
12	LOW			LOW
13	LOW			
14	HIGH			

Samples were drawn at regular intervals for the gravimetric determination of conversion. The dried samples were then dissolved in THF (1mg/ml) and filtered for Size Exclusion Chromatography (SEC) analysis. Analysis by Gel Permeation Chromatography (a type of SEC) provided information regarding the molecular weight and molecular weight distribution of the sample. Capillary Hydrodynamic Fractionation (CHDF) was used for particle size analysis of the emulsion samples and for observing if any secondary nucleation had occurred.

4.4 RESULTS AND DISCUSSION

4.4.1 DETERMINATION OF C_p^{sat}

Mass balance equations were used to determine the saturation constant of styrene (control, no RAFT agent) in the seed. It was found to be 5.61 mol dm^{-3} .

The concentration of RAFT agent in the separated monomer phase was determined after swelling and creaming by UV absorption spectroscopy. Mass balance allows one to obtain the moles of RAFT agent swelling the particles (aqueous phase solubility of the RAFT agents are very low and thus the aqueous phase concentration of the RAFT agent can be considered negligible). As the number of latex particles in the reaction vessel was known, the moles of RAFT in each particle could be determined and the RAFT concentration in the particles then calculated by using Equation 4.4

$$[RAFT] = \frac{\text{moles of RAFT}}{\text{swollen particle volume}} \quad (4.4)$$

where the swollen particle radius, r_s , is related to the unswollen radius, r_u , at a given monomer concentration inside the particles, C_p , by the following association:

$$\frac{r_s}{r_u} = \left(\frac{d_M}{d_M - C_p M_0} \right)^{1/3} \quad (4.5)$$

where d_M is the density of the monomer and M_0 is the molecular mass of the monomer. Under the selected experimental conditions the radius of the swollen particle, r_s equals 31.5 nm.

In Table 4.3 the RAFT agent concentration within the monomer phase before and after swelling is displayed, as is the change in the saturation constant values with the use of the different RAFT agents. The concentration of RAFT in the particles as calculated from Equation 4.4 is also given.

Table 4.3 Saturation constants in the presence and absence of the RAFT agents, and the concentration of the RAFT agent in the monomer layer and the particles

	Control	Cumyl RAFT	EMA RAFT	PBMA RAFT
C_p^{sat} (mol dm ⁻³)	5.61	5.54	5.97	5.63
[RAFT] in styrene – before swelling (mol dm ⁻³)		2.33×10^{-2}	2.33×10^{-2}	1.47×10^{-2}
[RAFT] in styrene – after swelling (mol dm ⁻³)		2.74×10^{-2}	3.01×10^{-3}	7.12×10^{-2}
[RAFT] in particle (mol dm ⁻³)		9.08×10^{-4}	1.63×10^{-3}	3.35×10^{-2}
Moles of RAFT per particle		1.17×10^{-22}	2.46×10^{-22}	4.43×10^{-22}

As can be seen in Table 4.3 the saturation concentration of styrene in the seed was 5.61 mol dm⁻³, which increased to 5.97 mol dm⁻³ when EMA RAFT was introduced and remained roughly constant with the introduction of Cumyl RAFT (5.54 mol dm⁻³) and PBMA RAFT (5.63 mol dm⁻³). The values obtained for the PBMA RAFT agent

were obtained using the UV calibration curve and must therefore be viewed with caution.

It can also be seen from Table 4.3 that the concentration of the RAFT agent in the monomer phase increases with the swelling of the seed, indicating that transport of the RAFT agent through the aqueous phase is poor. This could be due to the low aqueous phase solubility of the various RAFT compounds (refer to Chapter 3) and thus difficulties in transportation of the RAFT agent from the monomer droplets through the water phase and into the particles. The water solubility, C_W , of the various RAFT agents was in the region of 10^{-4} to 10^{-5} mol dm⁻³, which is significantly lower than the water solubility of styrene (5.0×10^{-3} mol dm⁻³)^[5] at 60°C.

The rate of transport from droplets into the particles can be calculated using Smoluchowski's equation (Equation 4.6), Equation 4.7 and the water solubility of the RAFT agents, where r is the radius of the particle and D_W is the diffusion in water.

$$k_e = 4\pi D_W r N_A \quad (4.6)$$

$$\text{Rate of Transport} = k_e C_W \quad (4.7)$$

The rate of transport (taking the limits of aqueous phase solubility of the RAFT agents into account) was approximately 10^6 s⁻¹. This suggests that on the time-scale of the swelling experiments (swelling took place overnight) transportation based on diffusion should not be a factor. There seems to be other factors that inhibit transportation, and these are currently being explored in the Laboratories of Eindhoven University of Technology.

From Table 4.3 it is evident that the number of moles of RAFT agent in the swollen latex particles increases in the order Cumyl RAFT, EMA RAFT, PBMA RAFT.

4.4.2 INHIBITION AND RETARDATION OBTAINED

Inhibition periods were observed in the seeded experiments by dilatometric techniques and the inhibition times observed for the different experiments given in Table 4.4.

Table 4.4 Summary of the conditions used in the seeded experiments along with the observed inhibition periods

Exp	[KPS]	[EMA RAFT]	[Cumyl RAFT]	[PBMA RAFT]	Inhibition time in minutes
1	HIGH		HIGH		29
2	HIGH		LOW		20
3	LOW		HIGH		730
4	LOW		LOW		155
5	HIGH	HIGH			117
6	HIGH	LOW			45
7	Very HIGH	HIGH			29
8	LOW	LOW			44
9	HIGH			HIGH	5
10	HIGH			LOW	5
11	LOW			HIGH	4
12	LOW			LOW	3
13	LOW				5
14	HIGH				3

The dissociation constant, k_d for the persulfate initiator^[1] at 60°C is $5.3 \times 10^{-6} \text{ s}^{-1}$. This equates to a half life of approximately 36 hours. Both the dissociation constant and the half life of the initiator is strongly dependant on the reaction temperature and increasing the reaction temperature to 80°C decreases the half life to approximately 3.5 hours.

At approximately 10% conversion, the emulsion polymerization was accompanied by the observation of phase separation, marked by a conspicuous red layer on top of the emulsion (when agitation was briefly ceased), which corresponds closely to the changeover from Interval II to III (refer to Equation 4.2). At high conversions (80-90%) this layer had turned to a lightly coloured pink, and the phase separation coagulates on the stirrer bar. NMR analysis of this coagulate revealed that it was polystyrene, and the colour suggested the presence of RAFT end groups, but the molecular weight of the chains was too high to gain much information on the chain end groups from NMR spectroscopy.

The inhibition periods observed at the low ($\approx 1.0 \times 10^{-4} \text{ mol dm}^{-3}$) and high ($\approx 5.0 \times 10^{-4} \text{ mol dm}^{-3}$) RAFT agent concentrations for the three RAFT agents at a high initiator concentration ($[\text{KPS}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$) are shown in Figure 4.3.

As can be seen from Figure 4.3, the addition of either EMA or Cumyl RAFT to the seeded system resulted in increased inhibition periods, while the addition of PBMA RAFT to the seeded system did not result in these increased inhibition periods.

The inhibition was more pronounced in the case of the EMA RAFT, with the inhibition periods increasing substantially with increase in RAFT concentration at constant initiator concentration.

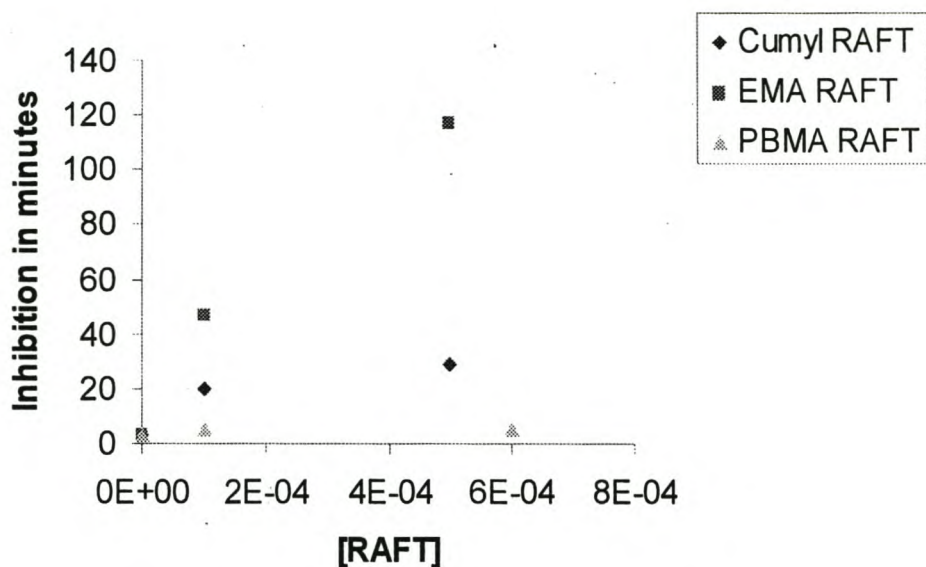


Figure 4.3 Observed inhibition periods in the seeded polymerizations of styrene in the presence of RAFT agents where $[KPS] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$.

When a lower initiator concentration ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$) was used with the above RAFT concentrations, so that the initiator concentration was equivalent to, or lower than the RAFT agent concentration, a substantial increase in the inhibition periods and retardation of polymerization in the cases of the Cumyl and EMA RAFT agents was seen. This decrease in the initiator concentration (and subsequent increase in the RAFT to initiator ratio) has no effect on the short inhibition period observed with the PBMA RAFT agent.

Conversion profiles for both low ($\approx 1.0 \times 10^{-4} \text{ mol dm}^{-3}$) and high ($\approx 5.0 \times 10^{-4} \text{ mol dm}^{-3}$) RAFT concentrations at a KPS initiator concentration of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ for the three different RAFT agents are given in Figures 4.4 and 4.5, respectively. The time is taken from when the reaction starts and as such does not include the observed inhibition periods.

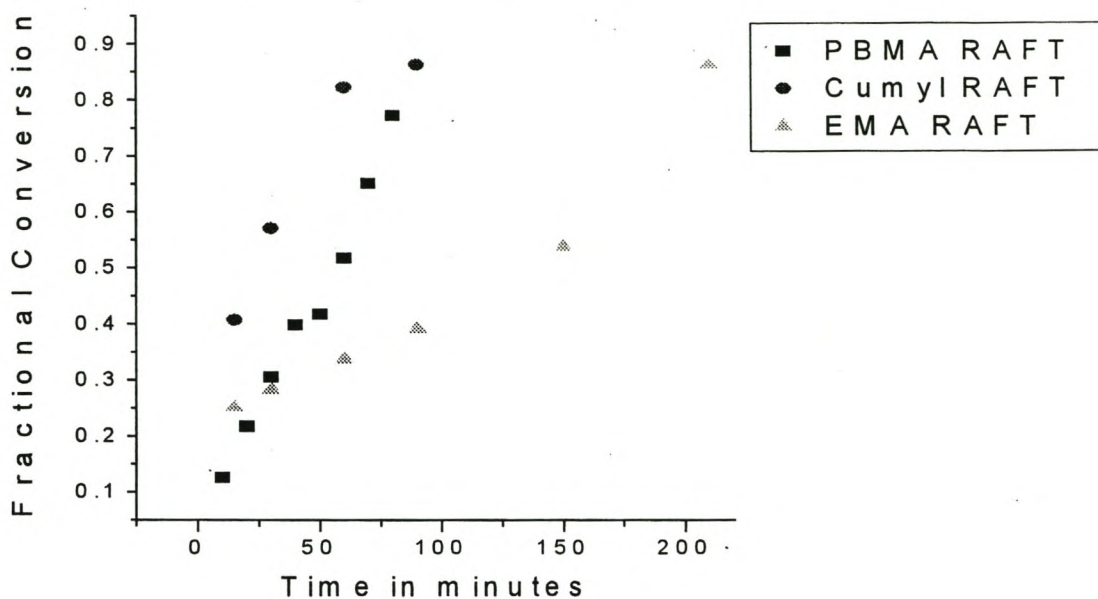


Figure 4.4 Effect of low RAFT agent concentration ($\approx 1.0 \times 10^{-4} \text{ mol dm}^{-3}$) on the seeded conversion profile of styrene with $[\text{KPS}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$.

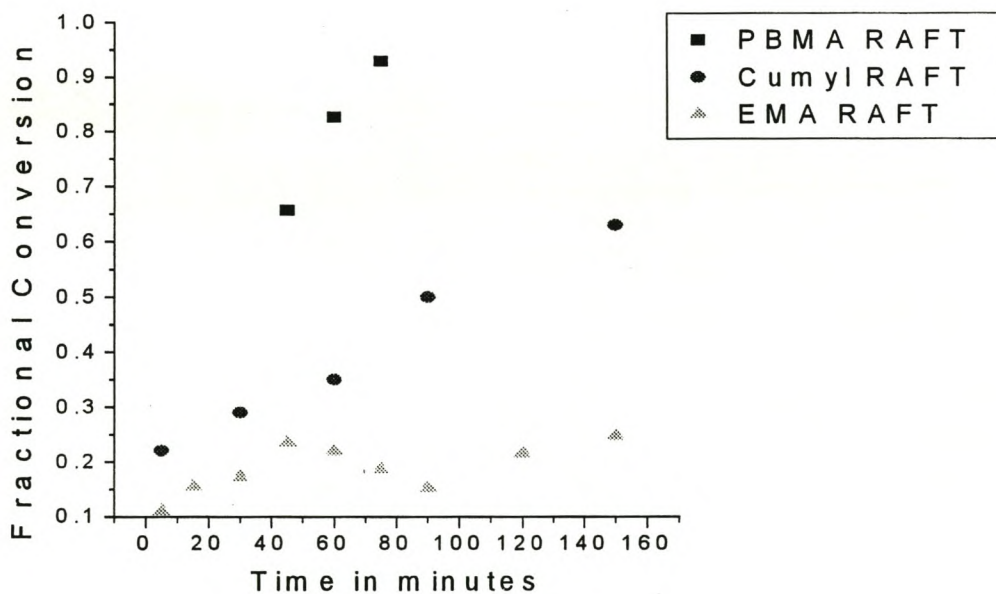


Figure 4.5 Effect of high RAFT agent concentration ($\approx 5.0 \times 10^{-4} \text{ mol dm}^{-3}$) on the seeded conversion profile of styrene with $[\text{KPS}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$.

It can be seen from the comparison of Figure 4.4 and Figure 4.5 that the ratio of initiator to RAFT agent (shown in the legend) plays a significant role in the reaction rate of the seeded emulsions where the Cumyl or EMA RAFT agent is concerned. This effect of retardation with decreasing initiator to RAFT agent concentration is further displayed in Figures 4.6, 4.7 and 4.8 where it can also be seen that the ratio of initiator to RAFT agent (which is shown in the legends) is less important at higher initiator concentrations.

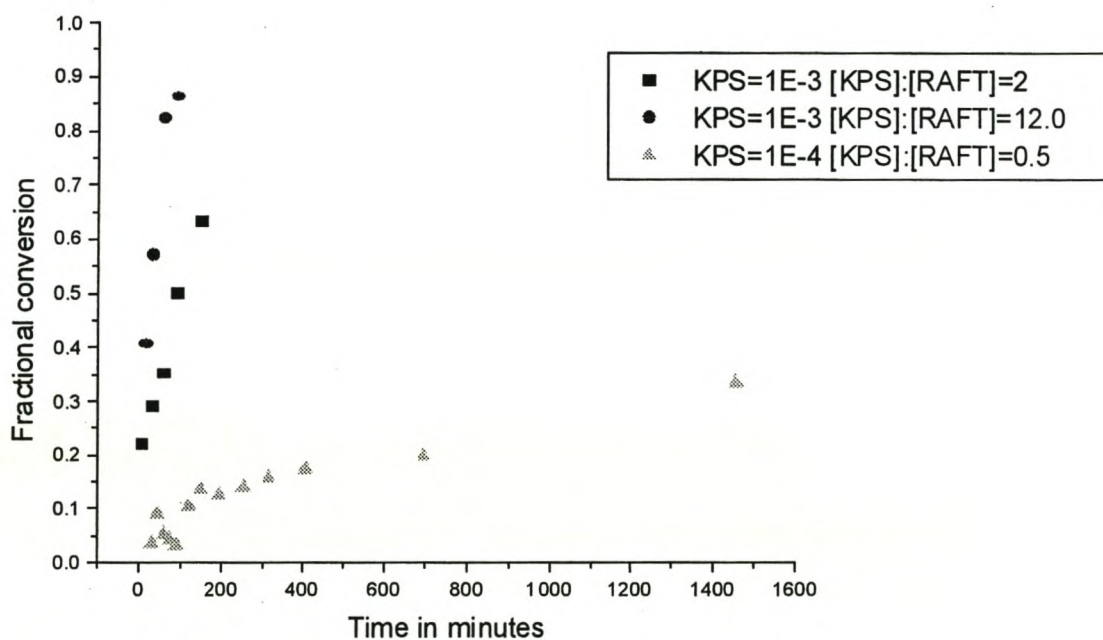


Figure 4.6 Conversion profile for seeded reaction containing Cumyl RAFT agent at various concentrations of RAFT agent and initiator.

