5. Living Radical Polymerization in Emulsion using RAFT.

Synopsis: This chapter describes the application of Reversible Addition–Fragmentation Transfer (RAFT) in emulsion polymerization. A brief introduction to emulsion polymerization is given, followed by the application of living radical techniques in this heterogeneous medium, which is discussed on a theoretical level with references to the literature. Seeded emulsion polymerizations of styrene in the presence of two RAFT agents are then investigated. It is found that the polymerizations are significantly retarded by the presence of RAFT agent and it is proposed that exit from the particles after fragmentation was the main cause of retardation. The development of the molar mass distribution and the polydispersity deviate from the ideal ‘living’ behavior, found in homogeneous systems. Slow, continuous transportation of RAFT agent into the particles is postulated as a possible cause for this phenomenon. Besides, colloidal stability was found to be poor and irreproducible. The use of nonionic surfactants was found to improve the stability. Ab initio emulsion polymerizations are conducted as well, with the aim of exploring the effect of RAFT on the nucleation process. The reaction kinetics were distinctly different from those in conventional emulsion polymerization, indicated by the absence of an Interval II with constant polymerization rate.

5.1. Emulsion Polymerization

5.1.1. Introduction

A new challenge confronting living radical polymerization is its application in dispersed (i.e. heterogeneous) media. Water-borne polymerizations are an industrially preferred way to conduct radical polymerizations as they eliminate the need for organic solvents,\(^2\) provide a good medium to remove the heat of reaction and guarantee a product (i.e. latex) that has a relatively low viscosity and is easy to
handle. Emulsion systems are relatively cheap and robust, with low sensitivity to impurities. The polymerization results in a relatively low viscosity latex that has a high solids content. Because of these advantages, emulsion polymerization has developed into an economically important process, responsible for effecting 40–50% of free-radical polymerizations. These, in turn, constitute approximately 30% of the total worldwide production of polymers. 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. 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. If living radical polymerizations could be conducted in such systems, the range of possible industrial applications and products will be greatly enhanced through intelligent design of the polymer architecture.

The advances and developments made in the field of emulsion polymerization concerning kinetics and thermodynamics to derive the mechanism, have been documented by Gilbert. The fundamental mechanisms of the polymerization process dictate what the properties of the polymer and latex will be, given particular operating conditions (e.g. 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.

5.1.2. A Qualitative Description

Without completely repeating here the classical descriptions of the emulsion polymerization mechanism that are available in numerous text books, the key features that will be important in the discussion of living radical emulsion polymerization will be briefly reviewed. Traditionally, emulsion polymerizations are considered to be a three-stage process, as shown in Scheme 5.1.

The reaction starts in *Interval I* from a mixture of water, monomer(s), surfactant and initiator. The water soluble initiator is dissolved in the continues water phase. The monomer is emulsified by agitation. A small quantity of monomer dissolves in the water phase, while most of it is present in the form of droplets (d>1µm), stabilized by surfactant. The remainder of the surfactant is dissolved in the aqueous phase at a concentration above the critical micelle concentration (CMC) such that a large number of micellar aggregates (d≈5nm) is present. Hydro-
philic radicals, generated by dissociation of the initiator, are formed in the water phase. These radicals react with monomer dissolved in the water phase, so oligomers are formed. Provided that no termination takes place, monomer units are added until a critical chain length, $z$, is reached where the oligomer becomes surface active. At this point, the oligomeric radical will enter a micelle, swollen with monomer. Droplet entry can be neglected as the total surface area of the droplets phase is several orders of magnitude smaller than that of the micelles. The radical will continue to grow, thereby consuming monomer which is replenished by diffusion from the droplets, through the water, into the growing particle.

For small particles (<100nm, depending on the monomer used), the zero–one assumption is used, meaning that any polymer particle contains either none or just a single growing radical. If a radical enters a particle that already contains another growing radical, instantanious termination will take place due to the extremely high, local concentration of radicals. This again reduces the number of radicals to zero, resulting in an on–off mechanism for any given polymer particle. Throughout Interval I, new particles are generated from micelles, increasing the number of polymerization loci and the polymerization rate. The polymer particles continue to grow and absorb an increasing amount of surfactant on their interface. This causes part of the micelles to dissolve. As this process proceeds, a point will be reached where all micelles have disappeared. Formation of new particles ceases. This point corresponds to the onset of Interval II and typically corresponds with a monomer conversion of 5–15%, depending on the actual recipe.
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Interval II is characterized by a constant number of particles and the presence of monomer droplets. The concentration of monomer at the locus of polymerization, i.e. inside the particles, remains roughly constant as the monomer droplets are able to supply the particles with monomer at the same rate at which it is consumed. The constant number of particles together with the relatively constant monomer concentration inside them cause the polymerization rate to be constant as well.

Interval III starts when the monomer droplets have disappeared completely. This point corresponds to a monomer conversion of 50 to 80%, depending on the recipe. The remaining monomer resides in the particles and polymerization continues, but at an ever decreasing rate as the monomer concentration gradually decreases.

Scheme 5.2 illustrates the kinetic events occurring in an emulsion polymerization and shows how these events are associated with chain growth. Entry and exit, processes of phase transfer, strongly depend on the partitioning of the radicals. For a specific monomer, this is governed largely by their water solubility. A radical, generated in the water phase, will either propagate or terminate. If the radical reaches its critical chain length, $z$, it will become surface active and enter a particle. Droplet entry is unimportant due to the comparatively small surface area of this phase compared with that of the micelles (Interval I) and particles (Interval II). This critical chain length, $z$, depends on the type of monomer and the oligomer end-group, but is in the order of 2–5 for common monomers like styrene and methyl methacrylate in polymerizations using a persulfate initiator. Once such a $z$-mer

\[ \text{Scheme 5.2. Several kinetic events occurring during emulsion polymerization. Initiator derived radicals (R$^\bullet$) propagate in the water phase to form short oligomeric radicals ($P_n^\bullet$) that can undergo termination or enter a particle. Upon entry, the radical will either terminate an already existing radical or propagate until termination or transfer occurs. Short transfer derived radicals can propagate or exit the particle leading to a large variety of possible fates, among which propagation, re-entry and termination are the most prominent.} \]
radical has entered a particle it is assumed not to desorb anymore, but rather to react inside the entered particle. If another radical was already present within this particle, it will be terminated (assuming again zero–one kinetics). Otherwise, the incoming radical will continue growing until it is terminated by a second incoming radical or until transfer takes place to either the monomer or a transfer agent. The short radical that is formed can reinitiate polymerization or exit into the water phase where it can terminate, propagate or re-enter a particle. Its fate depends on its partitioning and the concentration of monomer and radicals in the water phase. In general, exit events reduce the polymerization rate. The large number of variables, conditions, concentrations and types of ingredients indicate that emulsion polymerization is a remarkably complex system based on a mechanism of interrelated kinetic and thermodynamic events.