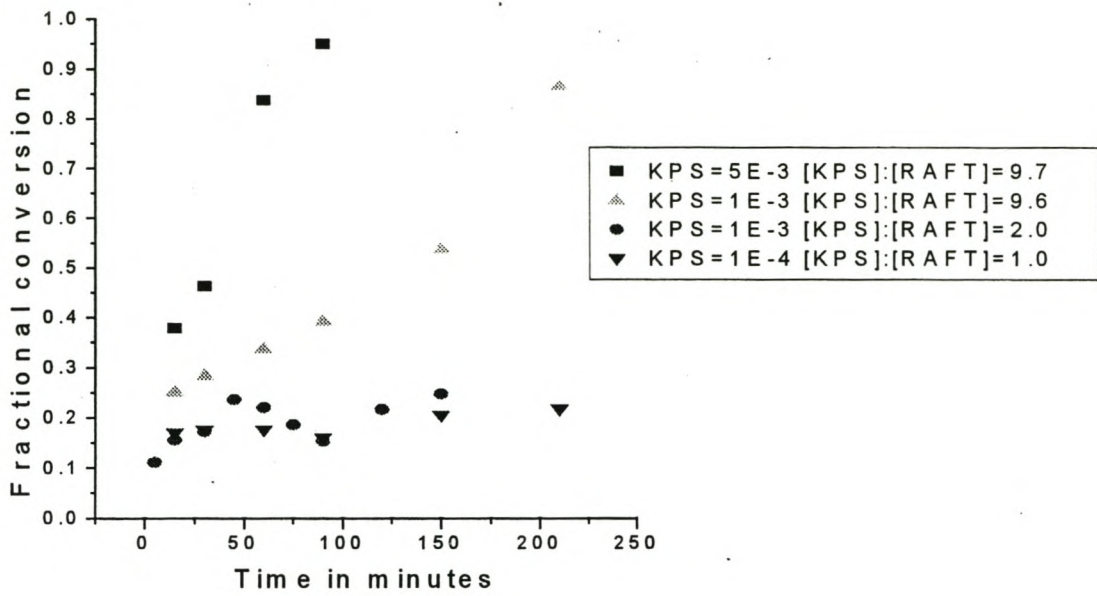


Figure 4.7 Conversion profile for seeded reaction containing EMA RAFT agent at various concentrations of RAFT agent and initiator.

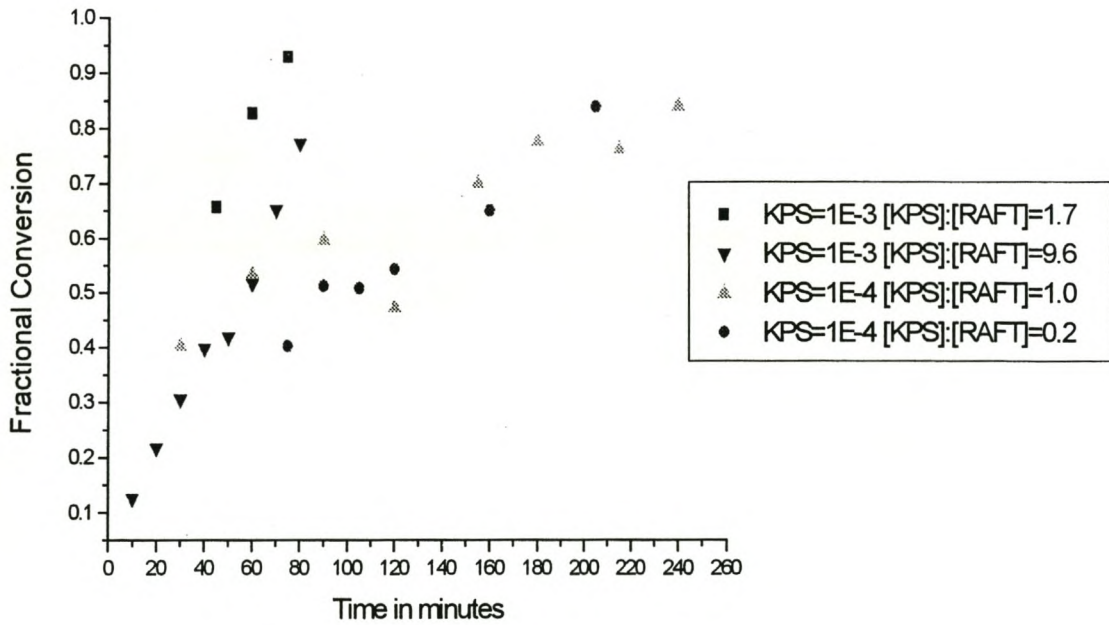


Figure 4.8 Conversion profile for seeded reaction containing PBMA RAFT agent at various concentrations of RAFT agent and initiator.

The reaction rate (dx/dt) was calculated from the derivative (or slope) of the conversion (x), time (t) data. The effect of increasing the Cumyl RAFT concentration on the reaction rate (Figure 4.6) was not as pronounced as the marked drop in reaction rate that was observed with increasing EMA RAFT concentration at a constant initiator concentration (Figure 4.7). Increasing the PBMA RAFT concentration in the seeded emulsion had no significant effect on the rate of polymerization at a constant initiator concentration, as shown in Figure 4.8.

The slope and intercept method^[1] is not a very reliable method to get entry and exit rate coefficients in emulsion polymerizations. The entry rate coefficient, ρ can however be approximated by this method to be $1.1 \times 10^{-4} \text{ s}^{-1}$. It must be noted that with the addition of RAFT agent to the emulsion system, the parameters will change and therefore the control experiments could not be used to determine any of the parameters for use in the RAFT experiments.

4.4.3 EXPERIMENTAL VALUES OBTAINED FOR \bar{n}

The average number of free radicals per latex particle, \bar{n} , is a kinetically determined quantity. A zero-one system is one in which conditions are such that the entry of a radical into a latex particle that already contains a growing radical, results in instantaneous termination. By definition, termination is not rate determining in such systems allowing the exclusion of this complex component of particle growth from consideration.

The conditions used in these seeded experiments were selected so that the system would be under zero-one conditions. This was done by tailor-making and using, a seed latex of sufficiently small particle size ($r_u = 21.9 \text{ nm}$) and high particle number (see Section 4.2.2). The seeded conditions were then selected so that the polymerization began in Interval II and quickly proceeded to Interval III (refer to Equation 4.2). The rate Equation 4.8 is used to determine \bar{n} in emulsion polymerizations:

$$\frac{dx}{dt} = \frac{k_p C_p N_c \bar{n}}{n_M^0 N_A} \quad (4.8)$$

where n_M^0 is the initial number of moles of monomer present per unit volume of water in the reactor, k_p is the propagation rate coefficient and $\frac{dx}{dt}$ is the reaction rate in s^{-1} . In Interval II, C_p is constant and equal to C_p^{sat} and N_c is also constant, allowing Equation 4.8 to be rewritten for Interval II as

$$\frac{dx}{dt} = A\bar{n} \quad (4.9)$$

In Interval III, C_p decreases monotonically as a function of conversion and neglecting the volume contraction due to polymerization, the Equation 4.10 can be derived^[1] for the determination of \bar{n} in Interval III.

$$\frac{-d \ln(1-x)}{dt} = \frac{k_p \bar{n}}{V_s N_A} \quad (4.10)$$

where V_s is the swollen particle volume.

The seeded experiments were monitored by CHDF and it was found that no secondary nucleation occurred, thus N_c remained constant throughout the seeded experiments and the Equations 4.9 and 4.10 could be utilized.

The average value of \bar{n} was determined by plotting $-\ln(1-x)$ against time, fitting a straight line to the points and obtaining the derivative (see Equation 4.10). Table 4.5 summarizes these \bar{n} values at an initiator concentration of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$.

It must be noted that an average value for \bar{n} is shown in Table 4.5. Where \bar{n} decreases with increasing conversion in the control experiment (\bar{n} just under $1/2$ in the beginning of the polymerization) and increases with conversion in the experiments containing RAFT agent (initial values are very low). It can be said that the \bar{n} values for the RAFT experiment and the control experiment converge towards each other at high conversions.

Table 4.5 Comparison of the values obtained for \bar{n} for different RAFT agents at an upper and lower concentration, at a KPS initiator concentration of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$

Experiment	Average \bar{n}
Control	0.10
[EMA RAFT] = $5 \times 10^{-4} \text{ M}$	0.0028
[EMA RAFT] = $1 \times 10^{-4} \text{ M}$	0.014
[Cumyl RAFT] = $5 \times 10^{-4} \text{ M}$	0.018
[Cumyl RAFT] = $9 \times 10^{-5} \text{ M}$	0.10
[PBMA RAFT] = $6 \times 10^{-4} \text{ M}$	0.20
[PBMA RAFT] = $1 \times 10^{-4} \text{ M}$	0.067

The average number of free-radicals per particle decreased with increasing EMA or Cumyl RAFT concentration, but increased with increasing PBMA RAFT concentration. Of the three RAFT agents used, EMA RAFT had the greatest influence on the average number of free-radicals, dropping the number drastically.

4.4.4 GPC RESULTS

GPC analysis was carried out using a WATERS Model 510 pump, WATERS Model WISP 712 autoinjector, Model 410 refractive index detector and Model 486 UV detector (at 254 nm). The columns used were a PLgel guard $5 \mu\text{m}$ $50 \times 7.5 \text{ mm}$ precolumn, followed by 2 PLgel mixed-C $10 \mu\text{m}$ $300 \times 7.5 \text{ mm}$ columns (40°C) in series. THF was used as eluent (flow rate 1.0 mL/min) and calibration was done using polystyrene standards ($M = 580$ to 7.1×10^6). Data acquisition was performed using WATERS Millennium 32 (v3.05) software.

A UV detector was used for the GPC analysis of the seeded experiments so that the polystyrene was detected but not the PMMA seed.

In living polymerization the molecular weights increase in a predictable and linear manner with conversion according to the relationship^[6]:

$$Mn(calc) = \frac{[monomer]}{[CTA]} x M_0 \quad (4.11)$$

where x is fractional conversion and M_0 is the molecular weight of the monomer.

It is important to note that Equation 4.11 does not hold in Interval II of an emulsion polymerization, as the monomer concentration in the particles is constant due to replacement of the reacted monomer in the particles by monomer from the monomer droplets. Muller^[8] has derived equations for the determination of theoretical M_n values for the case where monomer addition (feed) is equivalent to the monomer depletion due to polymerization. These equations do not include a conversion factor x .

In Interval III, Equation 4.11 is valid as there are no monomer droplets present in the system that could replace the consumed monomer in the particles. The experimental conditions for these experiments have been designed so that the polymerization moves into Interval III within the first 10% of conversion, ensuring that the usage of Equation 4.11 for the prediction of the number average molecular weight is valid.

The number-average molecular weights (experimental and predicted) and the polydispersities obtained for the Cumyl RAFT seeded emulsions are given in Figures 4.9 and 4.10, respectively.

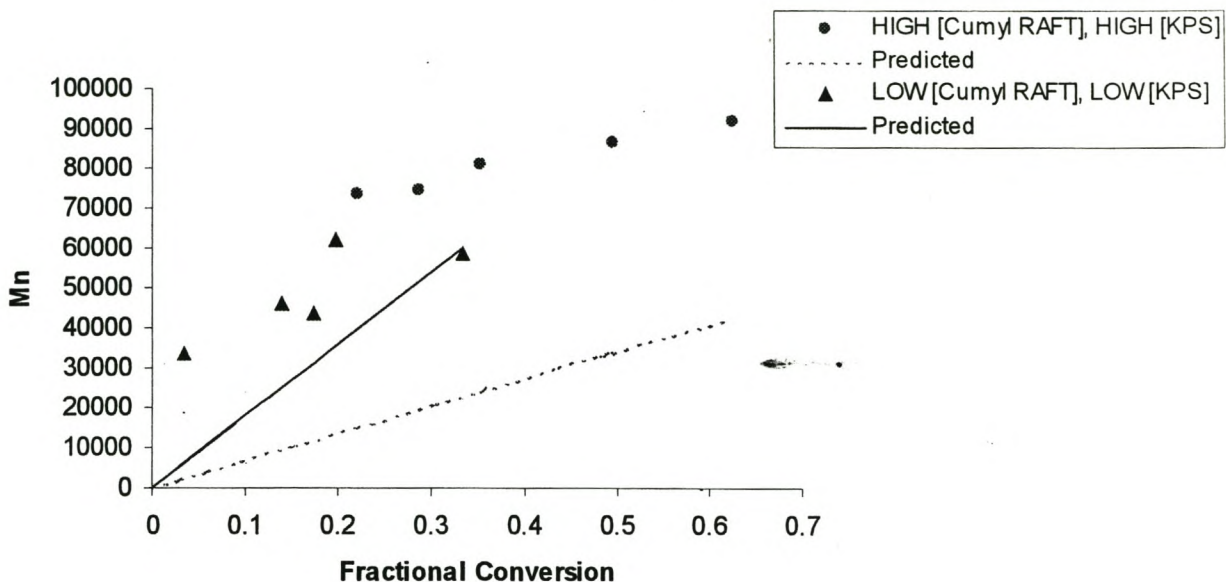


Figure 4.9 Number average molecular weights obtained experimentally and calculated theoretically as a function of conversion for the seeded emulsion polymerization with Cumyl RAFT.

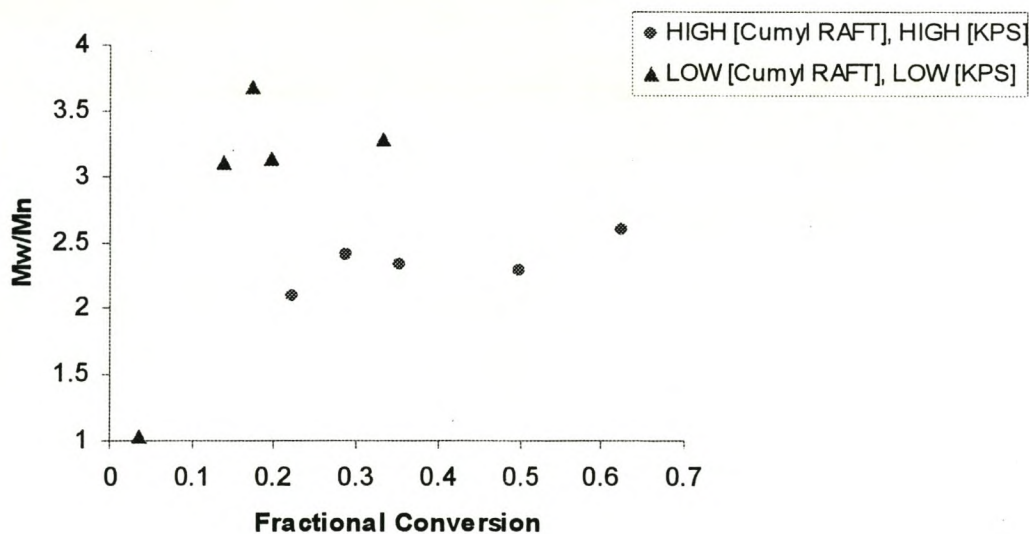


Figure 4.10 Mw/Mn (polydispersity) obtained for two seeded emulsions with Cumyl RAFT agent and KPS initiator.

From Figure 4.9 it can be seen that there is a somewhat linear increase in the M_n values after a fractional conversion of 0.2. These values were higher than the predicted M_n values. This indicates that there was far less RAFT agent initially involved in the polymerization than that which was added to the system. The approximate linear increase in M_n values suggests that the system has 'living' character albeit with a broad distribution.

In Figure 4.10 it is seen that the obtained polydispersities in the Cumyl RAFT seeded system were high, meaning that M_w (the weight distribution which is more sensitive to lower molecular weights) was much larger than M_n (the number distribution, which is more sensitive to the higher molecular weight fractions^[7]). This indicated that there was a large range of chain lengths, with a portion of very high molecular mass polymer which is suggestive of bimolecular termination. The low amount of RAFT agent initially present in the particles seems to be responsible for the corresponding high M_w/M_n values. It is clear from the increasing M_n values that the system is living although there is no control of the polydispersity as is the case in bulk and solution experiments.

In the EMA RAFT experiments a high initiator to RAFT agent ratio (≈ 10) was required to overcome inhibition/retardation and obtain conversion on an acceptable timescale. At these high ratios a linear increase in M_n with conversion was not observed and the number distribution remained relatively constant with increasing conversion, as shown in Figure 4.11. This indicates that there is a lack of living character in systems where a high initiator to RAFT agent was employed.

The polydispersity values were high and increased with increasing conversion, as shown in Figure 4.12.

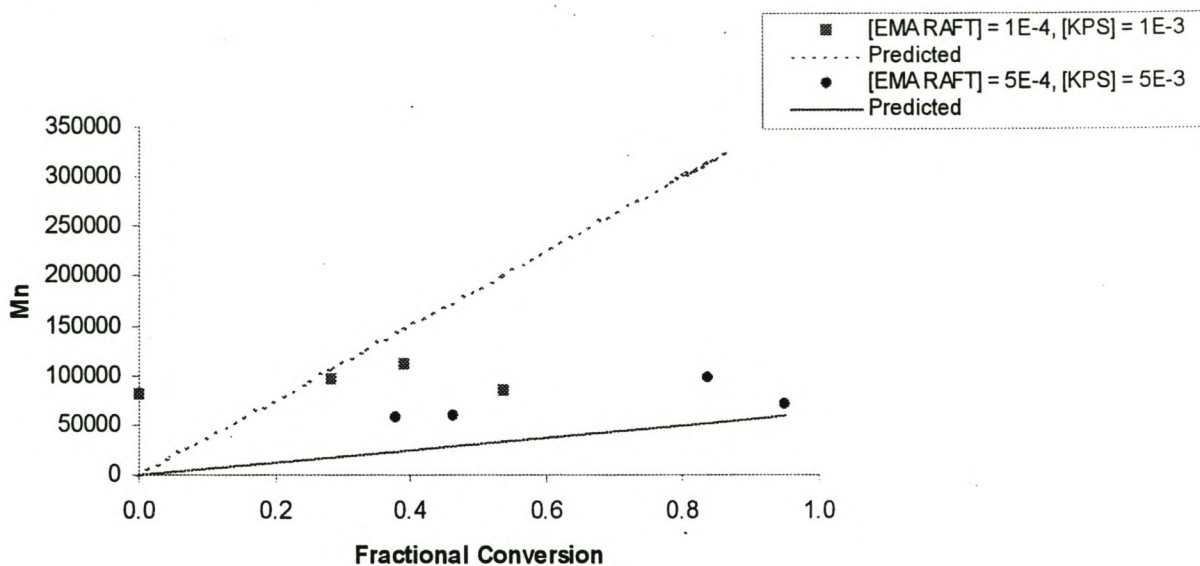


Figure 4.11 Experimental and predicted M_n values for EMA RAFT seeded emulsions where the initiator concentration is an order of magnitude greater than the RAFT concentration.