5.1.3. Living Radical Polymerization in Emulsion

The desire to conduct living radical polymerizations in emulsion is not only based on the preferential use of existing processes and technology but there are advantages intrinsic to the heterogeneous system as well. From the outlook of living radical polymerization, an advantageous effect is to be expected from the reaction in a compartmentalized system. The quality of all living radical processes is influenced by the amount of bimolecular radical termination. In atom transfer radical polymerization (ATRP) and nitroxide mediated polymerization (NMP), equilibria are designed to yield a low radical concentration and in systems based on reversible transfer, initiator is used in a small amount to retain the living character of the polymerization. For this reason, application in bulk and solution is limited by the low rates of polymerization (see the remarks made at the end of section 2.1.2 on page 34).

Emulsion polymerization provides an ideal alternative to overcome this problem. High rates with little termination are found in emulsions due to the compartmentalization of the radicals in individual particles, in which radicals in one particle have no access or contact with radicals in another. High rates are achieved by controlling the number of particles by choice of surfactant and initiator concentrations. In conventional emulsion polymerization, very high molar masses are found, showing that bimolecular termination is not prevalent and thus the main chain stopping events are primarily through transfer to monomer.
One of the key factors for a successful living radical emulsion polymerization is to get the deactivator at the locus of polymerization and to keep it there. Another qualifying factor is the undisturbed occurrence of Interval I, when particles are generated. During this stage, a relatively high radical production rate is desired in order to create a large number of particles, as growth of existing particles competes with the generation of new ones for the surfactant. This clearly conflicts with the desire for a low concentration of active species or radicals that prevails amongst the living polymerization techniques. Furthermore, chain growth in the water phase should not be hindered extensively, as this will prevent the growing radicals reaching their critical chain length required for entry. Despite their similarities in approach, some crucial differences exist between the application of living polymerizations based on reversible termination (section 2.1.1) and those based on reversible transfer (section 2.1.2).

**Reversible Termination**

The typical approach that is taken in the living radical schemes that rely on reversible termination (NMP and ATRP), is to start with a certain amount of low molar mass, dormant species from which radicals are generated (one starts on the left hand side of the equilibria in Schemes 2.4 and 2.5). In this case, the generation of active radicals and persistent radicals is balanced. The activation–deactivation equilibrium is however designed to yield a low concentration of radicals and therefore results in a slow nucleation process during Interval I, which is known to lead to a very broad particle size distribution in the final dispersion. The initiator should generate radicals in the water phase in order to prevent droplet nucleation, which would cause the system to behave like a miniemulsion polymerization (see Scheme 6.1, page 140). The partitioning of the deactivator should find a suitable balance between the water and organic phases such that water phase radicals have a chance to grow and enter while still allowing rapid transportation of the deactivator from the droplets to the polymerization loci in order to prevent uncontrolled polymerization. Alternatively, one can start on the right hand side of these equilibria using a conventional initiator combined with nitroxide (Scheme 2.4, page 23) or the metal complex in its higher oxidation state (Scheme 2.5, page 24). This reverse approach has the advantage that the conventional initiator can provide the desired nucleation, but requires a carefully balanced quantity with respect to the deactivating species. Water phase propagation should not be hindered by reversible deactivation as in this case, entry will be postponed as the chains will not be able to reach their critical chain length for entry.
Notwithstanding these theoretical issues, conventional\textsuperscript{8,9} and reverse\textsuperscript{10,11} ATRP have been used to obtain polymer dispersions once practical problems, like the hydrolysis of initiator,\textsuperscript{13} were overcome. The drastic change in kinetics interferes with the conventional nucleation mechanism causing a relatively broad particle size distribution with sometimes visually observable particles. The colloidal stability is difficult to reproduce, resulting in the appearance of a distinct organic phase\textsuperscript{8} during the reaction, massive coagulation or sedimentation of polymer.\textsuperscript{13} When all reaction components are designed to be located at the locus of polymerization, polymer of predetermined molar mass is obtained and polydisperisities are fairly low. An unlucky choice of ligand or initiator will cause the polymerization to be inhibited or to proceed uncontrolled.\textsuperscript{12,13}

Nitroxide mediated emulsion polymerizations have been restricted to styrene and confined to high temperatures (above the normal boiling point of water, under high pressure) calling for special equipment and causing coagulation during the reaction in both \textit{ab initio}\textsuperscript{14} and seeded\textsuperscript{15} reactions. The polymerizations are extremely slow and polydisperisities (1.4–2.0) cannot match the low values obtained in homogeneous systems.

**Reversible Transfer**

Living radical polymerizations based on reversible transfer are potentially more convenient because they, in principle, do not change the reaction rate. Additionally, once the initial transfer agent has been consumed, the transfer activity resides completely in polymeric species. The transfer event that occurs between active and dormant polymers (b, Scheme 2.8, page 27) will not give rise to small radicals that are subject to exit events. When this situation is attained, polymerization rate and phase transfer events in the polymerization will not be different from a conventional emulsion polymerization without transfer agent. Up to this point, the reaction will largely resemble an emulsion polymerization with a conventional transfer agent. Such systems are thoroughly investigated as in the majority of industrial emulsion polymerization recipes, chain transfer agents are used to limit the molar mass of the product. Three aspects are of importance when considering the use of large quantities of RAFT agent.
First, the concentration of transfer agent in the water phase should be relatively low. Deactivation of chains that propagate in this medium is undesired as it will give rise to large amounts of water soluble oligomers and, depending on the partitioning of the radical that is formed, preventing entry and thereby lowering the polymerization rate or hampering nucleation.

A second consideration concerns transport phenomena. An important prerequisite for living emulsion polymerization is that all chains grow for an equal period of time. This requires a rapid reaction of the transfer agent or dormant species at the locus of polymerization in the early stages of the reaction. This may prove to be a problem in RAFT polymerizations as transportation of highly reactive transfer agents with a poor water solubility is under diffusion limitation. This has, for instance, been documented for the seeded emulsion polymerization of styrene in the presence of \( n \)-dodecyl mercaptane,\textsuperscript{16,17} as well as in \textit{ab initio} reactions.\textsuperscript{18} The transfer constant of the mercaptane is approximately 15 for similar reactions in homogeneous media.\textsuperscript{19} When the seeded system contains a large number of small particles, the transfer agent is consumed at roughly 50\% monomer conversion. This is virtually identical to a similar experiment conducted in bulk.\textsuperscript{20} When the seed material consisted of a much smaller number of larger particles, the transfer agent was found to last longer, up to 80\% conversion.\textsuperscript{16} This is attributed to the change in surface area of the droplet and particle phases and not as much to the different kinetics of the two systems (zero–one vs. pseudo-bulk). The phase transfer events apparently form the rate determining step in the diffusion process. The most important transport barrier was found to be the phase transfer from the monomer droplets into the water phase.\textsuperscript{16} The RAFT agents used in this work have even higher transfer constants.\textsuperscript{21,22} In a homogeneous medium, they are typically consumed within the first 10\% of conversion and thereby lay a serious demand on their transportation rate. Therefore, a well-dispersed system with a large droplet–water interface is essential.