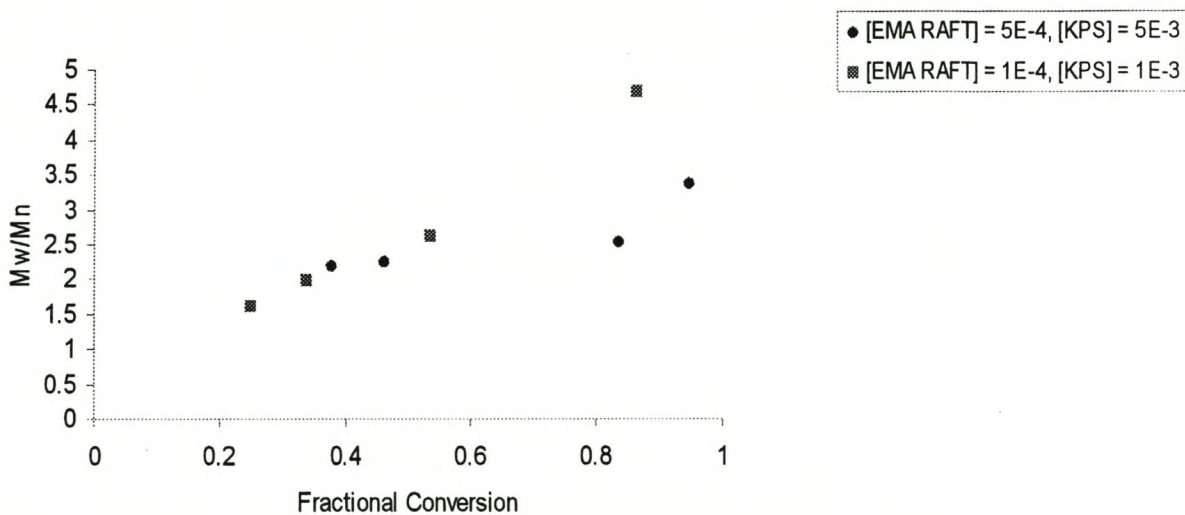


Figure 4.12 Polydispersity values obtained in EMA RAFT seeded emulsions.

The M_n values obtained for two of the PBMA RAFT seeded experiments are displayed in Figure 4.13 from where it can be seen that there is an approximately linear increase in M_n values with conversion although these values are far higher than those predicted by Equation 4.11.

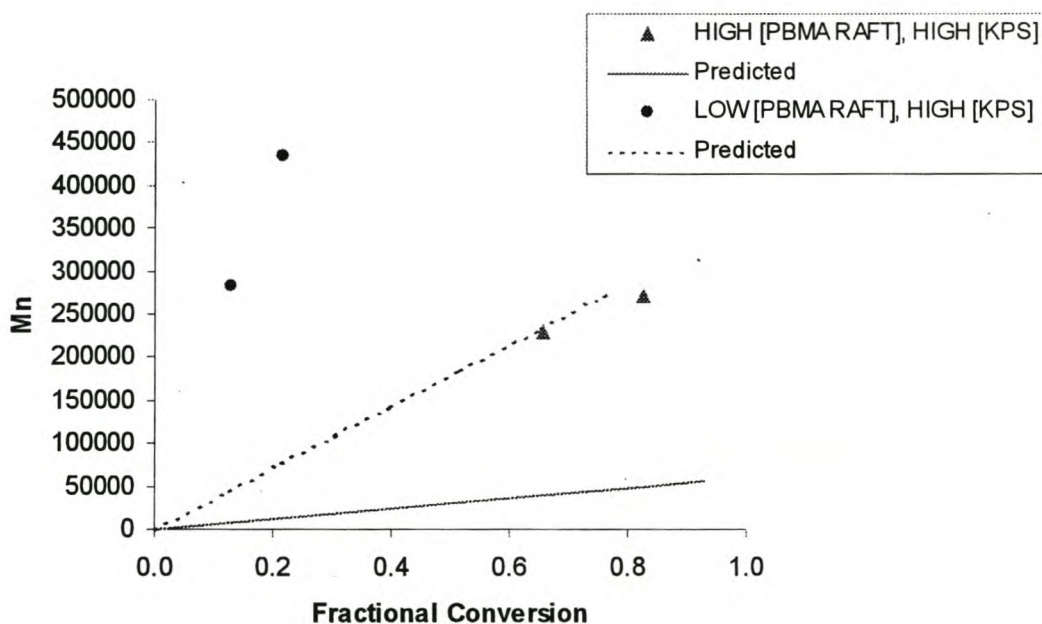


Figure 4.13 Predicted and experimental values of M_n as a function of conversion for the seeded styrene polymerizations containing PBMA RAFT.

The polydispersities obtained with the PBMA RAFT seeded emulsions were high; values ranged between 2 and 4. Portions of the molecular weights obtained with the PBMA RAFT agent in emulsion were much higher than when the EMA or Cumyl RAFT agent was used; so high in fact that the M_n and M_w/M_n values were not able to be calculated due to the samples having a portion of their molecular masses higher than the calibration standards that were used for the GPC.

A typical GPC profile (log distribution) obtained in the seeded experiments with added RAFT agent is shown in Figure 4.14. The distributions were first normalized and then scaled according to conversion.

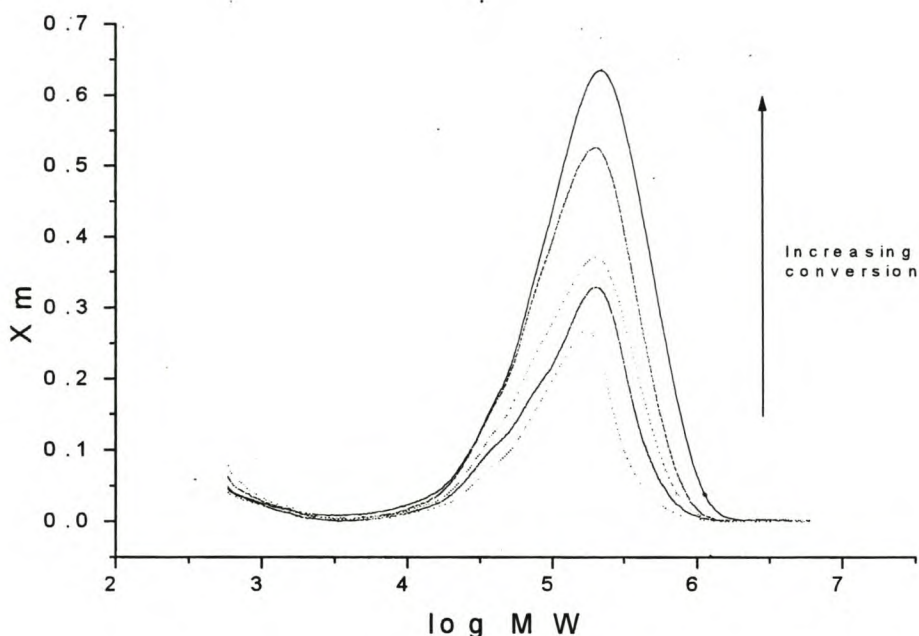


Figure 4.14 GPC chromatogram (log distribution) of a seeded emulsion polymerization of styrene at 60°C in the presence of Cumyl RAFT agent. $[KPS] = 10^{-3} \text{ mol dm}^{-3}$ and $[Cumyl \text{ RAFT}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$.

Little, or no shift in molecular weight with increasing conversion was found in the seeded emulsion experiments. Higher molecular weights were formed over time but the lower molecular weight chains were still present.

4.5 DISCUSSION

On addition of the EMA and Cumyl RAFT agents to the seeded system, an increase in inhibition periods was noted and once the polymerization started, it was significantly retarded in comparison to the control experiments where no RAFT agent was present. This inhibition and retardation effect was more prominent in the EMA RAFT polymerization than in the Cumyl RAFT polymerization while the increase in inhibition periods and retardation were insignificant in the PBMA RAFT seeded emulsions. A high initiator concentration (10^{-3}) was necessary to achieve acceptable polymerization rates in the presence of RAFT agent (10^{-4}). The ratio of initiator

concentration to RAFT agent concentration was also an important factor in the seeded polymerizations, with a smaller ratio leading to increased inhibition and retardation in the presence of Cumyl or EMA RAFT agent.

The phenomena of inhibition and retardation in the EMA and Cumyl RAFT experiments but not in the PBMA RAFT experiments, suggested that the inhibition and retardation was due to the exit of radicals from the particles. Exit from the particles lowers \bar{n} by orders of magnitude and therefore a low rate of polymerization is achieved. It is noticed from the performed seeded experiments that it does not take a lot of RAFT agent to lower \bar{n} drastically.

The coefficient for desorption of monomeric free radical (exit) from a particle with swollen radius, r_s , is given by:

$$k_{dm} = \frac{3 D_{mon} D_w}{\left(\frac{C_p}{C_w} D_{mon} + D_w \right) r_s^2} \quad (4.12)$$

where D_{mon} is the diffusion coefficient for monomeric free radicals and D_w is the diffusion coefficient of the monomeric free radical in the water phase.

The possibility of escape can then be determined by using Equation 4.13:

$$P_{(es)} = \frac{k_{dm}}{k_{dm} + k'_p C_p} \quad (4.13)$$

where k'_p is the propagation rate coefficient for monomeric radical formed by transfer.

Using Equations 4.12 and 4.13, it could be visualized that desorption will be higher for a radical species that has a higher aqueous phase solubility, and a lower k'_p .

Using the approximation that D_w is 1.6×10^{-5} for the three radicals formed after fragmentation of the RAFT agents, the diffusion coefficient of the monomeric free radicals, D_{mon} , the escape rate coefficient, k_{dm} and the possibility of escape, $P(es)$

was determined. These calculated values for the individual RAFT agents are given in Table 4.6.

Table 4.6 Diffusion coefficient for the monomeric free radicals, D_{mon} , the escape rate coefficient, k_{dm} and the possibility of escape, $P(es)$ determined for the three RAFT agents

	Cumyl radical (Cumyl RAFT)	EMA radical (EMA RAFT)	PBMA radical (PBMA RAFT)
D_{mon}	1.5 E-5	1.5 E-5	8.2 E-7
k_{dm}	3.15×10^3	7.98×10^4	4.4×10^3
$P(es)$	0.25	0.87	0.1

On fragmentation of the original dithioester compounds, the solubility of the leaving radical increases in the order PBMA, Cumyl, EMA RAFT agent (see Section 3.3 and Figures 3.11, 3.12 and 3.13) and thus more exit would be expected from the EMA RAFT agent followed by the Cumyl RAFT. This was reflected in the $P(es)$ values given in Table 4.6. The oligomeric leaving species formed upon fragmentation of the PBMA RAFT was not expected to exit as it should have very low aqueous phase solubility – this is in good accord with the absence of inhibition and retardation in the PBMA experiments.

It is important to note that it is not only a monomeric radical (1-mer) that can exit, but also oligomeric species with a sulfate end group. Consider the species portrayed in Figure 4.15, where addition followed by fragmentation will lead to a styrene 2-mer with a sulfate end group (which increases the water solubility of the species) which could possibly exit.

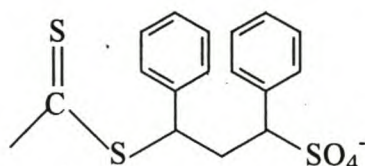


Figure 4.15 Intermediate RAFT compound with sulfate end group.

A suggested hypothesis for the inhibition, retardation and red layer formation observed in emulsions containing RAFT agent, and the resulting M_n values obtained is given in the following sections.

4.5.1 INHIBITION

In the initial stages of the emulsion polymerization process, oligomeric radicals enter the latex particles and undergo transfer to the RAFT agent. This is followed by the fragmentation of the original RAFT agent with the subsequent 'creation' of a new radical species that is able to act as an initiating species, or exit (if it is a short chain radical). Upon exit of the radical, it can either terminate in the aqueous phase or re-enter another particle and terminate or propagate, with termination processes reducing the average number of free radicals per particle. Retardation in bulk experiments with increasing amounts of RAFT agent has been observed at Eindhoven University of Technology, suggesting that aqueous phase termination is not responsible for the retardation and that the system is suggested to follow Limit 2a (negligible aqueous phase termination with complete re-entry and minimal re-escape).

This exit is the main reason for the observed inhibition. The higher the exit rates then the longer the apparent inhibition times. There is a drastic decrease of approximately two orders of magnitude of \bar{n} due to exit (Limit 2a), which means that there is a very drastic retardation period which manifests itself as an inhibition period. Once the concentration of RAFT agent becomes low enough, cessation of the inhibition period occurs and polymerization commences.

4.5.2 RETARDATION

Fresh RAFT agent diffuses into the particles in Interval II resulting in exit and thus a reduction in \bar{n} and also polymerization rate. At the changeover to Interval III (at approximately 10% conversion) most of the RAFT agent is in the particles, however transport of residual RAFT agent that is still present in the system is enough to give a marked reduction in polymerization rate due to exit. This rate of replenishment of RAFT agent is calculated by Equations 4.6 and 4.7 to be in the order of 10^6 s^{-1} , indicating that replenishment of consumed RAFT agent will occur during the timescale of the experiment.

It is important to note that even when inhibition periods are similar for various RAFT agents, the rate of reaction is still determined by the type of RAFT agent.

4.5.3 THE RED LAYER

Due to the inhibition time monomer droplets containing RAFT agent are stung. If a radical enters a droplet and reacts with RAFT agent the probability of escape of the incipient RAFT fragmented radical is small due to the large size of the droplet. This means that one has a pseudobulk system in which one radical in principle can react with all the RAFT agent in the droplet to form many oligomeric chains. The diffusion rate of these oligomers decreases and therefore transportation slows drastically, and consequentially a red layer is formed after all the monomer has been transported into the particle. The observation of the red layer correlates with the changeover from Interval II to III (at approximately 10% conversion).

During the lengthy inhibition period, monomer droplets are being stung by initiating radicals, resulting in the formation of oligomeric to polymeric dithioesters, which can not be successfully transported through the aqueous phase to the latex particles^[9]. The rate of diffusion of these oligomerics is given by Smoluchowski's equation where the coefficient of diffusion is calculated using the reptative power law given in Equation 4.14:

$$D_i = \frac{D_{mon}(W_p)}{i^2} \quad (4.14)$$

where i is the degree of polymerization and $D_{mon}(W_p)$ is the diffusion coefficient of the monomeric species at a specific weight fraction of polymer.

It can be visualized that the diffusion coefficient decreases quickly on increasing chain length, resulting in a drastic reduction in transportation with increasing chain length.

4.5.4 MOLECULAR WEIGHT AND DISTRIBUTION

M_n increases with conversion suggesting that it is a 'living' process. Continuous transport of RAFT agent into the particles affects the molecular weight and the distribution. The initial number average molecular weight, $M_{n,initial}$ will be far higher than predicted as all the RAFT agent is not initially contained in the particles, and M_n should then follow Equation 4.11 for the RAFT agent initially present in the particles, $[RAFT]_{initial}$.

As RAFT diffuses into the particles, smaller chains are being formed and at the same time the polymer chains formed initially grow, causing an increase in polydispersity and an increase in M_n but at a much lower rate as predicted by Equation 4.11. Since fresh RAFT agent diffuses into the particles in Interval II we get exit and thus reduction in \bar{n} and thus rate. At the changeover to Interval III, most of the RAFT agent is in the particles and there is a broad distribution of polymer chains having a dithioester end-group in the particles. In Interval III, all these chains will grow at the same rate, thus M_n increases and the polydispersity remains relatively constant. The further decrease in polydispersity is probably due to termination (radical-radical) or transfer to monomer. The rate of increase of M_n after 10% conversion is consistent with the above postulate.

If transfer reactions are taken into account in the zero-one model that Gilbert uses^[1], and assuming the different limits, values for the average number of radicals per

particle, \bar{n} can be obtained. With increasing RAFT concentration one sees a reduction in \bar{n} (Limit 2a). This would correspond to a reduction in reaction rate. Usage of the RAFT concentrations calculated from the experimental M_n values, a KPS concentration of $1 \times 10^{-3} \text{ mol dm}^{-3}$ and a transfer constant^[10] of the order 10^3 leads to the following theoretical \bar{n} values for the Cumyl and EMA RAFT agents at a RAFT concentration of $\approx 5 \times 10^{-4} \text{ mol dm}^{-3}$:

Cumyl RAFT: $\bar{n} = 0.023$ (Experimental $\bar{n} = 0.018$)

EMA RAFT: $\bar{n} = 0.0047$ (Experimental $\bar{n} = 0.0028$)

As can be seen, the theoretical prediction gives quite a good approximation to the experimentally obtained values. Greater reduction in \bar{n} with the EMA RAFT than with the Cumyl RAFT is rightly predicted, as is the lowering of \bar{n} with increase in RAFT concentration.

4.6 BIBLIOGRAPHY

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CHAPTER 5

AB INITIO STUDIES

5.1 BACKGROUND

In Section 4.1, the three different intervals of polymerization in an emulsion system have been discussed, and the complications noted. The advantages of avoiding particle formation by performing seeded experiments were mentioned. Despite the advantages associated with the avoidance of particle formation, in this study, *ab initio* work was deemed necessary to ascertain the effect of the RAFT agents on particle nucleation. It was also hoped that the *ab initio* studies would elucidate more mechanistic information about the emulsion polymerization of styrene in the presence of a RAFT agent, that could be viewed and interpreted in the light of the mechanistic information acquired from the seeded studies.

5.2 EXPERIMENTAL

Two sets of experiments were performed. The first was designed to determine the sensitivity of the RAFT emulsion on different reaction conditions while the second was designed to compare the effects of RAFT concentration and the structure of the RAFT agent.

5.2.1 VARIATIONS IN REACTION CONDITIONS

Variations on the emulsion procedure were adopted to determine the RAFT emulsion reaction sensitivity to certain factors; these were:

- Rigorous degassing to eliminate the presence of oxygen was carried out to determine the sensitivity of the polymerization system to dissolved oxygen.

- The oxygen centred initiator used (KPS) was substituted with a carbon-centred, water soluble initiator (ACPA, 4,4-azobis(cyanovaleric acid)) to see if the inhibition period was due to a reaction of the oxygen-centred radical with the RAFT agent.
- The effect of changing the monomer from the highly insoluble styrene to the more water soluble MMA monomer was also investigated.

The concentration of RAFT agent in the reactions (at a constant initiator concentration) was varied to see the effect of different initiator to RAFT agent ratios on the emulsion polymerization reaction.

The experimental set-up used is depicted in Figure 5.1 and a short summary of the performed experiments is given in Table 5.1.

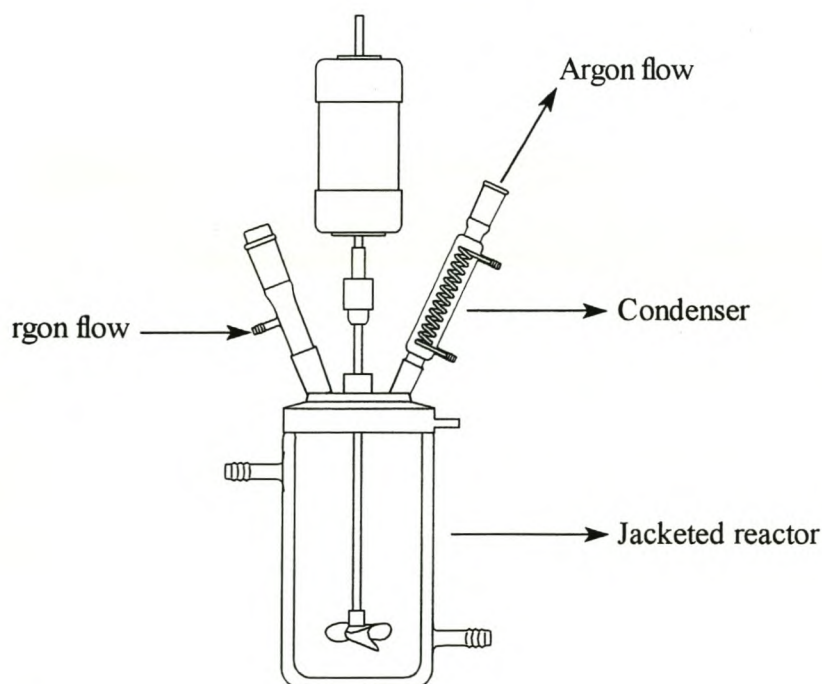


Figure 5.1 Experimental set-up used in the *ab initio* experiments.

Table 5.1 Summary of the conditions for the initial *ab initio* experiments

Exp	Comments	[EMA RAFT]	[KPS]
A	Control, no RAFT		2.1×10^{-3}
B	Control, no RAFT		5.2×10^{-4}
C		4.5×10^{-3}	2.2×10^{-3}
D		4.8×10^{-3}	7.0×10^{-4}
E		7.8×10^{-4}	2.4×10^{-3}
F	Freeze-evac degassing	2.7×10^{-3}	2.4×10^{-3}
G	ACPA as initiator	2.7×10^{-3}	2.1×10^{-3}
H	MMA as monomer	2.9×10^{-3}	2.5×10^{-3}

Experiments A through to E were carried out according to the following procedure. Deionized water was charged to a glass jacketed reactor and degassed for 1 hour at 60°C by the bubbling through of Argon gas while the reactor contents were being stirred. The surfactant was then added to the reactor and agitation was allowed to proceed for a further ½ hour at the reaction temperature. The RAFT agent (not present in Experiments 1 and 2) was then dissolved in the styrene monomer from which the inhibitor had already been removed by passing it through an inhibitor removal column. The monomer (and EMA RAFT agent) was then added to the reactor and emulsification was allowed to proceed for 5 minutes before the addition of the pre-dissolved and pre-heated initiator.

Experiments F through to H were carried out with rigorous degassing of the monomer and RAFT agent through three freeze-evacuated-thaw cycles. This rigorous degassing of the monomer for use in a robust system such as an emulsion was done to determine if the large inhibition periods in the *ab initio* system were due to some type of reaction between the RAFT agent and the dissolved oxygen, resulting in the inhibition of the polymerization reaction. Small amounts of dissolved oxygen are common in an emulsion system and are usually responsible for a short inhibition period before polymerization gets underway, where the free radicals generated from the initiator react with the oxygen molecules (free radical scavengers). The experimental procedures followed for Experiments A through to E

were adapted for Experiments F through to H, with the inclusion of rigorous degassing of the monomer and an increase in the emulsification period to 1 hour.

Experiment G was carried out with ACPA (4,4-azobis(cyanovaleric acid)) as the initiator, instead of KPS, under the same conditions as Experiment F. This change from an oxygen-centered initiator (and initiating radical) to a carbon-centered initiator (and carbon-centered initiating radical) was made to see if the inhibition period was due to reaction of the EMA RAFT agent with an oxygen-centered radical. The structures of the different initiators are given in Figures 5.2 and 5.3.

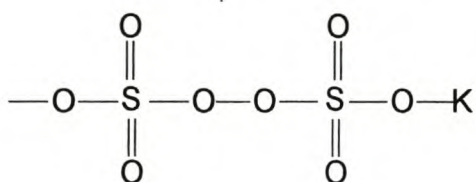


Figure 5.2 Structure of the oxygen-centred initiator, potassium persulfate.

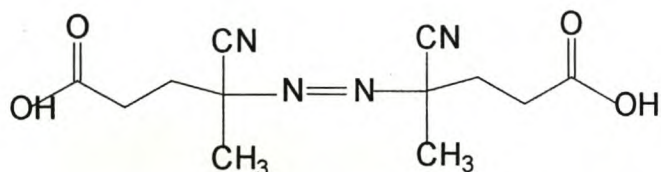


Figure 5.3 Structure of the carbon-centred initiator, 4,4-azobis(cyanovaleric acid).

Experiment H was carried out under the same conditions as Experiment F, with the replacement of the highly water insoluble monomer styrene with MMA monomer. MMA has a higher propagation constant than styrene and a water solubility two orders of magnitude greater than that of styrene. The aqueous phase concentration of MMA monomer is therefore expected to be higher and the z-mer longer^[1]. This may lead to the reduction of the inhibition period as the initiator used in the system is water soluble and the initiation reaction should occur in the aqueous phase between the initiating radical and the monomer – the probability of this occurring should be greater when the aqueous phase concentration of the monomer is higher.

5.2.2 VARIATIONS IN RAFT STRUCTURE AND CONCENTRATION

A second range of experiments was performed in which the type of RAFT agent, at a range of different concentrations, was varied to determine the effect of RAFT agent structure and concentration on the emulsion polymerization. A summary of the different RAFT concentrations that were employed is given in Table 5.2.

Table 5.2 Summary of RAFT agent concentrations in the second range of experiments, with $[KPS] = 2 \times 10^{-3} \text{ mol dm}^{-3}$

	[Cumyl RAFT]	[EMA RAFT]	[PBMA RAFT]
HIGH	5.2×10^{-3}	5.2×10^{-3}	4.7×10^{-3}
MIDDLE	2.6×10^{-3}	2.7×10^{-3}	2.4×10^{-3}
LOW	1.1×10^{-3}	1.0×10^{-3}	8.7×10^{-4}

The procedure adopted for the second range of the experiments was similar to the reaction conditions used for Experiment F. Here the degassed monomer was transferred via a pump from the reactor (where it was degassed, and placed under Argon) to a 250 ml, 3 necked round bottomed flask reaction vessel, which was stirred by means of a magnetic stirrer.

5.3 RESULTS AND DISCUSSION

5.3.1 DIFFERENT REACTION CONDITIONS

A summary of the effect of reaction conditions on the inhibition periods is given in Table 5.3. It can be seen from these results that the inhibition period in the control experiments were not noticeable. The inhibition times, similar to those of the seeded experiments, increased with EMA RAFT concentration, as can be seen in Figure 5.4.

Table 5.3 A summary of the effect of experimental conditions on the inhibition periods obtained

Exp	Comments	[EMA RAFT] mol dm ⁻³	[KPS] mol dm ⁻³	Inhibition time in min
A	Control, no RAFT		2.1 x 10 ⁻³	None
B	Control, no RAFT		5.2 x 10 ⁻⁴	None
C		4.5 x 10 ⁻³	2.2 x 10 ⁻³	540
D		4.8 x 10 ⁻³	7.0 x 10 ⁻⁴	510
E		7.8 x 10 ⁻⁴	2.4 x 10 ⁻³	90
F	Freeze-evac degassing	2.7 x 10 ⁻³	2.4 x 10 ⁻³	210
G	ACPA as initiator	2.7 x 10 ⁻³	2.1 x 10 ⁻³	360
H	MMA as monomer	2.9 x 10 ⁻³	2.5 x 10 ⁻³	No conversion

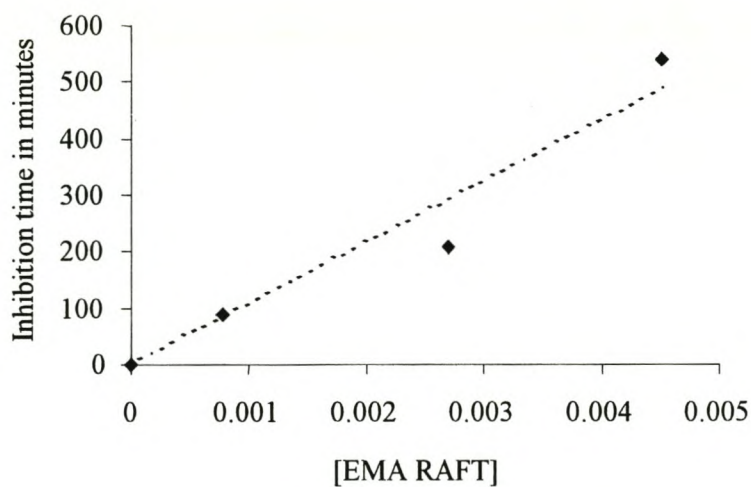


Figure 5.4 The effect of EMA RAFT addition on the inhibition times displayed in the *ab initio* emulsion polymerization at 60°C, with [KPS] $\approx 2 \times 10^{-3}$ mol dm⁻³.

From Experiment F, which was carried out with rigorous degassing of the seed latex, the monomer and chain transfer agent, we ascertained that the inhibition period was not overly sensitive to the amount of dissolved oxygen present in the system.

From Experiment G, which was carried out using ACPA as the initiator instead of KPS, a longer inhibition period was noted than when KPS was used as the initiator in the same system. The inhibition period is therefore not merely due to a side reaction of the oxygen-centered initiating radical with the EMA RAFT agent, as the inhibition period was even more prominent when a carbon-centered initiator was used.

Due to MMA having both a higher water solubility and propagation constant than styrene, it can be expected that the z-mer for MMA will be longer than that of the styrene monomer.

From Experiment H, which was carried out using the more water soluble MMA monomer instead of styrene, it can be seen that no conversion was obtained, even after a lengthy period. This is postulated to be due to an equilibrium being reached between the original RAFT agent and the RAFT radical (generated by the immediate reaction of the persulfate radical with the dithioester compound) that has reacted with MMA monomer, as nearly the same chemical species was obtained as the original EMA RAFT agent. If the fragmentation rate coefficient is slow then termination of the equilibrium radical (**B**) by other radicals would result in significant retardation/inhibition. (See Figure 5.5)

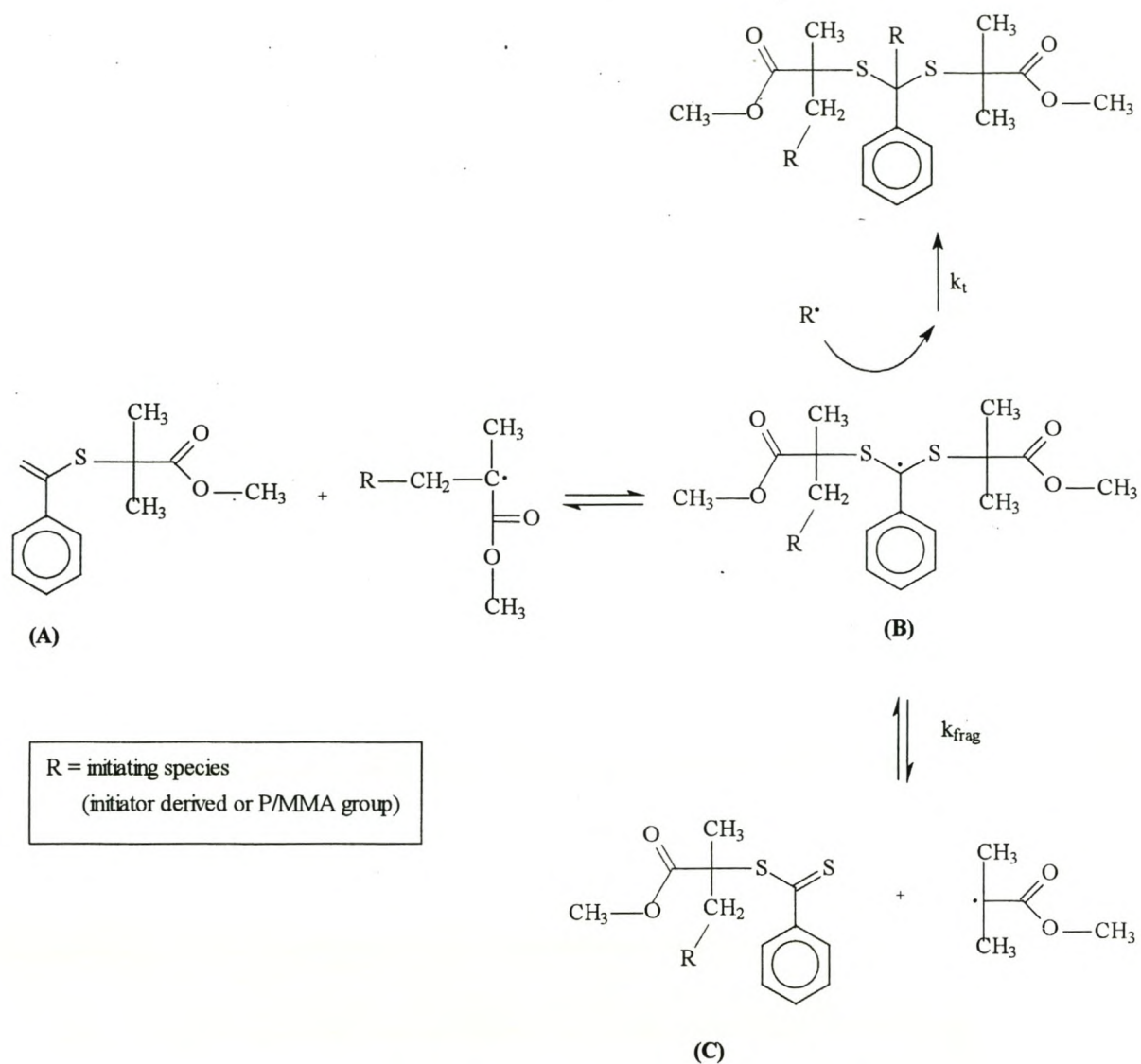


Figure 5.5 Reaction of EMA RAFT agent with MMA radical species, displaying the equilibrium that is set in between chemically similar species (A) and (C) and the termination of the intermediate (B).

5.3.2 VARIATIONS IN RAFT STRUCTURE AND CONCENTRATION

Results obtained from the second set of *ab initio* experiments are now presented in the form of a comparison between different RAFT agents and RAFT agent concentrations.

At about 10% conversion, phase separation of an intensely red coloured layer was observed in the reactor. This 'red layer' decreased in surface volume throughout the polymerization until it coagulated on the stirrer bar at approximately 80 to 90% conversion.

5.3.2.1 Inhibition periods

The increase in inhibition times with increasing RAFT concentration was evident from the conversion profiles, for the various RAFT agents at three different concentrations, as shown in Figures 5.6, 5.7 and 5.8.

From Figure 5.6 it is seen that, although there is an inhibition period with the Cumyl RAFT emulsion, the inhibition remained almost constant with increasing Cumyl RAFT concentration.

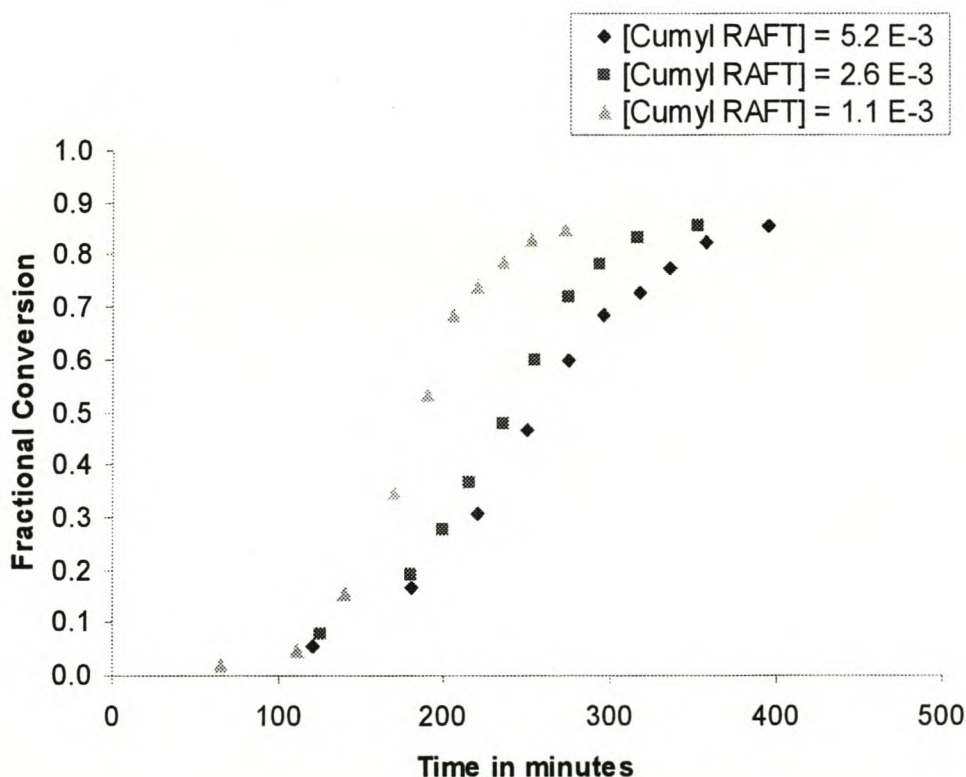


Figure 5.6 Conversion time profile for varying Cumyl RAFT concentrations at a KPS concentration of 2.2×10^{-3} M.