A third important aspect of the RAFT process in emulsion that needs to be considered is the effect of exit of the transfer species \( R \) (Scheme 5.3) on the rate and control of molar mass. Whang \textit{et al.}\textsuperscript{23} found that the addition of the transfer agent, \( \text{CBr}_4 \), in seeded emulsion polymerization significantly retarded the rate of polymerization. In a more complete study of the kinetics\textsuperscript{24} (using gamma relaxation) of transfer for \( \text{CBr}_4 \) and \( \text{CCl}_4 \) they found that exit of the incipient transferred radical from the particles was the main source of retardation. The fate of these radicals depend on the radical concentration in the aqueous phase (Scheme
Cross-termination of the exited radical occurred primarily with radicals in the aqueous phase when the radical concentration was high and radicals in the particles via re-entry when the radical concentration in the aqueous phase was low. The results also supported, that exit is diffusion controlled during Interval II. The size of the particles, the diffusion coefficient and the partition coefficient of the exited free radical in the water phase determine the value of the exit rate coefficient.

The heterogeneity of emulsion polymerizations and the kinetic effects of transfer agents result in a mechanism of a complex network of fundamental reaction steps. The work described so far in the literature with reversible transfer is largely focused at low reactivity reagents. Xanthates were used to prepare homopolymers, block copolymer structures and also to increase the number of particles. When the monomer was fed slowly to the system and instantaneous conversions were high, a linear increase of the molar mass with conversion was observed. In batch reactions, the xanthate system is similar to a reaction with a conventional transfer agent. Experiments with seeded systems demonstrated that these agents strongly increase the exit rate and that, for an unclarified reason, the entry efficiency is reduced. The combination of effects results in a much lower polymerization rate.

Scheme 5.3. RAFT agents applied in emulsion polymerizations. 2-phenylprop-2-yl dithiobenzoate or Cumyl-RAFT where \( R = 1 \), 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate or EMA-RAFT, in which \( R = 2 \) and 2-cyanoprop-2-yl dithiobenzoate or Cyano-RAFT with \( R = 3 \), are all known to allow the living radical polymerization of styrene in homogeneous systems. For the application in heterogeneous systems, their partitioning and that of the expelled radicals, \( R \), over the different phases is of importance as well. Radical 1 is the cumyl radical \( \cdot \text{C(CH}_3\text{)}_2\text{C}_6\text{H}_5 \) and 2 the ethyl methacrylate radical \( \cdot \text{C(CH}_3\text{)}_2\text{COOC}_2\text{H}_5 \). Refer to Scheme 2.8 on page 27 for the details of the addition–fragmentation equilibrium. RAFT agents in which \( R = 3 \) and 4 are used in ab initio polymerizations.
Reports on emulsion polymerizations with highly reactive RAFT agents are scarce. Butyl methacrylate has been polymerized in semi-batch emulsion polymerizations, using rather unusual feed conditions.\textsuperscript{33} This is presumably to have all the RAFT agent reacted inside the particles at the beginning of the reaction. Beside homopolymers, block copolymers have been made consisting of a polystyrene part and a polymethyl or butyl methacrylate part.\textsuperscript{34} Straightforward batch polymerizations have not been reported and, for unknown reasons, RAFT agents of moderate activity performed better than high reactivity reagents.\textsuperscript{21} The emulsion stability was not addressed and particle sizes were not given. Uzulina \textit{et al.}\textsuperscript{35,36} found that living characteristics were observed but with up to 40\% coagulation. They had more success with a hydrophilic transfer agent although only in combination with styrene. The use of methacrylates yielded high polydispersities.

### 5.1.4. Research Target

Obviously, the use of these reagents is not as straightforward as might be expected. It is the aim of this work to gain insights into the mechanisms operating for the RAFT process in the presence of droplets. Seeded systems are extremely useful for this purpose, since they eliminate many variables and can explore the effects of exit and droplets on the rate and control of molar mass in RAFT systems. Two RAFT agents with comparably high $C_{T,RAFT}$ were used in this study (see Scheme 5.3) each having a different leaving group $R$. \textit{Ab initio} experiments were conducted to investigate the effect of RAFT agent on the nucleation process.

| Table 5.1: Probability of escape, $P_{\text{exit}}$, Determined for RAFT agents with Cumyl and EMA Leaving groups. |
|---------------------------------|-----------------|------------------|
|                                 | Cumyl           | EMA              |
| $k_p^{1}$ (dm$^3$·mol$^{-1}$·s$^{-1}$) \textsuperscript{a)} | 1705            | 9390             |
| $k_{\text{doe}}$ (s$^{-1}$) \textsuperscript{b)}          | 3.98·10$^3$     | 6.89·10$^4$     |
| $P_{\text{exit}}$                      | 0.29            | 0.56             |

\textsuperscript{a)} $k_p^{1}$ was determined for 1 by $\langle k_p^{1} \rangle_{STY}$ \textsuperscript{37} by being multiplied by 5 (reasonable for small radical reactions); for 2, $\langle k_p^{1} \rangle_{EMA}$ \textsuperscript{38} was multiplied by 5 and also by 2 to compensate for the reactivity ratio of EMA to STY.\textsuperscript{39}

\textsuperscript{b)} The unswollen radius was 20nm, which gave a swollen radius of 29.5nm.
5.2. Seeded Emulsion Polymerizations

5.2.1. Background Theory

Probability of Exit for R

Exit events can reduce the reaction rate significantly. The more water soluble the leaving group (R) the greater the extent of exit. The leaving radicals from Cumyl-RAFT and EMA-RAFT are the cumyl radical (1) and 2-(ethoxycarbonyl)prop-2-yl radical (2), respectively. The coefficient for desorption of a monomeric free radical (exit) from a particle with swollen radius $r_s$ is given by Eq. 5-1:

$$k_{dM} = \frac{3D_{R_w}}{r_s^2} \frac{[R]_w}{[R]_p} \quad (5-1)$$

The probability of exit can then be determined by using Eq. 5-2:

$$P(exit) = \frac{k_{dM}}{k_{dM} + k_p^1 [R]_p} \quad (5-2)$$

where $D_{R_w}$ is the diffusion coefficient of R in water, $[R]_p$ and $[R]_w$ are the concentrations of R in the aqueous phase and particle, respectively, and $k_p^1$ is the propagation rate coefficient for R to monomer. Using the approximation that $D_{R_w}$ is $1.6 \times 10^{-9}$ m$^2$·s$^{-1}$ for the two radicals and $[R]_w$ is similar to the monomer equivalent, $P(exit)$ was determined (see Table 5.1). It can be seen that 2 has a far greater probability of escape than 1. This suggests that retardation should only be effective when RAFT agent is present in the system. Assuming a high value for $C_{T,RAFT}$ (found experimentally to be approximately 6000 for polymeric RAFT agents derived from the dithiobenzoate moiety), all RAFT agent should be consumed in the first few percent of monomer conversion (see Eq. 5-5). After this transformation, exit should no longer be the dominant retardation mechanism.