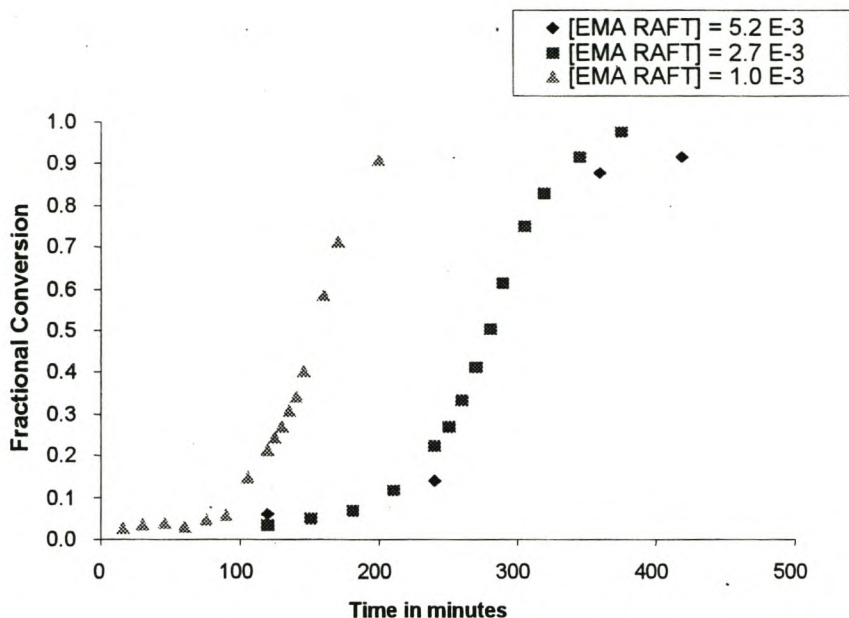


Figure 5.7 Conversion time profile for varying EMA RAFT concentrations at a KPS concentration of 2.1×10^{-3} M.

From Figures 5.7 and 5.8 it is evident that the inhibition period in both the EMA RAFT and the PBMA RAFT *ab initio* emulsions, increases markedly with increasing RAFT concentration (and subsequent lowering of the initiator to RAFT ratio).

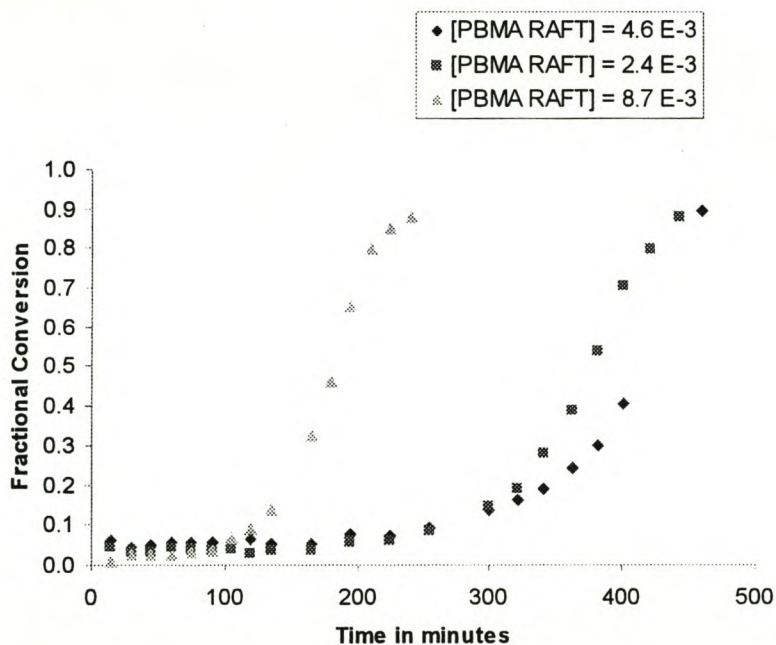


Figure 5.8 Conversion time profile for varying PBMA RAFT concentrations at a KPS concentration of 2.0×10^{-3} M.

Conversion time profiles at different RAFT concentrations, for the three different RAFT agents, are displayed in Figures 5.9, 5.10 and 5.11. At low RAFT concentrations (Figure 5.9), the inhibition periods displayed by the three different types of RAFT agents were quite similar, with the EMA RAFT emulsion displaying the smallest inhibition period. On increasing RAFT concentration (Figure 5.10 through to Figure 5.11) the increasing inhibition period was more prominent in the case of PBMA RAFT, followed by the EMA RAFT emulsion.

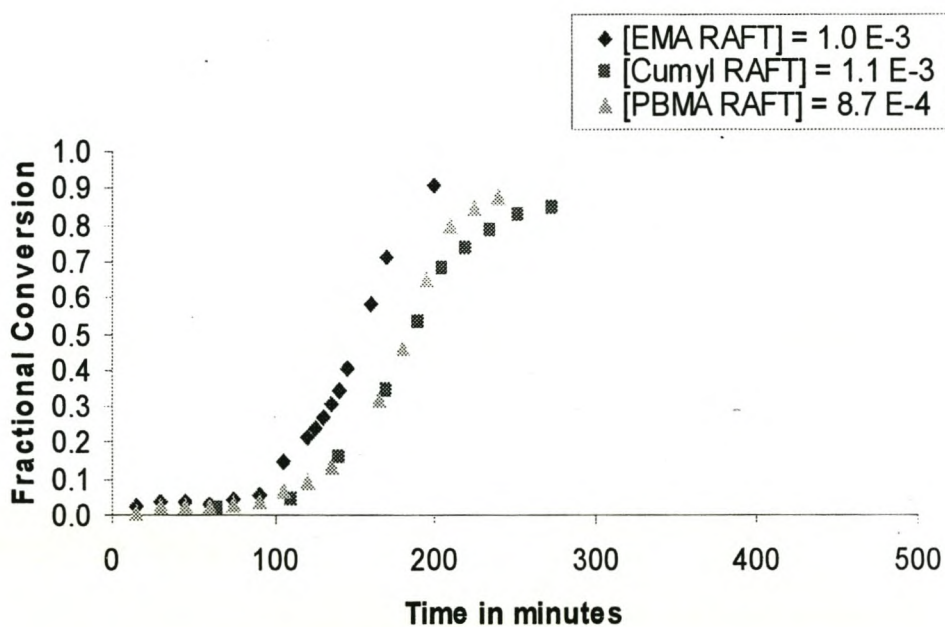


Figure 5.9 Conversion time profile for low RAFT concentrations ($1 \times 10^{-3} \text{ M}$) with $[\text{KPS}] = 2 \times 10^{-3} \text{ M}$.

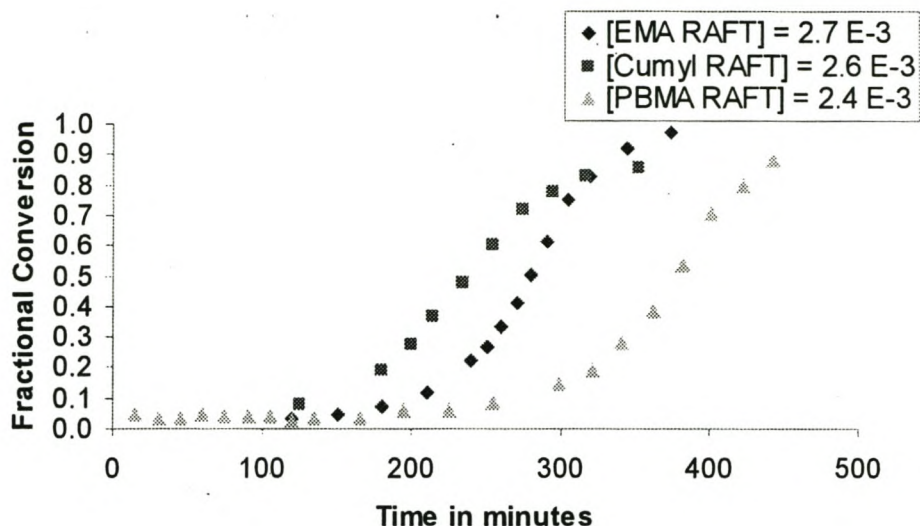


Figure 5.10 Conversion time profile for medium RAFT concentrations ($\approx 2.5 \times 10^{-3} M$) with $[KPS] = 2 \times 10^{-3} M$.

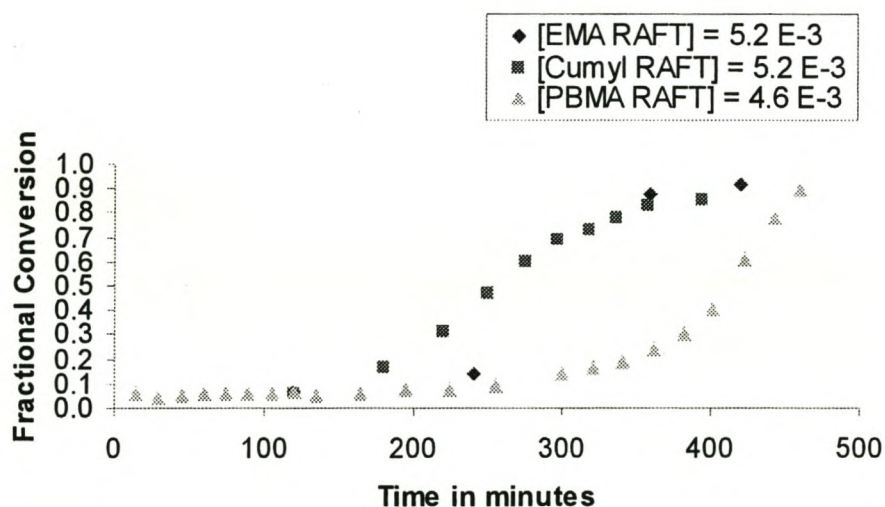


Figure 5.11 Conversion time profile for high RAFT concentrations ($5 \times 10^{-3} M$) with $[KPS] = 2 \times 10^{-3} M$.

The inhibition times found in these *ab initio* experiments were much longer than those observed for the seeded experiments at equivalent RAFT and initiator concentrations (see Section 4.4.2)

5.3.2.2 Rate retardation

The reaction rate profiles for the separate RAFT agents, given as experimental points, at different concentrations, are given in Figures 5.12 through to 5.14. The RAFT concentrations designated by High, Mid and Low were as follows:

High : $5 \times 10^{-3} \text{ mol dm}^{-3}$

Mid : $2.5 \times 10^{-3} \text{ mol dm}^{-3}$

Low : $1 \times 10^{-3} \text{ mol dm}^{-3}$

The concentration of the persulfate initiator was $2.2 \times 10^{-3} \text{ mol dm}^{-3}$ for all the experiments.

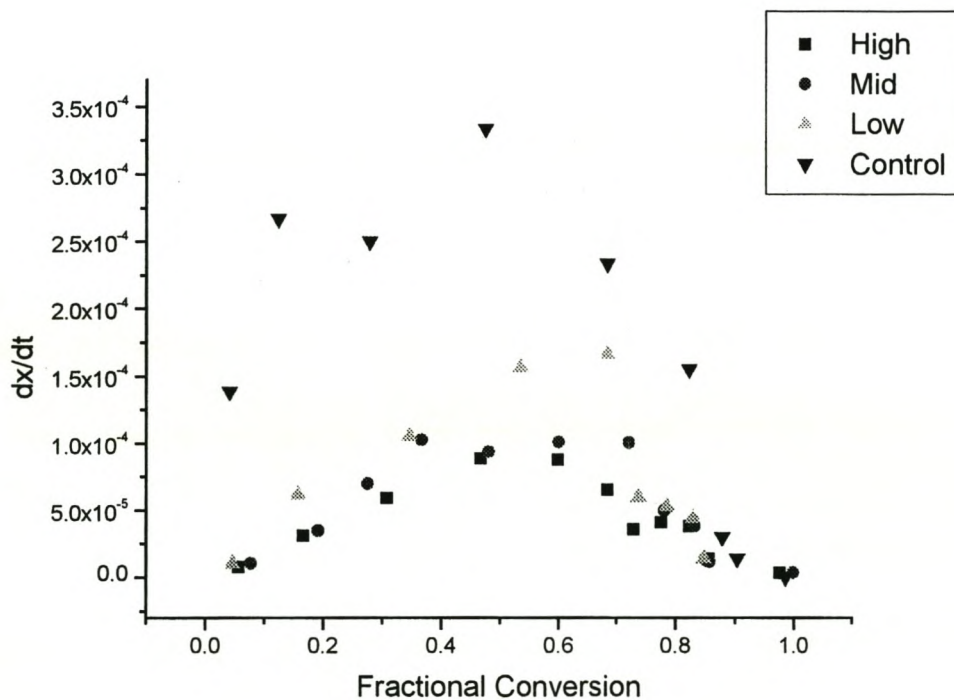


Figure 5.12 Reaction rate profile for ab initio experiments with Cumyl RAFT agent.

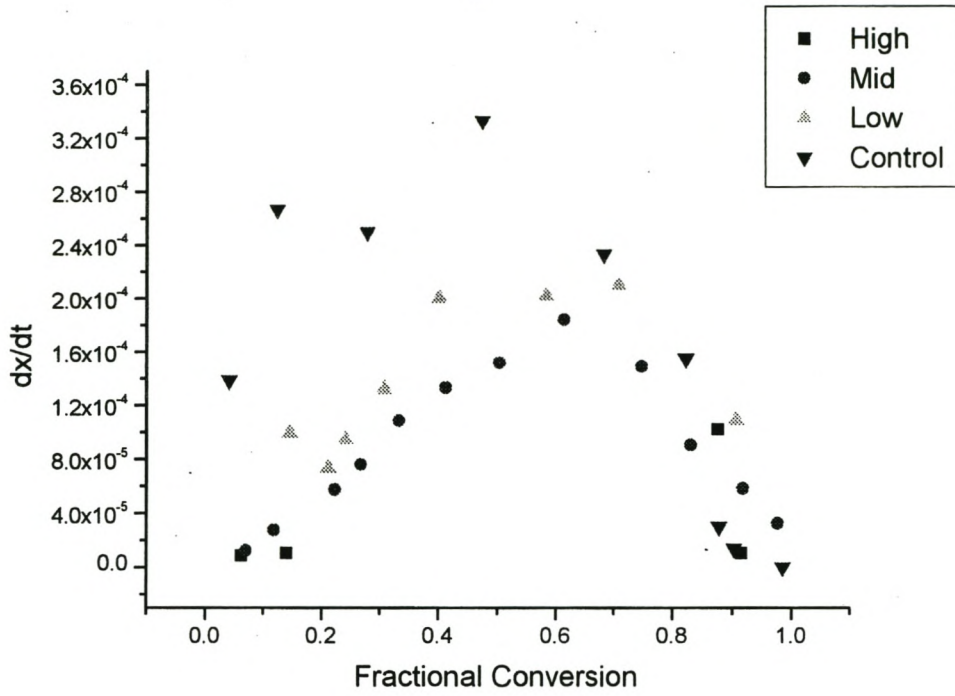


Figure 5.13 Reaction rate profile for *ab initio* experiments with EMA RAFT agent.

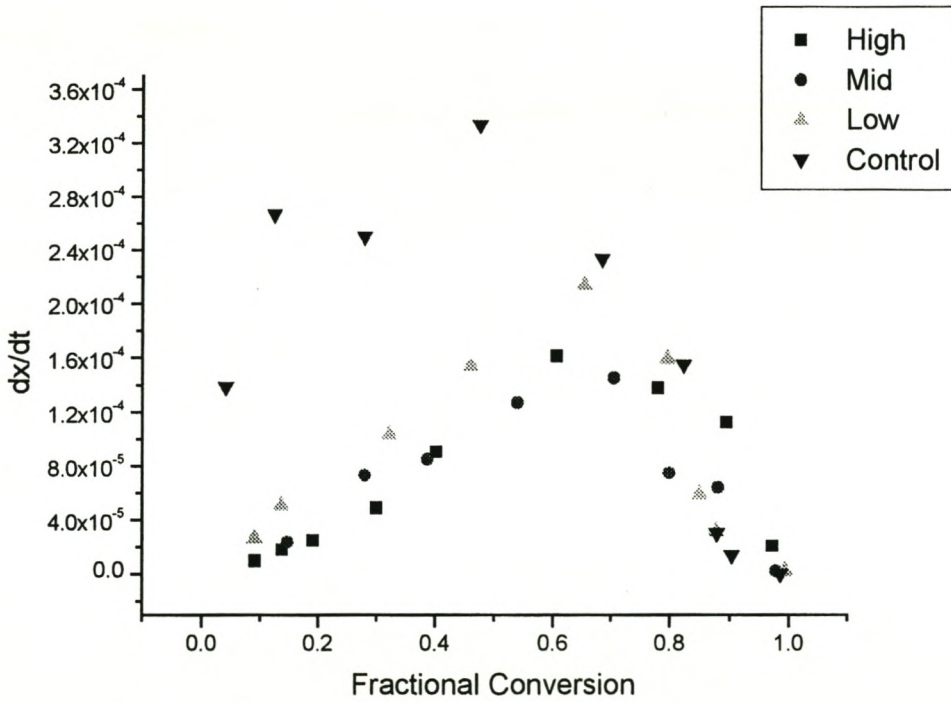


Figure 5.14 Reaction rate profile for *ab initio* experiments with PBMA RAFT agent.

From the reaction rate profiles it was evident that the addition of RAFT agent to the system resulted in retardation of the polymerization reaction. With increasing amounts of RAFT agent, greater retardation was observed, although this slowing down of the reaction rate with increasing RAFT concentration was not as noteworthy as the change in reaction rate from the control experiment (no RAFT agent present) to the experiment with a low concentration of RAFT agent.

In a 'normal' emulsion polymerization, one would see three different phases of the reaction rate (as discussed in section 2.1.2):

1. Firstly, an increase in the reaction rate in the early stages of the polymerization is observed - synonymous with Interval I where particle formation is occurring.
2. Secondly, a period of constant reaction rate is observed - coinciding with Interval II where the particle number is constant and the monomer concentration in the particles is constant.
3. Lastly, a decreasing rate of polymerization is observed - corresponding to Interval III where the monomer concentration in the particles is decreasing due to the depletion of monomer droplets in the system.

In the control experiment we saw that the changeover from Interval I to Interval II occurred between $x = 0.10$ and 0.15 , and below which we have an increasing rate of polymerization (dx/dt). During Interval II the reaction rate remained relatively constant, until the changeover to Interval III at $x \approx 0.6$, after which the reaction rate declined.