Molar masses and Polydispersities in RAFT Systems

The equations used to predict the molar mass and polydispersity (PD) of polymer produced by the RAFT method in bulk or solution are those derived by Müller et al. for living processes involving active and dormant species. The
equations are obtained via the method of moments. For values of $C_{T,RAFT}$ much greater than one, the $\overline{M}_n$ and PD can be closely approximated by the following expressions:

$$\overline{M}_{n,th} = \gamma \cdot x \cdot FW_{mon} \quad (5-3)$$

$$PD = \frac{1}{\gamma \cdot x} + \left[ 2 + \frac{\beta - 1}{\alpha - \beta} (2-x) \right] \frac{-2 \alpha (1-\alpha)}{(\beta^2 - \alpha^2) x^2} \left[ 1 - (1-x)^{1+\beta/\alpha} \right] \quad (5-4)$$

where $\gamma$ is $[M]_0/\{RAFT\}_0$, $FW_{mon}$ is molar mass of monomer, $x$ is the fractional conversion, $\alpha$ is $[P_n]/\{RAFT\}$ and $\beta$ is $C_{T,RAFT}$. The concentration of RAFT as a function of conversion is given by:

$$\{RAFT\}_x = (1 - \alpha) \cdot \{RAFT\}_0 \cdot (1-x)^\beta \quad (5-5)$$

The assumptions made in these expressions are that the steady-state radical concentration ($\{P_n\}$) is very low, the efficiency of the RAFT agent is 100% and bimolecular termination events are negligible. For equations 5-3 to 5-5 to be valid for a seeded emulsion polymerization, the RAFT agent must be transported from the droplets to the particles at the rate of transfer during Interval II.

5.2.2. Experimental Design

Design of the Seed Latex

The design of the seed is crucial for understanding the events that control the molar mass distribution. The size of the seed particles must be as small as possible to explore the effects of exit, since exit is inversely proportional to the particle radius squared (see Eq. 5-1). However, the seed must have a minimum size, otherwise the concentration of monomer will change drastically during particle growth. This, to a good approximation, is determined by the Morton equation and shows that for particles with unswollen radius greater than $\approx 20–30$ nm the monomer concentration inside the particle remains relatively constant during Interval II. Therefore, the unswollen seed radius for these styrene polymerizations was chosen to be approximately 20 nm.

In addition, a hetero-seed, consisting of polymethyl methacrylate (PMMA), was used so that the molar mass distribution (MMD) of polystyrene (PS) could be observed exclusively, by UV detection ($\lambda=254$ nm) since PMMA has no UV
absorption at this wavelength. For the purpose of these experiments, polymer immiscibility was neglected. This assumption seems valid due to the presence of monomer (which acts as a plasticizer), the very small size of the seed, and the low molar mass polymer being produced. Another important design parameter is the number of particles, which must be high in order to avoid secondary nucleation. Therefore, \( N_c \), the number of particles per unit volume of water, chosen for this work was approximately \( 4 \cdot 10^{17} \text{dm}^{-3} \).

### Polymerizations in Seeded Systems

The experimental conditions were chosen so that the changeover from Interval II to III occurred close to 10% conversion. This still gives us information on the influence of droplets, and its effect on the MMD. In addition, the effects of exit and transportation of RAFT on the rate up to the changeover can be studied.

### Deviations from Zero–One Conditions

Zero–one conditions are obeyed when the size of the seed is sufficiently small such that entry of a \( z \)-mer radical (i.e. \( \text{SO}_{4}(\text{STY})_z \)) into a particle already containing a growing chain results in instantaneous termination. The criteria for zero–one conditions have been described by Maeder and Gilbert. In simple terms, it depends upon the probability of termination upon entry of a small radical to that of propagation to form polymer.

Based on the mechanism of the RAFT process, the system may not obey the zero–one condition. For example, if entry of a \( z \)-mer should react first with a dormant species, then a long polymeric radical (active species) is formed. This can either react with monomer or terminate with the already growing chain. The chances of long–long chain termination are highly unlikely, and so the probability of bimolecular termination is reduced significantly. This means that two or more radicals can reside in the same particle. In the presence of RAFT, the probability of termination was calculated using Eq. 5-6, where the same values as Maeder and Gilbert were used. The results that follow are based on the seeded system starting in Interval II:

\[
P(\text{termination})_z = \frac{k^L_z / (N_A V_s)}{k^L_z / (N_A V_s) + k_p C_p + k_{tr,RAFT}[RAFT]_p}
\]  

(5-6)
In this formula, $k_{t,z}^{L}$ is the termination rate constant of a $z$-mer and a long chain radical, $N_A$ is Avogadro’s number, $V_s$ is the particle volume, $k_p$ the propagation rate coefficient and $k_{tr,RAFT}$ the transfer rate coefficient. The concentrations of dormant species inside the particles, $[RAFT]_p$, used were $1.5 \times 10^{-3}$ and $10.5 \times 10^{-3}$ mol·dm$^{-3}$, which are the lowest and highest RAFT agent concentrations applied in this study. The value $z = 3$ was used for styrene and an unswollen radius of 20nm.

The probability of termination without RAFT was found to be 0.82, but this probability will rapidly increase to unity as the chain grows. Addition of RAFT decreased the probability to 0.65 and 0.28 for $[RAFT]_p$ of $1.5 \times 10^{-3}$ and $10.5 \times 10^{-3}$ mol·dm$^{-3}$, respectively. The results clearly show that zero–one conditions may not hold when high concentrations of RAFT are used. However, it should be noted that the chain length of the dormant and active species is a function of both RAFT agent concentration and conversion according to Eq. 5-3. Consequently, the long–long termination assumption used may not be valid up to conversions of approximately 10%. Nevertheless, this shows that the RAFT system can deviate from zero–one conditions by simply increasing the amount of dormant species (or initial RAFT agent).

### 5.2.3. Results and Discussion

The concentration of monomer and RAFT agent in the separate monomer phase after creaming was determined by UV absorption spectroscopy. Table 5.2 shows the saturation concentration of monomer in the presence of the RAFT agents. The $[STY]_p^{sat}$ of styrene in the PMMA seed was 5.61 mol·dm$^{-3}$, which remained roughly constant when Cumyl-RAFT was added to the monomer but increased to 5.97 mol·dm$^{-3}$ for EMA-RAFT. It can also be seen that the concentration of Cumyl-RAFT in the particles is much less than EMA-RAFT. Water solubilities, $[RAFT]_w^{sat}$, of both RAFT agents are in the region of $10^{-4}$ to $10^{-5}$ mol·dm$^{-3}$, which is much lower than $[STY]_w$ (5·10$^{-3}$ mol·dm$^{-3}$ at 50°C).

Seeded emulsion polymerizations of styrene were carried out at 60°C in an argon atmosphere. The KPS and RAFT concentrations used are given in Tables 5.3 and 5.4 (pages 120 and 121). In all polymerizations, the appearance of the emulsion at the beginning of the reaction was a lighter shade of pink due to the red color of the RAFT agents. In the course of polymerization, a conspicuous red layer on top of the emulsion (when agitation was briefly ceased) was then observed. It was found
that the appearance of the red layer occurred shortly after the commencement of polymerization. At conversions of approximately 10%, which for these systems is the changeover from Interval II to III, a red coagulum was formed. NMR and GPC analysis of the red coagulum showed low molar mass polystyrene ($M_p=2100\text{ g mol}^{-1}$) without the presence of the initial RAFT agent.