It could also be seen in the reaction rate profiles that no true steady state was achieved for the *ab initio* RAFT emulsions. The reaction rate increased with increasing conversion and little or no plateau was present in the reaction rate before the reaction rate started to decrease at a fractional conversion, x , of approximately 0.7 . This suggests that there is no Interval II in the *ab initio* emulsion polymerization with added RAFT agent. That is, N_c or C_p is changing with conversion. If N_c is changing throughout the reaction then nucleation is taking place throughout the polymerization. Particle size analysis by CHDF was carried out on the reactions to

monitor the particle size development with conversion. From the CHDF data the development of the particle sizes with conversion could be traced and Figure 5.15 gives an example of the evolution typically obtained in the *ab initio* RAFT experiments. It should be noted that the lower cut-off limit for the CHDF is a particle diameter of approximately 20 nm. The increase in the average particle size and particle size distribution broadening with increasing conversion can be seen from Figure 5.15.

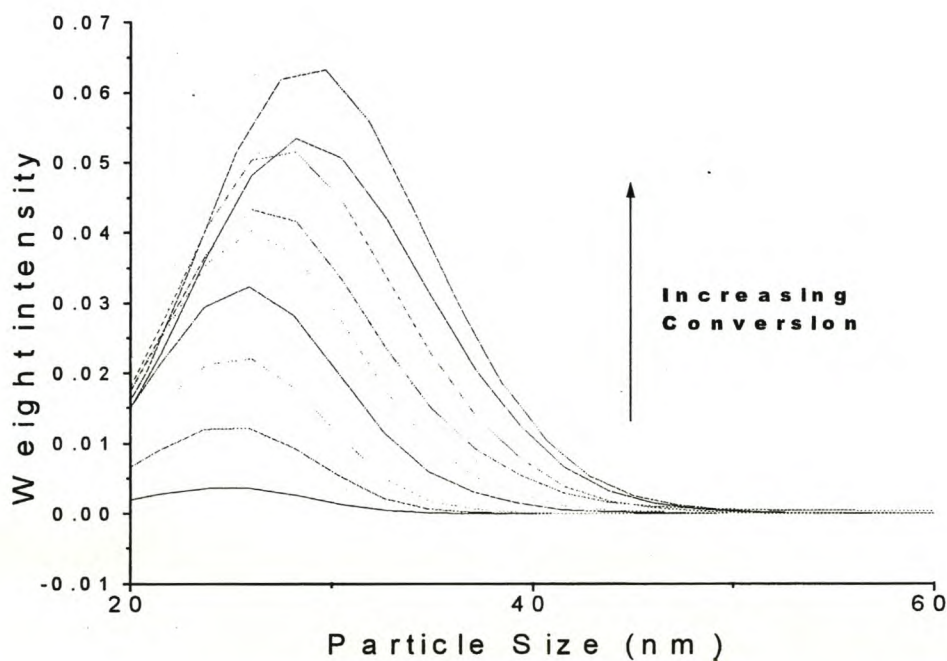


Figure 5.15 Evolution of particle sizes for the *ab initio* emulsion of styrene in the presence of Cumyl RAFT with KPS as initiator.

The value of C_p must then be changing throughout the polymerization. This change in the monomer concentration in the latex particles could be due to the fact that C_p^{sat} is a marked function of r_u for small particles ($r_u < 30$ nm, which is in the particle size region that we are working with) as predicted by the Morton equation^[2].

5.3.2.3 GPC data

5.3.2.3.1 Number-average molecular weights

The M_n values obtained experimentally at the different RAFT concentrations as well as the predicted M_n value (from Equation 4.11) are given in Figures 5.16 through to 5.18 (High through to Low RAFT concentrations) for the three different RAFT agents.

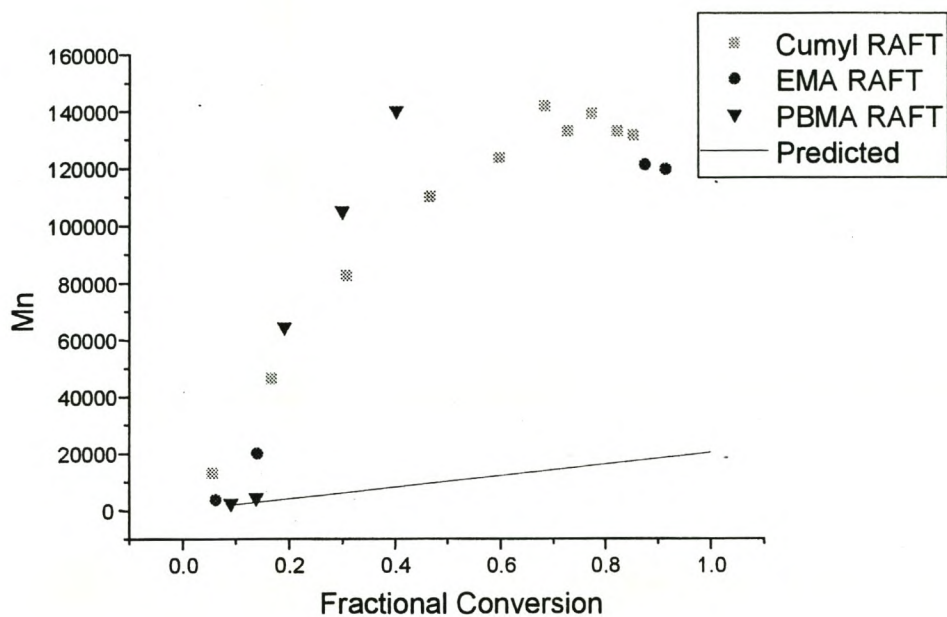


Figure 5.16 M_n values obtained experimentally and the predicted M_n for High RAFT agent concentrations.

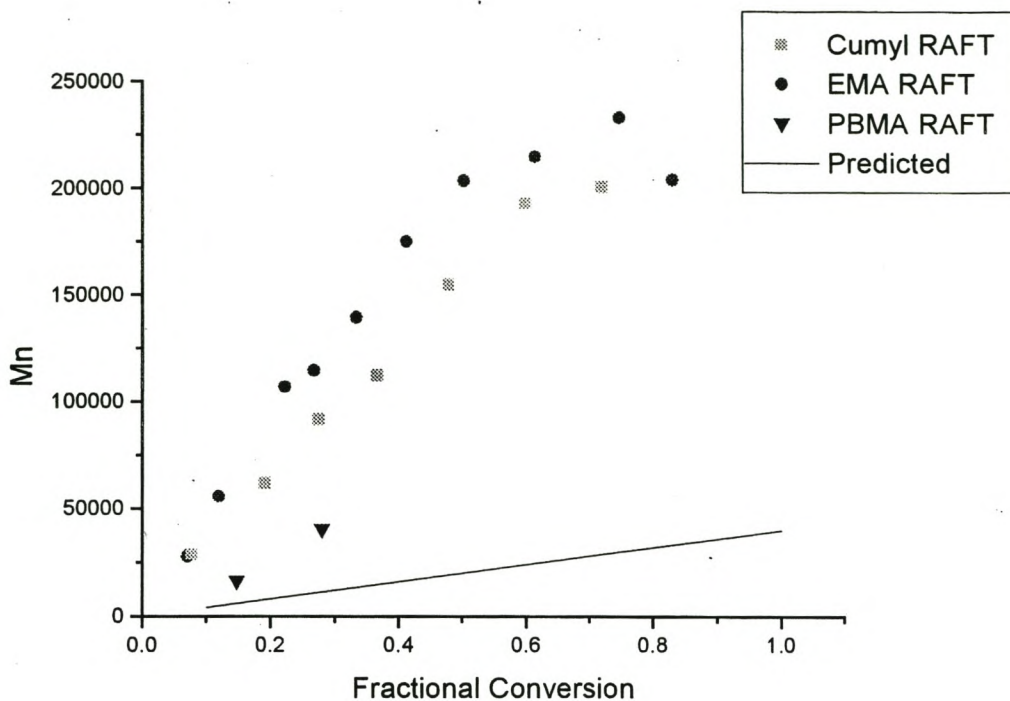


Figure 5.17 Mn values obtained experimentally and the predicted Mn for Middle RAFT agent concentrations.

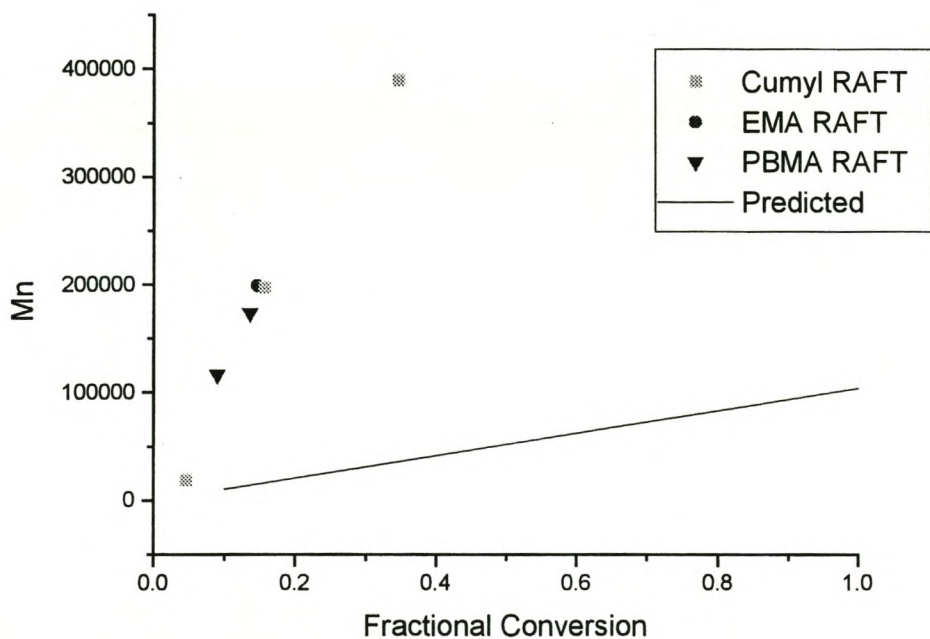


Figure 5.18 Mn values obtained experimentally and the predicted Mn for Low RAFT agent concentrations.

At High, Low and Middle RAFT concentrations for the Cumyl, EMA and PBMA RAFT agents, the experimentally obtained values for the number-average molecular weight, M_n were much higher than the predicted values. It could also be seen that the experimental M_n value did in fact increase with conversion. It was also found that the experimental M_n values decreased with increasing RAFT concentration.

Portions of the high molecular weight fractions present in the emulsion samples that were drawn over time were above the GPC calibration curve, and the values thus obtained for the M_n and M_w values were subsequently unreliable. We therefore did not include them in the above graphs. The PBMA experiments gave a large amount of high molecular weight material and therefore M_n or M_w/M_n data was not considered for these samples.

^1H NMR analysis was performed on the red sticky coagulate and it was seen from the NMR spectra that it was polystyrene. The molecular weight of the polymer was however too high to gain conclusive evidence on the presence of RAFT endgroups. The intense red colour of the coagulate indicated that there were chromophoric groups (from the RAFT agent) in the polymer chains.

5.3.2.3.2 Polydispersity

The experimental values obtained for the polydispersity (M_w/M_n) of the *ab initio* samples for the different RAFT agents are given in Figures 5.19, 5.20 and 5.21.

It is evident from these Figures that the polydispersities of the *ab initio* samples were very high. This means that the weight distribution M_w was much larger than the number distribution M_n . The polymer chains being grown in the RAFT emulsions were not of uniform length, and resulted in rather broad molecular weight distributions. It should be noted that at fractional conversions greater than 0.3, the polydispersities appear to be relatively constant.

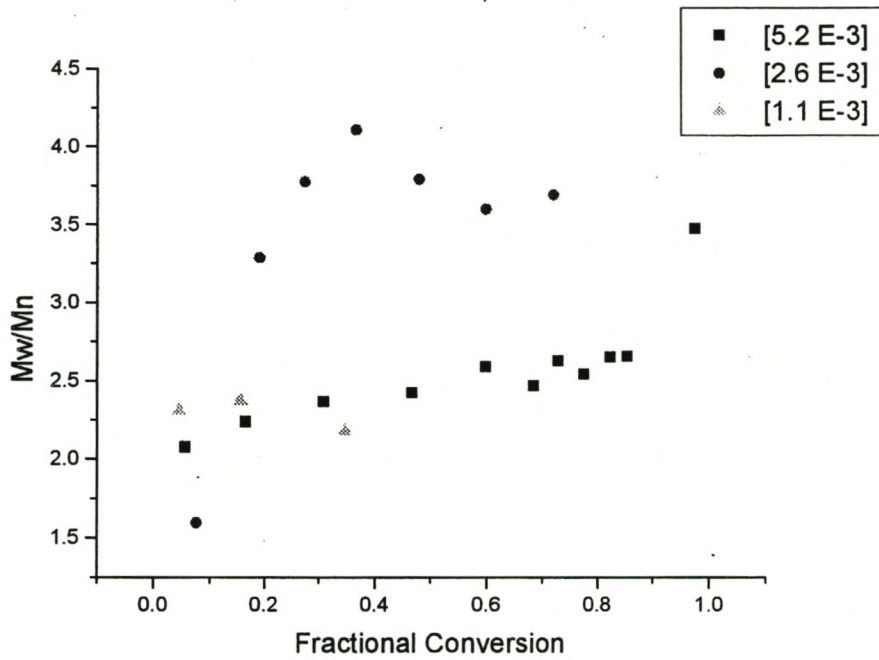


Figure 5.19 *Mw/Mn values obtained at High, Middle and Low concentrations of Cumyl RAFT agent.*

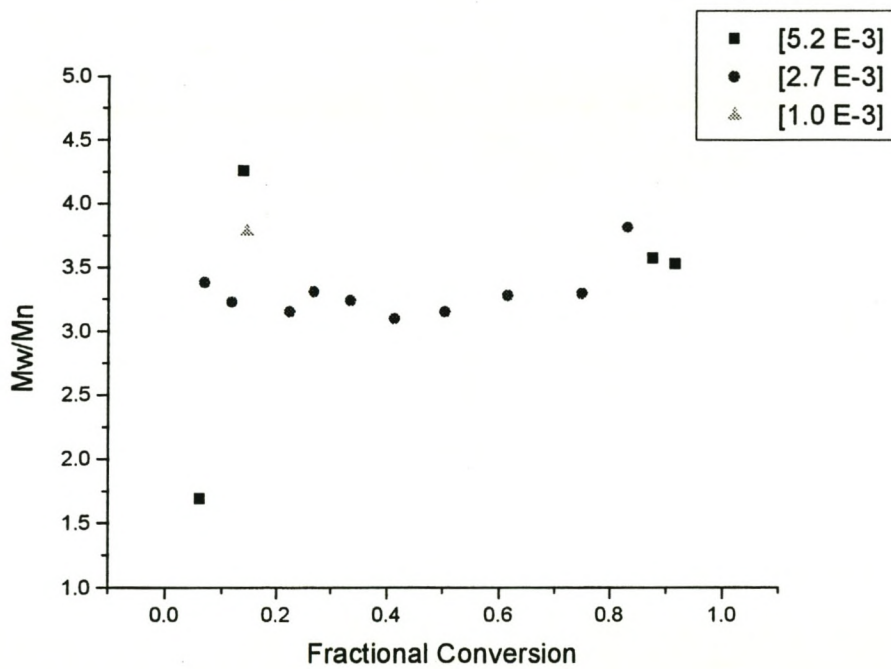


Figure 5.20 *Mw/Mn values obtained at High, Middle and Low concentrations of EMA RAFT agent.*

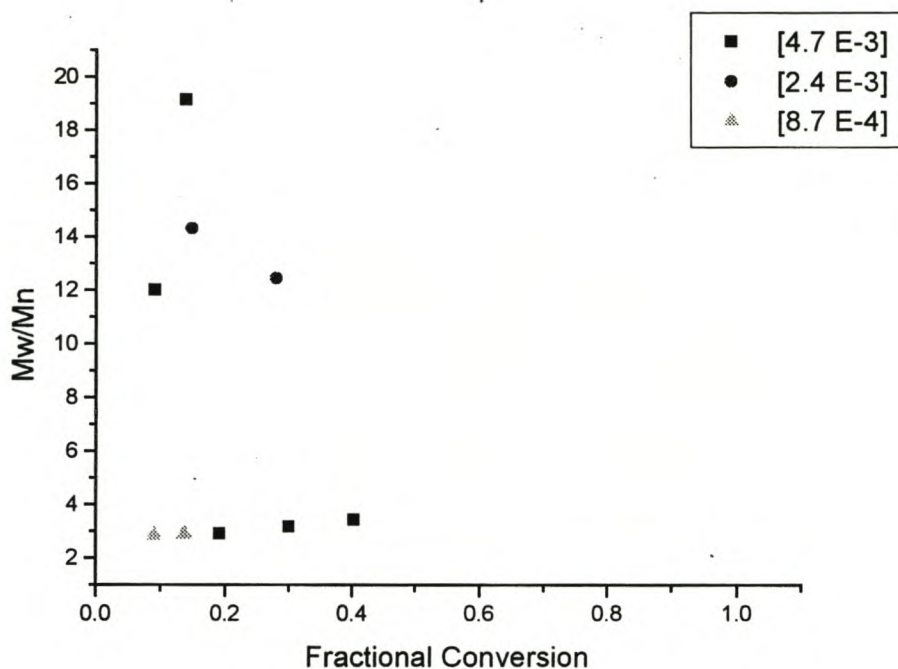


Figure 5.21 *Mw/Mn* values obtained at High, Middle and Low concentrations of PBMA RAFT agent.

5.3.2.3.3 GPC traces

Examples of the differential log MWD, $x(M)$ (derivative with respect to the logarithm of molecular weight) obtained from the GPC data for the different emulsion polymerizations are illustrated in Figures 5.22 through to 5.25. The same trends were seen at the different concentrations of the individual RAFT agents, only one example of the distribution obtained from each of the different RAFT *ab initio* emulsion experiments is given. The areas underneath the individual distributions were first normalized and were then scaled according to conversion.