The formation of this red layer is still unclear. One could be led to believe that transportation of the RAFT agents into the particle is slow on the polymerization time-scale. The rate of transportation can be calculated from Eq. 5-7, which is derived from Smoluchowski’s equation:

$$\text{Rate of transportation} = 4\pi D_{RAFT, w} r N_A [RAFT]_w$$  \hspace{1cm} (5-7)

Using a diffusion coefficient, $D_{RAFT, w}$, similar to that of two styrene chain units,$^{2,59}$ the rate of transportation is approximately $10^6\text{ s}^{-1}$. This value is much larger than the rate of propagation, and on the time-scale of the reaction, diffusion should not be a factor. Therefore, the red layer seems to be more likely due to low molar mass dormant species swollen with monomer. The diffusion$^{16,17,51}$ of these species is extremely slow on the reaction time-scale, and therefore, transportation into the particles is slow. Once the changeover from Interval II to III has occurred, these dormant species coalesce to form the red coagulum, which is not in the emulsion samples analyzed with GPC.

The conversion profiles of these seeded experiments at different KPS and Cumyl-RAFT concentrations are given in Figures 5.1 and 5.2. The starting time was taken when KPS is added to the reaction mixture. At a high KPS concentration (Figure 5.1), the rate decreased as the RAFT concentration was increased. Similarly at low KPS (Figure 5.2) the trend is repeated but the retardation in rate is less drastic. In the case of EMA-RAFT, at a high KPS concentration (Figure 5.3) the

### Table 5.2: Saturation Concentrations of Monomer in PMMA Seed at 60 °C in the Presence of RAFT Agent and the Concentration of RAFT Agent in the Monomer Layer and in the Particles.

<table>
<thead>
<tr>
<th></th>
<th>Control (mol·dm$^{-3}$)</th>
<th>Cumyl-RAFT (mol·dm$^{-3}$)</th>
<th>EMA-RAFT (mol·dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[STY]$^{sat}_{w}$</td>
<td>5.61</td>
<td>5.54</td>
<td>5.97</td>
</tr>
<tr>
<td>[RAFT] in styrene before swelling</td>
<td>$2.33\cdot10^{-2}$</td>
<td>$2.33\cdot10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>[RAFT] in styrene after swelling</td>
<td>$2.74\cdot10^{-2}$</td>
<td>$3.01\cdot10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>[RAFT] in the particle</td>
<td>$9.08\cdot10^{-4}$</td>
<td>$1.63\cdot10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>
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rate also decreased as a function of EMA-RAFT concentration. Therefore, a very high KPS concentration (5 times higher) was required to gain similar rates to that of the control experiment (i.e. without RAFT agent). At low KPS concentration a conversion of about 20% was reached similar to the control experiment. A comparison of the conversion profiles between the Cumyl-RAFT and EMA-RAFT agents at high KPS concentration are given in Figure 5.4. It can clearly be seen that the retardation effect was more predominant for the EMA-RAFT compared to the Cumyl-RAFT polymerizations.

Retardation using RAFT agents has been observed in bulk and solution experiments (see e.g. section 2.3 and ref. 21). The possible explanations given (see page 43) do not explain the difference in rates between the Cumyl- and EMA-RAFT agents, since the free-radical chemistry will be identical, once the initial RAFT agent has been consumed. Therefore, it is believed that the main retardation effect for the two RAFT agents used in these emulsion systems is due to the higher exit rate of 2 compared to 1 from the particles (see section 5.2.1), in line with what Lichti et al. found for normal transfer agents. This also suggests that the destabilization of the emulsion by the RAFT caused a slow rate of transportation of RAFT into the particles by possibly substantially decreasing the surface area of the droplets (producing an organic layer on top of the reaction mixture). At a high KPS

Figure 5.1. Conversion profiles of styrene in the presence of Cumyl-RAFT (1) at a high KPS concentration (1·10⁻³ mol·dm⁻³) at 60°C. Control experiment (□); Low Cumyl (▲, exp. 2); High Cumyl (■, exp. 1).

Figure 5.2. Conversion profiles of styrene in the presence of Cumyl-RAFT (1) at a low KPS concentration (1·10⁻⁴ mol·dm⁻³) at 60°C. Control experiment (□); Low Cumyl (▲, exp. 4); High Cumyl (■, exp. 3).
concentration, the most probable cause of termination of $R$ is with radicals in the aqueous phase. Whereas at low KPS concentrations, termination between re-entry of $R$ into particle with a growing chain is the most probable process.

It should be noted, however, that retardation is effective during Interval II and III. A possible reason, despite the fact that droplets are no longer present in Interval III, is further transportation of RAFT agent into the particles from the water phase.

The influence of both Cumyl-RAFT and KPS on the evolution of $M_n$ and polydispersity with fractional conversion is given in Table 5.3. At high RAFT and KPS concentrations (exp. 1), the $M_n$ increased with conversion, but the PD remained in the range of 2.1 to 2.6. In addition, the $M_{n,\text{th}}$ values calculated with Eq. 5-3 were far lower than experimental. When the RAFT concentration was lowered (exp. 2) only one $M_n$ value could be obtained. Beside this, part of the MMD was beyond the exclusion limit of the SEC columns, and therefore only peak molar masses ($M_p$) are given. The $M_n$ at 41% conversion was more than two times larger than $M_{n,\text{th}}$, with a polydispersity of 2.33. In exp. 3 conversions of 14% were reached in 25 hours, and therefore only two $M_n$ data points were taken, in which these values were again higher than $M_{n,\text{th}}$. Experiment 4, at the lowest RAFT and KPS concentrations investigated, showed the closest correlation between $M_n$ and $M_{n,\text{th}}$. The polydispersities were high, however, in the range of 3.1 to 3.7. These results demonstrate that for all experiments the $M_n$ increased with conversion and the polydis-
persities remained relatively constant. Furthermore, the $M_{n,th}$ is always lower than $M_n$ obtained experimentally. Still, the increase in $M_n$ indicates the living character of the polymerization.

The influence of EMA-RAFT on the MWDs is collected in Table 5.4. In the case of high EMA-RAFT, the $M_n$ values in exp. 5 (very high KPS) increased with conversion and are slightly larger than the $M_{n,th}$, with polydispersities in the range of 2.1 to 3.4. Conversely, at a lower KPS concentration (exp. 6) the $M_n$ values are far greater than theory with polydispersity indices as high as 6.4. In the cases where the RAFT concentration is low, the $M_n$ values are in fact below that of theory, in which the polydispersities increased for exp. 7 but remained approximately constant for exp. 8. The results suggest that both the ratio of RAFT agent and KPS

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(Cumyl-RAFT)</th>
<th>(KPS)</th>
<th>$x$</th>
<th>$M_n \times 10^{-4}$</th>
<th>$P_D$</th>
<th>$M_{n,th} \times 10^{-4}$</th>
<th>$M_n \times 10^{-4}$</th>
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<td>High</td>
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</tr>
<tr>
<td></td>
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<tr>
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<td></td>
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<td>5.5·10⁻³</td>
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<td>0.33</td>
<td>5.84</td>
<td>3.28</td>
<td>5.98</td>
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</table>

a) The concentrations for RAFT and KPS were determined for the monomer volume and water plus the seed latex volume, respectively.
b) Conversion data are placed in the order of the polymerization time.
c) The theoretical number average molar mass was calculated using Eq. 5-1
d) The molar mass distribution exceeded the exclusion limits of the applied SEC columns, so the peak molar masses are given.
concentrations had a more pronounced influence on the MWD for EMA-RAFT compared to Cumyl-RAFT experiments. This is presumably due to the different fates and reaction rates of the exited radicals.

The very broad molar mass distributions, even at low KPS concentrations, are a consequence of continuous transportation of RAFT into the particles during Interval II and a small amount during Interval III, where small chains are continually being formed. Therefore, it is not unexpected to find polydispersity indices much larger than one. The higher values of \( \overline{M}_n \) observed experimentally suggest that there is a much lower than the expected amount of dormant species available for reaction inside the particles. This is also supported by the argument put forth for retardation (i.e. slow transportation of RAFT into the particles).

The deviation of \( \overline{M}_n \) from theory is also caused by the concentration of KPS. The more KPS, the greater the deviation from theory. These results suggest that bimolecular termination due to entry is no longer negligible at high KPS concentra-

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[EMA-RAFT]</th>
<th>[KPS]</th>
<th>( x )</th>
<th>( \overline{M}_n \times 10^{-4} )</th>
<th>PD</th>
<th>( \overline{M}_{n,inh} \times 10^{-4} )</th>
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<td>9.84</td>
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<tr>
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<td>High</td>
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<td>6.77</td>
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</table>
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Table 5.5: The Effect of Variations in Experimental Conditions on the Inhibition Time in Ab Initio Emulsion Polymerizations.

<table>
<thead>
<tr>
<th>Experiment $^a$</th>
<th>[EMA-RAFT] concentration $^b$ (mol·dm$^{-3}$)</th>
<th>Initiator concentration $^b$ (mol·dm$^{-3}$)</th>
<th>Inhibition time (min.)</th>
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</thead>
<tbody>
<tr>
<td>AI-1</td>
<td>—</td>
<td>2.1</td>
<td>—</td>
</tr>
<tr>
<td>AI-2</td>
<td>—</td>
<td>0.52</td>
<td>—</td>
</tr>
<tr>
<td>AI-3</td>
<td>4.5</td>
<td>2.2</td>
<td>540</td>
</tr>
<tr>
<td>AI-4</td>
<td>4.8</td>
<td>0.70</td>
<td>510</td>
</tr>
<tr>
<td>AI-5</td>
<td>0.78</td>
<td>2.4</td>
<td>90</td>
</tr>
<tr>
<td>AI-6 $^c$</td>
<td>2.7</td>
<td>2.4</td>
<td>210</td>
</tr>
<tr>
<td>AI-7 $^c$, $^d$</td>
<td>2.7</td>
<td>2.1 $^b$</td>
<td>360</td>
</tr>
<tr>
<td>AI-8 $^c,d$</td>
<td>2.9</td>
<td>2.5</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ Recipes further consisted of 200g water, 0.6g SDS and 24g styrene.

$^b$ Potassium persulfate (KPS) is used as the initiator, except in AI-7 where 4,4’-azobis(4-cyanopentanonic acid) is used.

$^c$ The mixture of monomer and RAFT was degassed using three freeze-evacuate-thaw cycles.

$^d$ Methyl methacrylate was used as the monomer.

So, over the time of the reactions, the amount of chains formed from initiator can be similar to those formed by the RAFT agents, consequently reducing the $\langle M_n \rangle$. Whereas at low KPS concentrations (exp. 4 and 8), the $\langle M_n \rangle$ values were closer to theory, suggesting only a small proportion of chains were formed from initiator. Therefore, the deviation from theory is proposed to be a combination of the lower than expected amount of RAFT agent available for reaction and the amount of initiator decomposed, which both act concomitantly to increase and decrease $\langle M_n \rangle$, respectively.

5.3. Ab Initio Emulsion Polymerizations

Ab initio emulsion polymerizations were conducted to investigate the effect of RAFT agents on particle nucleation. It was also hoped that the ab initio studies would reveal 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.

Two sets of experiments were performed. The first series 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 structure.
5.3.1. Variations in Reaction Conditions

Details of the first series are given in Table 5.5. In this series the sensitivity of the reaction towards three different aspects was investigated:

1. sensitivity towards oxygen.
2. sensitivity towards potassium persulfate and its derived radicals.
3. specific issues with styrene monomer.

Emulsion polymerizations are in general tolerant towards trace amounts of oxygen. It could be a possibility, however, that when RAFT is added to the system, it is oxidized to form strongly inhibiting or retarding compounds. Based on this hypothesis, experiments AI-6 to AI-8 were conducted using an organic phase that had been thoroughly deoxygenated before use. The water phase was deoxygenated in all cases (see ‘Procedures for ab initio polymerizations’ on page 131). Another possibility is that potassium persulfate reacts with the RAFT agent in an unknown way, causing retardation and possibly forming inhibiting or retarding side-products. Dithioesters are known to be susceptible to oxidation by strong oxidizing agents and also in their specific identity as RAFT agent, mention has been made of this process. Finally, styrene was replaced with methyl methacrylate to investigate the effect of monomer partitioning (AI-8). A higher concentration of monomer in the water phase will accelerate propagation and possibly promote entry.

5.3.2. Variations in RAFT Concentration and Structure

The experiments in this second series (Table 5.6) share the common characteristic that a red layer of organic material is formed at around 10% conversion. As the reaction proceeds, monomer is depleted from this phase and the red material coagulates on the stirrer bar in the form of a viscous oil.

Table 5.6: Type and Concentration of RAFT Agents in the Second Series of Experiments.

<table>
<thead>
<tr>
<th>RAFT Concentration $\times 10^3$ (mol·dm$^{-3}$)</th>
<th>Cumyl</th>
<th>EMA</th>
<th>PBMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>5.2</td>
<td>5.2</td>
<td>4.7</td>
</tr>
<tr>
<td>Medium</td>
<td>2.6</td>
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<td>2.4</td>
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<tr>
<td>Low</td>
<td>1.1</td>
<td>1.0</td>
<td>0.87</td>
</tr>
</tbody>
</table>

a) $[\text{KPS}] = 2.2 \times 10^{-3}$ mol·dm$^{-3}$. For further details see the experimental section on page 131.
Figure 5.5 shows the inhibition times for the various types and concentrations of RAFT. When RAFT agent is added to the polymerization, an inhibition period is observed. At low concentrations, the type of RAFT agent is unimportant, but when the concentration is increased, a distinct difference is found between Cumyl-RAFT on the one hand and both EMA-RAFT and PBMA-RAFT on the other. The inhibition times imposed by Cumyl-RAFT seem to level off, whereas those induced by both other RAFT agents increase when more RAFT is used.