It can be seen from the differential log MWDs that there was an increase in the maximum of $x(M)$ with increasing conversion, up to about 60% conversion after which the maximum of the differential log MWD remained unchanged. The low molecular mass material did not appear to be growing, indicating the presence of 'dead' chains.

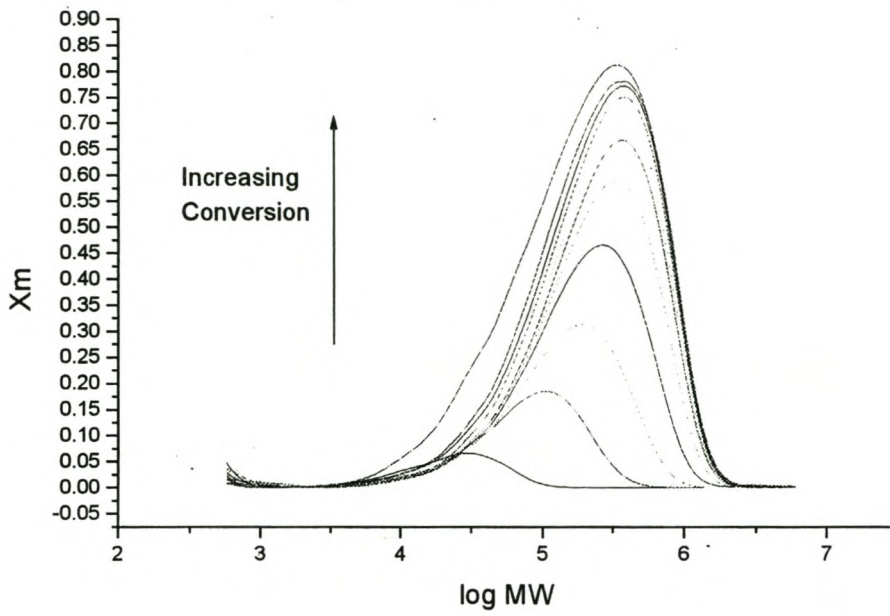


Figure 5.22 Log molecular weight distributions at High Cumyl RAFT concentration with increasing conversion.

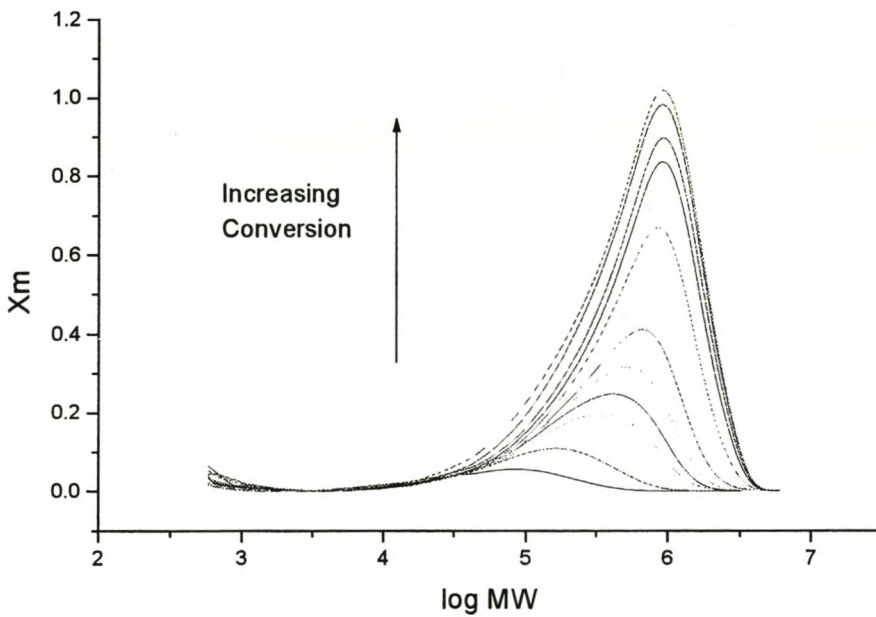


Figure 5.23 Log molecular weight distributions at Middle EMA RAFT concentration with increasing conversion.

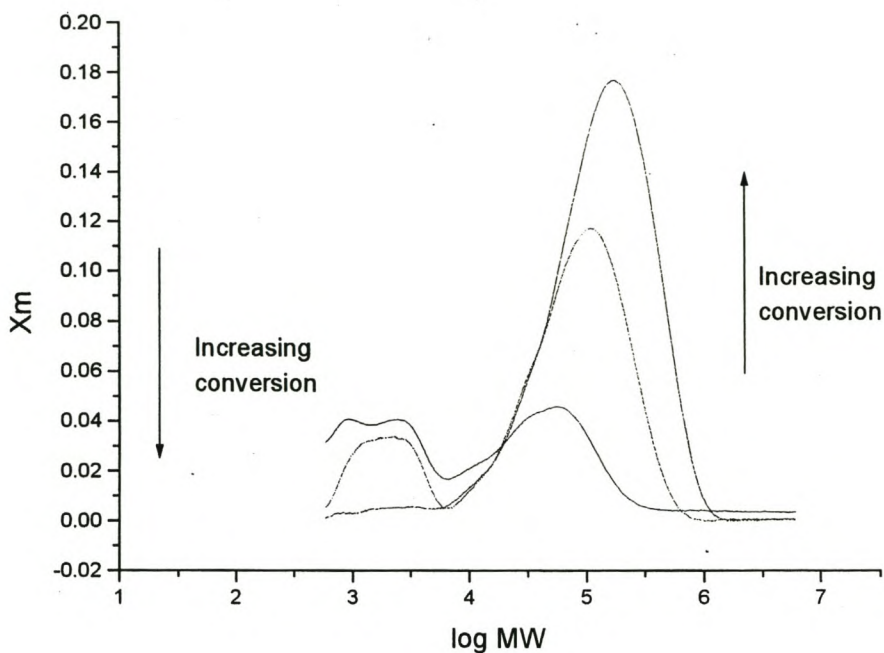


Figure 5.24 Log molecular weight distribution for low conversions (9, 14 and 20%) in the ab initio polymerization with High concentrations of PBMA RAFT.

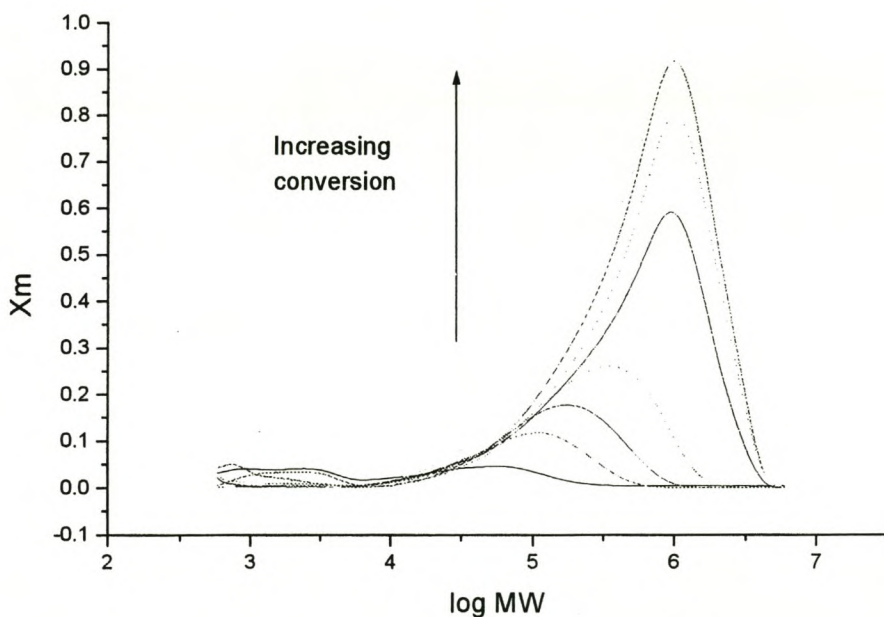


Figure 5.25 Log molecular weight distribution for increasing conversions (up to full conversion) in the ab initio polymerization with High concentrations of PBMA RAFT.

The same trend was seen in all the PBMA RAFT experiments, with a bimolecular molecular weight distribution evident at low conversions, contributing towards the high polydispersity values. The low molecular weight fraction did not appear to grow with increasing conversion, and therefore become less significant with increasing conversion, resulting in a decrease in the polydispersity values.

5.4 DISCUSSION

5.4.1 INHIBITION

Long inhibition periods, up to 5 hours, were observed in the *ab initio* emulsion polymerizations with added RAFT agent. These inhibition periods increased with increasing RAFT concentration. At low RAFT concentrations the inhibition periods observed for the different RAFT agents were similar, but on increasing the RAFT concentration the inhibition period observed increased more significantly with the PBMA RAFT. The Cumyl RAFT reactions displayed the least increase in inhibition time with increasing conversion.

These inhibition periods could be due to the exit of R' (radical arising from the fragmentation of the RAFT agent, see Figure 2.8) from the particles, which then acts as a primary radical terminator, retarding the particle nucleation in Interval I.

During these long inhibition periods the stinging of monomer which would lead to some polymerization taking place in the monomer droplets was highly likely.

5.4.2 RETARDATION

After the long period of inhibition observed in the *ab initio* RAFT emulsion polymerizations is over and the polymerization had begun, the radical flux was lower

than in the control experiment where no significant inhibition was seen. This decrease in the radical flux would lead to reduced reaction rates.

Transportation of the RAFT agents into the particles during the polymerization would result in continuous exit from the particles, and thereby reduce the reaction rate.

The *ab initio* experiments with RAFT agent did not appear to have an Interval II steady state reaction, but rather seemed to go directly from Interval I (with increasing reaction rate) to Interval II (with decreasing reaction rate). It is postulated that the mechanism of rate retardation is similar to the effect of inhibitors and retarders in *ab initio* experiments

Inhibitors and retarders (even in very small quantities) have been shown to have a dramatic effect on nucleation kinetics and hence on the particle number and the particle size distribution^[1], and concomitantly on the duration of Interval I and on the overall polymerization rate. This large change can be explained by the nucleation mechanism. First one notes that that concentration of particles is very small in an emulsion polymerization ($= 10^{-7} \text{ mol dm}^{-3}$). As an inhibitor/retarder would be present in the micelles, and as micelles are dynamic quantities, it is expected that the inhibitor/retarder would move from micelle to micelle. Hence when a young, surface active radical enters a micelle hoping to eventually become a 'mature' particle, it is likely to encounter an inhibitor molecule (if present) and terminate. If the number of inhibitor molecules is comparable to the number of micelles then the rate at which precursor particles become sufficient in number and size to capture all new radicals is reduced. If the interfering species is a retarder rather than an inhibitor, then the rate of growing to a mature latex particle will be truly slowed down rather than proceeding by punctuated growth.

5.4.3 Mn VALUES

The Mn values increased in a linear fashion with increasing conversions but the experimental Mn values were much higher than the predicted Mn values (from Equation 4.11). This was due to a lower RAFT concentration being present in the

particles, than what was expected from the amount of RAFT agent added to the system.

The long inhibition periods characteristic of these RAFT *ab initio* experiments would result in the stinging of the monomer droplets and subsequent polymerization in the monomer droplets. This would lead to the formation of highly water insoluble oligomers/polymers that could not be transported through the aqueous phase into the latex particles. When polymerization occurs in the monomer droplets, transfer to RAFT agent will occur and result in the RAFT agents being incorporated into the highly water insoluble oligomers/polymers. These compounds containing the dithioester moiety are then unable to be transported through the aqueous phase to the loci of polymerization, to control the polymerization. As the monomer is depleted in the droplets, the oligomers/polymers will solubilize by association with the weakly soluble RAFT agent, so compounding the inefficient transport to the particles and the occurrence of a red separating phase.

The RAFT concentration in the particles is therefore lower than expected, and the experimental values obtained for M_n are therefore higher than expected.

5.4.4 M_w/M_n

High values of M_w/M_n were obtained in all the RAFT *ab initio* experiments. This broad polydispersity indicated that together with dead chains formed from bimolecular radical-radical termination, a broad distribution of chain lengths with dithioester end-groups were present. The latter is supported by the appearance of a relatively constant polydispersity with conversion.

The different rates of growth of small particles (below 30 nm radius), in comparison to larger particles (ones above 30 nm radius) could also result in the broad polydispersity values. The concentration of monomer inside small particles is size dependant and hence the volume growth rate is also size dependant.

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CHAPTER 6

DISCUSSION AND FUTURE DIRECTIONS

6.1 OVERVIEW

Emulsion polymerizations containing RAFT as chain transfer agents were carried out using two different experimental systems: Seeded and *ab initio*. These experiments were performed to determine the feasibility of the RAFT process as a method of exercising control in emulsion experiments, and to gain insight into the mechanisms and kinetics of the emulsion process in the presence of the dithioesters.

The seeded experiments were carried out to gain information on entry and exit processes taking place in the presence of RAFT agent. The *ab initio* experiments were performed to determine the effects of the RAFT agent on the nucleation process. Different RAFT agents were used to determine the effect of variation of the RAFT structure on the emulsion reaction.

In the seeded experiments the seed particles were swollen overnight with styrene and the RAFT agent to facilitate transport of the water insoluble RAFT agent into the latex particles. The seeded experiments were designed so that polymerization would commence in Interval II and move immediately into Interval III (below 10% conversion) so that the majority of the polymerization would take place in the absence of monomer droplets. This is in contrast to the *ab initio* experiments where most of the polymerization occurs in the presence of monomer droplets, and no latex particles are present for swelling at the beginning of the polymerization.

Emulsion polymerization is a complex process, which is further complicated by the addition of RAFT agent to the system. The presence of these dithioester compounds has a number of effects on the seeded and *ab initio* emulsion polymerizations, which have already been discussed in Chapter 4 and 5. A

comparison of the results obtained in the seeded and *ab initio* experiments will now be discussed and reasons for the results will be suggested.

6.2 INHIBITION PERIODS

A significant increase in inhibition times was observed on addition of RAFT agent to the emulsion systems and increasing inhibition times were observed with increasing RAFT concentration. The inhibition periods were much longer for the *ab initio* experiments than for the seeded experiments.

The phenomenon of inhibition can be explained by radical exit (from the particles or micelles) due to the transfer and fragmentation of the RAFT agents, with the exited radical then acting as a primary radical terminator. The exit results in negligible aqueous phase termination and re-entry of the radical into another particle and minimal re-escape from this particle (Limit 2a). This exit and termination would lead to severe rate retardation (seen as an inhibition period) as well as the retardation of particle nucleation in Interval I. Exit in the seeded reactions was more prominent where the EMA RAFT agent was used (and can be likened to exit in an MMA polymerization) than with the Cumyl or the PBMA RAFT agents. No inhibition period was noted for the seeded emulsion polymerizations containing the PBMA RAFT, but long inhibition times were observed in the *ab initio* reactions containing the PBMA RAFT.

During these long inhibition periods the stinging of monomer droplets and the subsequent polymerization in the monomer droplets was highly likely, resulting in oligomers and/or polymers in the monomer droplets.

6.3 RETARDATION

The probable reason for the decrease in reaction rate on addition of RAFT agent to both the seeded and *ab initio* emulsion systems is that transportation of small amounts of RAFT agent into the particles over time will result in continuous exit (due

to transfer and fragmentation of the RAFT agent), which in turn lowers the average number of free radicals per particle and therefore the rate of polymerization. Only a small amount of RAFT agent is required to lower \bar{n} drastically.

Increasing retardation in the presence of increasing amounts of RAFT agent has also been observed in bulk and solution polymerizations. The retardation therefore cannot be due to events occurring in the aqueous phase.

6.4 NUMBER AVERAGE MOLECULAR WEIGHT

It was seen in both the seeded and *ab initio* experiments that M_n increased with increasing conversion, but that the value obtained experimentally for M_n was much higher than the value predicted by Equation 4.11. This discrepancy between the predicted and the experimental value is due to an initially lower RAFT concentration being present and active in the polymerization locus than what is expected from the amount of RAFT that is added to the system.

The increase of M_n with conversion in the seeded systems indicates that the systems are 'living' systems, but due to the slow diffusion of the RAFT into the particles in Interval II, a broad distribution of chains with dithioester end-groups is obtained. This broad distribution of chains will grow in a 'living' manner in Interval III, and consequentially the resultant polydispersity will be broad.

Stinging of the monomer droplets is highly likely during the inhibition periods in both the seeded and *ab initio* experiments. This would lead to polymerization in the monomer droplets and the formation of oligomers/polymers with dithioester end-groups, resulting in the insoluble material found at the end of the reaction.

The observation of a red phase separation in both the seeded and *ab initio* experiments at approximately 10% conversion and coagulation of this intensely coloured phase between 80 and 90% conversion, is in agreement with the experimental result that all the RAFT agent is not present in the latex particles.

6.5 POLYDISPERSITY

The values of M_w/M_n obtained for both the seeded and *ab initio* emulsions were high, mostly in the region of 2 to 5. These are high polydispersity values and seem to indicate a lack of control that is found for bulk or solution experiments.

The perceived lack of control can be due to a number of factors. Firstly the concentration of RAFT agent initially in the particles was very low and diffusion of RAFT into the particles results in chains of varying length, which in principle all have the same capacity to grow via the RAFT mechanism.

Secondly bimolecular termination appeared to be occurring in both the seeded and *ab initio* experiments, resulting in high molecular weights and broad polydispersities.

6.6 GPC TRACES

The differential log MWD for the *ab initio* experiments showed an increase in the maximum of $x(M)$ with increasing conversion (up to about 60% conversion) after which the maximum of the differential log MWD remained unchanged. The differential log MWD for the seeded experiments showed no (or very slight) increase in the maximum at low conversions.

From the GPC traces it could be seen that some form of 'living' character was initially observed for the *ab initio* experiments when the W_p (weight fraction of polymer) was low, but as conversion, and therefore W_p increases the control is lost. No control was observed in the seeded experiments. This could be ascribed to the transfer process being under diffusion control^[1], where it was envisaged that the polymeric radical and the dormant polymeric (thiocarbonyl)sulfanyl compound would diffuse towards each other quite slowly, depending on both the W_p of the system and the chain lengths of the two reactants. This process is analogous to long-long bimolecular free radical termination^[2].