When the inhibition times are neglected and the polymerization rate is plotted as a function of the conversion (Figures 5.6 to 5.8), it can be seen that the addition of RAFT causes a drop in the reaction rate. In a conventional emulsion polymerization, one would first expect an increase in the reaction rate during Interval I, when the number of particles increases. Then during Interval II, the reaction rate will be fairly constant as both the number of particles and the monomer concentration inside them remain the same. Finally, during Interval III, the rate should decrease as the monomer is consumed. In the control experiment (i.e. without RAFT), the two changeovers seem to fall around 10% and 60% conversion. In the experiments in the presence of RAFT, no plateau is reached in the reaction rate – in other words, Interval II does not seem to exist. This implies that either the number of particles or the monomer concentration within the particles is changing during the reaction. Particle size analysis using capillary hydrodynamic fractionation (CHDF) revealed that the weight-average particle size for e.g. the Cumyl-RAFT samples ranged from 26–32nm throughout the reaction. For this reason, it is unlikely that nucleation takes place continuously. The small particle size, however, supports the other hypothesis of a changing monomer concentration. It is an established fact that the equilibrium monomer concentration is a marked function of the particle radius for particles with an unswollen radius below approximately 30nm as predicted by the Morton equation.\textsuperscript{45} As the particles grow, the monomer concentration inside will rise, thereby increasing the polymerization rate. A more noteworthy observation is the remarkably small particle size that is obtained in the presence of RAFT compared with that of the control experiment (≈95nm). Apparently, the presence of a large quantity of active and dormant oligomeric species improves the nucleation process, resulting in a large number of small particles. In the light of these findings, the reaction rate in the presence of RAFT can be considered very low, for a much larger number of particles would in an equivalent system imply a much higher reaction rate. The experimentally determined rate is however much lower over the entire conversion trajectory (Figure 5.6).
Figure 5.5. The effect of the concentration and structure of the RAFT agent on the inhibition period observed in ab initio emulsion polymerizations of styrene at 60°C and [KPS]=2·10⁻³ mol·dm⁻³. Cumyl-RAFT (●), EMA-RAFT (■), PBMA-RAFT (▲).

Figure 5.6. Reaction rate in ab initio emulsion polymerizations using Cumyl-RAFT. [RAFT]=0 (■); 1.1·10⁻³ (■); 2.6·10⁻³ (●); 5.2·10⁻³ (▲) mol·dm⁻³.

Figure 5.7. Reaction rate in ab initio emulsion polymerizations using EMA-RAFT. [RAFT]=0 (■); 1.0·10⁻³ (■); 2.7·10⁻³ (●); 5.2·10⁻³ (▲) mol·dm⁻³.

Figure 5.8. Reaction rate in ab initio emulsion polymerizations using PBMA-RAFT. [RAFT]=0 (■); 8.7·10⁻⁴ (■); 2.4·10⁻³ (●); 4.7·10⁻³ (▲) mol·dm⁻³.

Figure 5.9 gives an example of the development of the molar mass with conversion for the ‘medium’ RAFT concentrations. A linear relationship is apparent, but its slope is much larger than was to be expected, indicating that a living polymerization is taking place but with only a minor fraction of the RAFT agent in place. In the particular example given in Figure 5.9, the PBMA-RAFT performs slightly better than the other two compounds, but in the ‘low’ and ‘high’ concentration experiments, its behavior is very much the same as that of both EMA- and Cumyl-RAFT. The RAFT efficiency can be estimated from the molar mass and conversion.
data using Eq. 5-3. The results for the three Cumyl-RAFT experiments are depicted in Figure 5.10 and are qualitatively the same as those for the other RAFT agents. The concentration of RAFT actually participating in the reaction is only 10–20% of what was added to the reactor. From about 20% conversion onward the efficiency remains fairly constant or rises slightly. No specific trends on either the concentration or the type of RAFT agent could be found. The remainder of the RAFT agent obviously resides in the colored organic layer that is not sampled during the polymerization. The amount of RAFT that is lost in this manner depends on how large this phase grows and at what time during the reaction it starts to form. Poorly understood stability issues determine the RAFT efficiency in this case. Polydispersities in these polymerizations are generally high. Figure 5.11 gives the polydispersities for the polymerizations with Cumyl-RAFT. The results are again strongly affected by the stability issues. Results of the EMA-RAFT polymerizations are similar, with polydispersity ranging from 1.7 to 4.4. In the experiments with PBMA-RAFT, polydispersity went up to around 20, due to a multimodal molar mass distribution.

A last variation in RAFT structure that was tested comprises water soluble agents. Application of the sodium salt of 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid (compound 29 on page 83) and RAFT agents with poly(ethylene oxide) tails of various chain lengths (compound 32 on page 84) initially lead to solution
5.4. Emulsion Polymerizations with Nonionic Surfactants.

Evaluating the results reported in this chapter, living radical polymerization in emulsion polymerization appears to be possible. In both seeded and \textit{ab initio} systems, a linear relationship between the number average molar mass and conversion was observed under certain circumstances. Transportation of the RAFT agent and emulsion stability are problematic. Only a small proportion of the RAFT agent is active at the locus of polymerization and a conspicuous red organic layer is formed. In order to avoid transportation problems, miniemulsion polymerization is a straightforward alternative. These experiments have been conducted and results of these miniemulsion reactions are reported in the next chapter. The reason why nonionic surfactants are investigated in this section is that also in miniemulsion polymerization, stability problems were encountered and it was found that these problems could be largely avoided by the use of nonionic surfactants. Table 5.7 gives the experimental details of several successful emulsion polymerizations stabilized by nonionic surfactants. In total, the series consisted of around 40 experiments with varying monomers, RAFT agents and initiators at a number of concentrations. The PMMA latices used for the seeded polymerizations had the anionic surfactant.
Chapter 5

(Aerosol MA-80) removed by dialysis procedures after which Igepal890 was added to provide the required stabilization. The seed was swollen below saturation with monomer and RAFT agent. Polymerizations designed to start in Interval II, i.e., with monomer droplets present, had the remainder of monomer added before reaction to ensure that the RAFT agent was in the particles at the start of the reaction. Despite these precautions, a number of polymerizations starting in Interval II, but in Interval III as well, developed the same red organic layer as in the seeded polymerizations stabilized by SDS. In these cases, molar mass and polydispersity followed the same trends as those of the experiments with SDS shown in Tables 5.3 and 5.4 (pages 120–121). NI-1 is an example of a successful seeded emulsion polymerization. No signs of instability were observed. The efficiency of the transfer agent is around 50% as the experimental molar mass is about a factor of two larger than the expected molar mass. Polydispersity remained below 1.50 (Figure 5.12).

Ab initio polymerizations conducted with a nonionic surfactant lead to highly variable results, without any apparent relationship to the type and concentration of the surfactant, initiator or RAFT agent. Three examples of successful emulsion polymerizations are described in Table 5.7 and in Figures 5.13 and 5.14. Experimental molar masses are higher than expected under all circumstances, but the RAFT efficiency has clearly improved, relative to the experiments with SDS, reaching values of 45% (NI-2) to 85% (NI-4). Polydispersities are also much better than in the experiments with anionic surfactants, ranging from 1.1 to 1.7. Particle size distributions were determined by dynamic light scattering. The distribution were generally broad and averages varied from 65nm for NI-4 to 350nm for NI-3.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Monomer</th>
<th>Surfactant</th>
<th>Initiator</th>
<th>RAFT agent</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>type</td>
<td>quantity(b)</td>
<td>type</td>
<td>conc.(b)</td>
</tr>
<tr>
<td>NI-1</td>
<td>STY</td>
<td>13.7</td>
<td>Igepal890</td>
<td>_c)</td>
</tr>
<tr>
<td>NI-2</td>
<td>MMA</td>
<td>26</td>
<td>Tween20</td>
<td>6.8</td>
</tr>
<tr>
<td>NI-3</td>
<td>MMA</td>
<td>30</td>
<td>Tween20</td>
<td>2.6</td>
</tr>
<tr>
<td>NI-4</td>
<td>BMA</td>
<td>30</td>
<td>Tween20</td>
<td>26</td>
</tr>
</tbody>
</table>

a) Ab initio recipes (NI-1 to NI-3) are based on 160g water, seeded recipe NI-4 is based on 100g seed latex (8% solids) and 10g water. The anionic surfactant in this seed latex was replaced by Igepal890 before use.

b) Quantities in grams. Concentrations in mmol·dm⁻³, based on the total emulsion volume.

c) Igepal890 was present in the PMMA seed latex.
d) 4,4'-azobis(4-cyanopentanoic acid)
The performance of nonionic surfactants in emulsion polymerizations is clearly better than that of SDS. Like in the miniemulsion polymerizations described in the next chapter, the reason is not fully understood.

5.5. Conclusion

The use of seeded experiments has allowed mechanisms affecting the RAFT process in emulsion to be studied. One of the important aspects of this study was retardation in rate, which was greater for the EMA-RAFT compared with the Cumyl-RAFT. This has been proposed to be due to greater exit of the radicals from the particles, formed after fragmentation of the EMA-RAFT agent. It was also found that the presence of monomer droplets resulted in polymers with high polydispersities. This is proposed to result from continuous transportation of RAFT agent into the particles primarily during Interval II and a small proportion during Interval III. The red layer was also a result of the presence of droplets. Once the switch from Interval II to III occurred, the low molar mass species coalesced to form the red coagulum. Deviation from theory of $\overline{M}_n$ was due to high amounts of chains formed by radical–radical termination and the lower than expected concentration of RAFT agent in the particles caused by trapped dormant species in the red coagulum. Therefore, the ideal system should contain large particles to reduce exit, and a stable system should be sought to determine the effects of RAFT transportation into the particles.
From ab initio experiments it was learned that the RAFT agent causes severe inhibition and that it has a determental effect on the nucleation stage, which stretches it to such an extent that no separate Interval II could be observed. RAFT efficiencies in these batch reactions are low, while polydispersities are high. The use of nonionic surfactants increased the stability of the emulsion and lead to improved RAFT efficiencies in several cases. The polydispersities are much lower (1.1–1.7) than in the anionically stabilized systems, but the system is labile as small variations in the recipe lead to highly different results.

5.6. Experimental

**Materials:** Styrene and methyl methacrylate (Aldrich) were purified of inhibitor by passing through an inhibitor-removal column (Aldrich). Sodium dodecylsulfate (SDS, Fluka) and sodium peroxidisulfate (SPS, Merck) were used as received.

**RAFT agents:** The syntheses of the RAFT agents, 2-phenylprop-2-yl dithiobenzoate, 2-(ethoxycarbonyl)propyl-2-yl dithiobenzoate and 2-cyanoprop-2-yl dithiobenzoate, denoted here as Cumyl-RAFT, EMA-RAFT and Cyano-RAFT (see Scheme 5.3), are described in chapter 3, and follows literature procedures. PBMA-RAFT was prepared by a solution polymerization of butyl methacrylate (28 g) initiated by AIBN (7 g) and in the presence of bis(thiobenzoyl) disulfide (10 g) at 50°C. The average degree of polymerization was 3 and GPC analysis revealed that within this mixture of oligomers no species were present with an poly-styrene equivalent molar mass exceeding 600 g·mol⁻¹.

**Preparation of PMMA seed Latex:** The recipe for the preparation of the PMMA seed latex is given in Table 5.8. The surfactant, buffer and most of the water was charged to a 1.3 L 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 for 1 hr. with stirring. MMA monomer was then added to the reactor and the mixture was allowed to stir for 5 min. Initiator that had been dissolved in the remaining amount of water was then added to the reactor, after which the polymerization was allowed to proceed for 3 hr. The resulting latex was dialyzed for two weeks, with twice daily changes of deionized water to remove residual contaminants. The solids content after dialysis of 5.8% was much lower than expected, which is due to coagulation.
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 dynamic light scattering (Malvern 4700 multi-angle light scatterer with PCS for Windows). This strongly supports the production of a narrow particle size distribution. The PMMA seed was diluted in the seeded studies to give an \( N_c \) of \( 4.37 \times 10^{17} \) dm\(^{-3} \), which is above the critical particle number needed to avoid secondary nucleation.

**Procedure for seeded polymerizations:** 50 ml of the PMMA seed latex was measured into the dilatometer reactor and 78 ml of deionized water was added to the reactor to achieve a solids content of approximately 2.8% and an \( N_c \) of \( 4.37 \times 10^{17} \). The stirred latex was then purged with argon at 60 °C for 30 minutes. A small portion of SDS (0.032 g) (well below its CMC) was then added to prevent coagulation during the reaction. Styrene and RAFT agent were then added to the dilatometer reactor and swelling was allowed to proceed overnight at 60 °C.

KPS 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 added 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 decrease in height of the reaction mixture in the capillary tube. Samples were drawn at regular intervals for gravimetric determination of conversion. The dried samples were then dissolved in THF (1 mg·ml\(^{-1}\)) and filtered for Size Exclusion Chromatography (SEC) analysis. CHDF was used for particle size analysis of the emulsion samples to make sure that secondary nucleation was avoided.

**Procedures for \textit{ab initio} polymerizations:** Deionized water was charged to a glass jacketed reactor and degassed for 1 hour at 60 °C by purging with 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 1/2 hour at the reaction temperature...
ture. The RAFT agent (not present in AI-1 and AI-2) was then dissolved in the styrene. 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 AI-6 to AI-8 were carried out with rigorous degassing of the monomer and RAFT agent through three freeze–evacuate–thaw cycles and an increase in the emulsification period to 1 hour. Experiment AI-7 was carried out with 4,4′-azobis(4-cyanopentanoic acid) as the initiator, instead of KPS, under the same conditions as experiment AI-6.

**SEC Analysis:** SEC 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 mm 50×7.5 mm precolumn, followed by 2 PLgel mixed-C 10 mm 300×7.5 mm columns (40 °C) in series. THF was used as eluent (flow rate 1.0 mL·min⁻¹) and calibration was done using polystyrene standards (M = 580 – 7.1·10⁶ g·mol⁻¹). Data acquisition was performed using WATERS Millennium 32 (v3.05) software and processed further using GeePeeSee (beta 2).

**Determination of \([M]_{pSat}\):** The saturation monomer concentration within the seed latex particles, \([M]_{pSat}\), was determined by creaming experiments according to the method used by Ballard et al.\(^{55}\) The saturation concentrations of monomer were also determined in the presence of Cumyl-RAFT and EMA-RAFT agents. These were dissolved in the styrene monomer prior to the swelling of the seed. 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.

5.7. References

emulsion polymerization

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Chapter 5

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   See also the next chapter of this thesis.