6.7 FUTURE DIRECTIONS AND RECOMMENDATIONS

The emulsion system containing RAFT agents is complex and a lot has yet to be learned about the RAFT process in emulsion polymerizations. The effect of the RAFT agent on the reaction mechanisms and kinetics is intricate and although a lot of insight into the process has been gained through this work, the mechanisms and kinetics are not yet fully understood. Optimization of the RAFT process in emulsions has a long way to go, but this will require intimate understanding of the innate mechanisms.

The problem of inhibition in the emulsion system needs to be dealt with. As the inhibition appears to be due to exit, changes in the structure of the RAFT agent could perhaps eliminate or minimize this inhibition period. With minimization of exit and elimination of the inhibition period, the reaction rate should not be as negatively affected as the radical flux would not have decreased over time due to the decreasing initiator concentration and retardation due to exit would be minimized.

If the inhibition period can be eliminated, and all the RAFT agent is initially inside the particles then it follows that control should be more effective i.e. the M_n should increase in a linear fashion with conversion as predicted by the ratio of monomer to RAFT agent and less polydisperse polymer chains should be obtained.

As transportation of the RAFT agents is proving to be an important factor in the emulsion polymerizations, a seed could perhaps be prepared under starved feed conditions where the RAFT agent is added to the system in a small amount of monomer and once this has reacted more monomer could be added in the form of a feed or in batch. Rizzardo *et al.*^[3] has used this method (with a starved feed) to overcome the phase separation of the red layer (RAFT agent) observed when monomer droplets are present. It is important to note that if a more water soluble RAFT agent is used, that the problem of transfer of the RAFT agent into the particles may be alleviated but exit, and thus inhibition and retardation would be exacerbated.

More insight into the RAFT process in emulsions through further experiments, with a variety of RAFT agents, under a variety of different conditions, would be instrumental

in the eventual process of the optimization of RAFT as a means of controlled radical polymerization in emulsions.

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ADDENDUM

In Figures A1 through to A3 the NMR spectra of synthesized RAFT compounds – refer to Chapter 3, sections 3.1.1, 3.1.2 and 3.1.3 – are given. This is followed by the poster entitled 'Emulsion Polymerization in the Presence of RAFT' that was presented at the Controlled Radical Polymerization Conference held in San Francisco in September 1999.

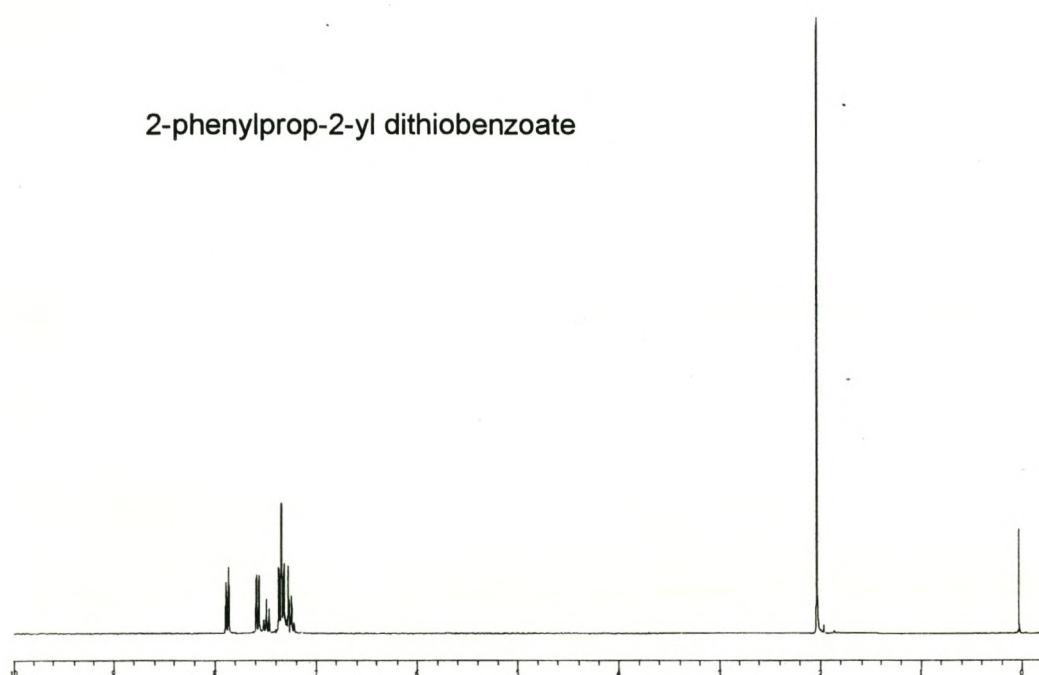


Figure A1 NMR spectra of 2-phenylprop-2-yl dithiobenzoate

2-(ethoxycarbonyl)prop-2-yl dithiobenzoate

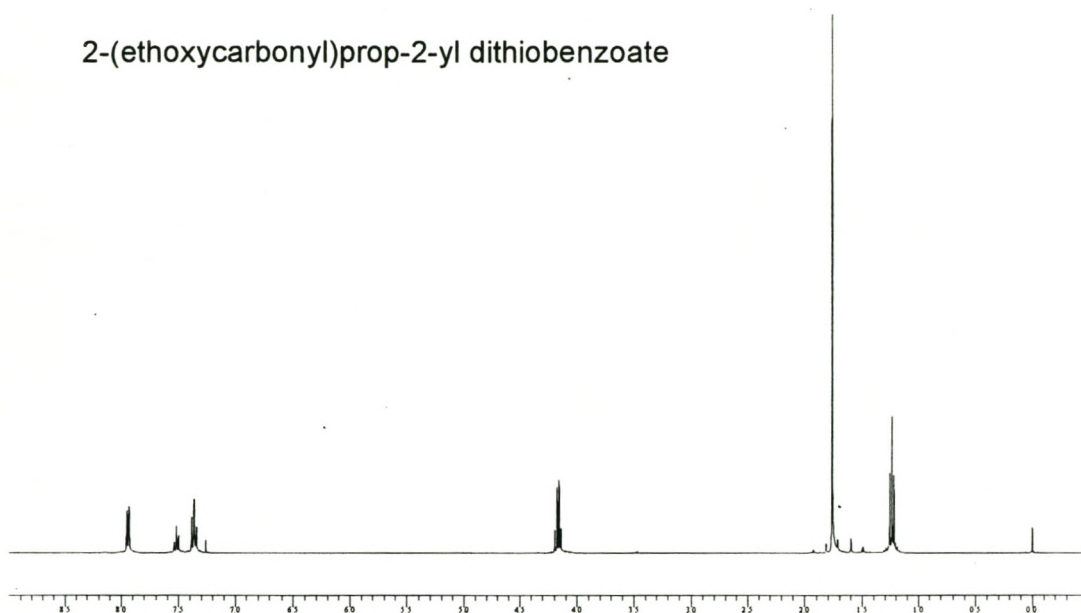


Figure A2 NMR spectra of 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate

ixed oligomeric PBMA RAFT species

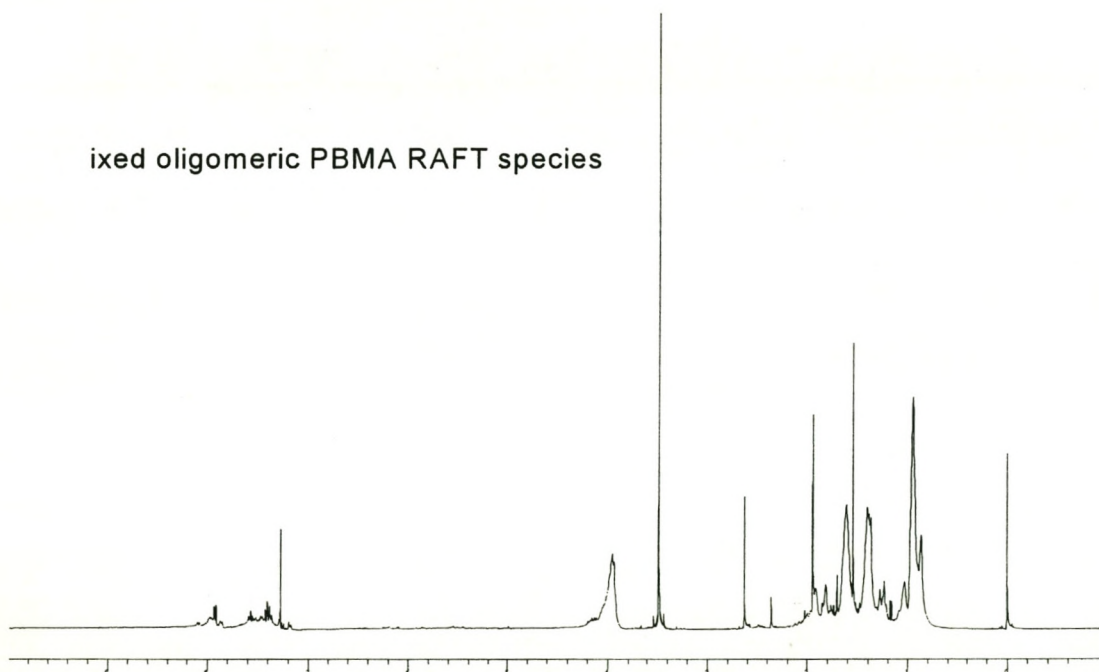


Figure A3 NMR spectra showing a crude mixture of PBMA oligomers with RAFT groups connected to them

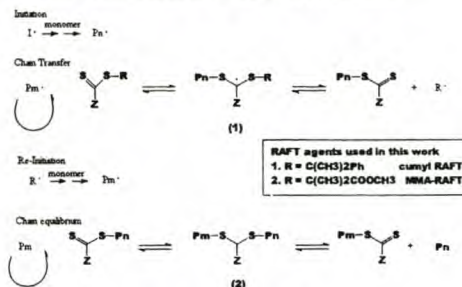
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Introduction

"Living" free-radical polymerizations allows one to produce polymers with narrow molecular weight distributions (MWDs). The main techniques^[1] explored are nitroxide-mediated living polymerization, atom transfer radical polymerization (ATRP), and more recently reversible addition-fragmentation chain transfer (RAFT). The nitroxide-mediated and ATRP processes rely on the persistent radical effect^[2], in which control is dictated by the ratio of persistent (nitroxide or metal) over active species (polymeric radicals). If this ratio decreases during the polymerization then bimolecular termination will be favoured and dead polymer is formed. In emulsion polymerizations the persistent species may exit the particles, depending upon both their partition and diffusion coefficients in the oil and water phases, and terminate with small radicals in the aqueous phase. Although one could envisage the use of highly insoluble compounds, nitroxide mediated and ATRP have other problems for use in emulsion. Nitroxide-mediated polymerizations require high temperatures (~123 °C), well above those used in conventional emulsion (60-80 °C). Colloidal stability at these temperatures becomes a major problem, and invariably leads to coagulation. The issue of ATRP is more from an environmental point of view, in which the elimination of heavy metals is becoming a critical aspect for industry.

The RAFT process can be used for a wide range of monomers and conditions^[3-6]. The persistent moiety is always attached to the chain-end of the polymer (see scheme 1) and thus will not exit during polymerization, and in principle the rate of polymerization should be comparable to that without RAFT agent. However, low initiator concentrations compared to RAFT are required to obtain narrow MWDs in bulk or solution. Experiments published so far were carried out in either solvent or in the case of bulk at high temperatures (styrene thermal initiation). The only emulsion polymerization was carried out with BMA at 80 °C, in which the BMA was fed in over a period of an hour. It is assumed that the authors chose these conditions to avoid the complexities arising from the gel effect.

The purpose of this work is to determine the optimal conditions for control of the RAFT process in emulsion polymerizations of styrene. Seeded experiments were first carried out at 60 °C in order to gain information of the effects of entry and exit due to the transfer and fragmentation processes of the two RAFT agents used in this work (see Scheme 1). *Ab initio* experiments were then carried out with varying RAFT concentrations.



Scheme 1: RAFT mechanism

Seeded Experiments

The seed was made of PMMA with an average diameter of 20 nm and number concentration of approximately 10¹³. The particle size and number were respectively chosen to keep the system under zero-one conditions^[5] and to avoid secondary particle nucleation^[6]. The saturation concentration of styrene in the seed was 5.5 mol dm⁻³, which increased to 5.97 mol dm⁻³ when MMA-RAFT was introduced and remained relatively constant with the cumyl RAFT (5.54 mol dm⁻³). The water solubility of MMA-RAFT is 10⁻⁴ and cumyl RAFT less than 10⁻⁴ (below the detection limit of the UV-Vis spectrometer). The effect of RAFT concentration on the inhibition time is shown in Fig 1. An increase in the RAFT concentration also increased the inhibition time, which for the highest RAFT concentration lasted for 12 hours.

The conversion-time data was obtained at both high and low concentrations for the two RAFT agents (see Fig 2). For these experiments the initiator concentration was increased by an order of magnitude, and the inhibition times were between 30 and 40 mins. The results show that the RAFT agents have a significant effect on the rate of polymerization (compared to the control). At high MMA-RAFT concentrations conversion reaches a maximum of 0.2 compared to almost 0.9 for low concentration after 2.5 hrs. For the cumyl case, there seems to be little effect of concentration on the rate. The reason for this difference between the two RAFT agents is postulated to be due to a number of factors:

- the concentrations of the RAFT agents inside the particles will be different and thus transportation will be an important parameter. It was found that polymerization started when a thin layer of red viscous liquid (found by NMR to be styrene oligomers with RAFT end-groups) was observed on the top of the emulsion.
 - The greater stability of the intermediate (2) for styrene with the cumyl RAFT compared to the MMA-RAFT^[7].
 - Termination of aqueous phase radicals by exit
 - Termination of particles that already contain a growing chain by re-entry.
- Both (c) and (d) will be greater for the MMA-RAFT, which is analogous to exit in an MMA emulsion polymerization^[8], where R· acts as a primary radical terminator. It can be seen that the rate is determined by a complex interplay between free-radical and colloidal chemistry.

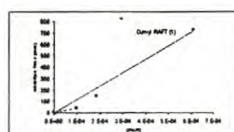


Figure 1: The effect of RAFT agents on the inhibition times at 60 °C and using a KPS concentration of 1x10⁻² mol dm⁻³.

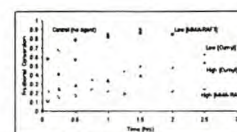


Figure 2: The effect of RAFT concentration on the conversion of seeded emulsion polymerizations of styrene at 60 °C. [KPS] = 10⁻² mol dm⁻³.

A typical GPC profile for these polymerizations is shown in Fig 3. Typical of all these experiments, there seems to be no control of the MWDs, in which the polydispersities increase with conversion from 2 to 2.7. It must be noted that the polydispersities are very dependent upon base line correction, and using different base line corrections, polydispersities as low as 1.5 were obtained.

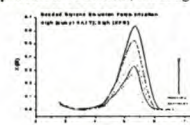


Figure 3: GPC chromatograms of a seeded emulsion polymerization of styrene at 60 °C initiated with KPS in the presence of the cumyl RAFT. [KPS] = 10⁻² mol dm⁻³; [cumyl RAFT] = 5x10⁻² mol dm⁻³.

Ab initio Experiments

The inhibition times (see Fig 4), similar to the seeded experiments, increased with RAFT concentration. However, the RAFT and initiator concentrations are approximately 10 times greater than that shown in Fig 1. This suggests that the mechanism of inhibition is most likely to be the same for the two systems, where exit of R· is highly likely and acts as a primary radical terminator, retarding particle nucleation in interval.

The conversion-time data was obtained using various concentrations of MMA-RAFT (Fig 5). The rate of polymerization is retarded with the increased concentration of MMA-RAFT agent. This could be due to the high exit rate, retarding nucleation, and thereby reducing the particle number concentration, Nc (where the rate of polymerization is proportional to Nc). This can occur by termination of the exited radicals, R·, either with radicals already present in the aqueous phase or re-entry into particles already containing a growing radical.

The GPC profiles with conversion are given in Fig 6 for all the RAFT concentrations. At high RAFT concentrations only one chromatogram was obtained due to the very slow rate of polymerization. More experiments under these conditions will be carried out to see if control is obtained. At the lowest concentration the RAFT agent acts as a normal chain transfer agent, reducing the Mn compared to polymerization without RAFT. It can be seen that between these two concentrations there is clear growth of the MWD with conversion. However, the polydispersities also increase with conversion, indicating that control is lost at medium to high weight fractions of polymer (wp).

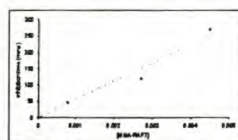


Figure 4: The effect of MMA-RAFT on the inhibition times at 60 °C and using a KPS concentration of 2.2x10⁻² mol dm⁻³.

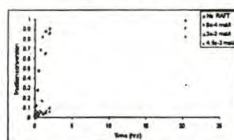


Figure 5: The effects of RAFT concentration on the conversion of *ab initio* emulsion polymerizations of styrene at 60 °C. [KPS] = 2.2x10⁻² mol dm⁻³.

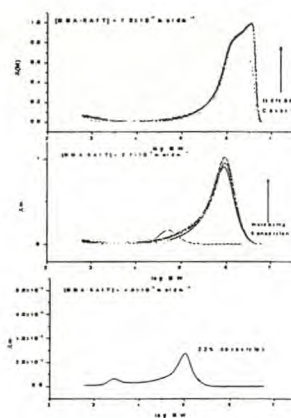


Figure 6: GPC chromatograms of *ab initio* emulsion polymerization of styrene at 60 °C initiated with KPS in the presence of the cumyl RAFT. [KPS] = 2.2x10⁻² mol dm⁻³.

Conclusion

The results show that little or no control of MWD is found for seeded emulsion polymerizations, where, as some control is found for *ab initio* polymerizations. A hypothesis derived from this work is that the RAFT process is sensitive to the weight fraction of polymer (wp) in the system. Control is observed initially for the *ab initio* experiments when the wp is low, but as conversion and, therefore, wp is increased control is lost. This is also found for seeded experiments, where the wp starts at approximately 0.4. The reason for the loss of control at high wp can be put down to the transfer process being under diffusion control^[9]. Where it is envisaged that the polymeric radical and the dormant polymeric (thiocarbonyl)sulfanyl compound will diffuse towards each other quite slowly, depending on both the wp of the system and the chain lengths of the two reactants. This process is analogous to long-long bimolecular free-radical termination^[10].

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