Chapter 1

Exposition

RAFT in Emulsion Polymerization: What Makes it Different?

Adapted from:

RAFT in Emulsion Polymerization: What Makes It Different.
Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G.
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Men occasionally stumble over the truth,
but most of them pick themselves up and hurry off as if nothing happened.

– Winston S. Churchill (1874–1965)

1.1 Abstract

Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization techniques have been the focus of a great deal of recent work. The combination of RAFT with emulsion polymerization, which is the method of choice for implementing most free-radical polymerizations on an industrial scale, has considerable technical potential: for example, in controlling physical properties and in eliminating added surfactants from surface coating formulations. However, considerable difficulties have been experienced in using RAFT in emulsion polymerization systems. Here, early progress in the application of RAFT techniques to emulsion polymerization is reviewed, summarizing the difficulties that have been experienced and the mechanisms that have been postulated to explain these difficulties. Possible origins include polymerization in droplets, water sensitivity of some RAFT agents, slow transport of highly hydrophobic RAFT agents across the water phase, and surface activity of some RAFT agents. The experimental and theoretical approaches to the work described in subsequent chapters are outlined.

1.2 Introduction

Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization techniques are part of a class of techniques for living or controlled radical polymerization. Living polymerization methods have been widely used to control molecular architecture, producing block copolymers,[1-3] gradient copolymers[2] and star polymers.[2,4,5] Additionally, the products of living polymerizations usually have quite narrow molecular weight polydispersity and the molecular weight is controllable.[4,6]

Living polymerizations have great potential for commercial products. One can control molecular weight, and can also produce block copolymers, in a way that is impossible with conventional free-radical polymerization. The molecular weight control and the capacity to grow block copolymers enhances many potential commercial applications. These include novel compatibilizers for polymer blends, novel mechanical properties such as improved impact strength, and synthesizing surface coatings by emulsion polymerization in the absence of any added surfactant[7] (which can yield environmental benefits, different film-forming properties and better adhesion).

Emulsion polymerization offers many advantages in terms of product and process control, and environmental benefits both in manufacture and in application. Its widespread consumer and industrial acceptance makes it ideal for industrial applications of living polymerizations. RAFT techniques have been described for many applications, but the use of this technology in emulsion (and miniemulsion) systems has not followed early optimistic projections. A summary of what makes RAFT/emulsion and (RAFT/miniemulsion) systems different from their classical emulsion and solution-RAFT cousins is presented here. A brief review of some of the problems, both solved and outstanding, of RAFT/emulsion systems is also included.

1.3 Principles of Living Polymerization

In general, ideal living polymerizations have the characteristics that all chains are initiated at the beginning of the reaction and continue to grow throughout the course of the reaction.[8] The distinction between classical and living polymerizations is illustrated in Fig. 1.1. In a classical polymerization, each chain is initiated, propagates and terminates in a short period of time relative to the length of the reaction. In a typical emulsion polymerization, which takes many hours to go to complete conversion, the lifetime of a single chain is of the order of seconds; chains that grow early in the reaction will experience quite different growing conditions compared to chains that grow at the end of the reaction (*e.g.* monomer concentration). However, in an ideal living polymerization, each chain experiences the same growing conditions over the course of the reaction.[9,10] The result is that the chains produced are more similar to each other than in a classical polymerization.[11] By making the time over which each chain grows commensurate with that of the overall reaction, block and gradient polymers may be produced, and the polymer produced has a reduced molecular weight polydispersity.[11] Some of the advantages of this are as follows.

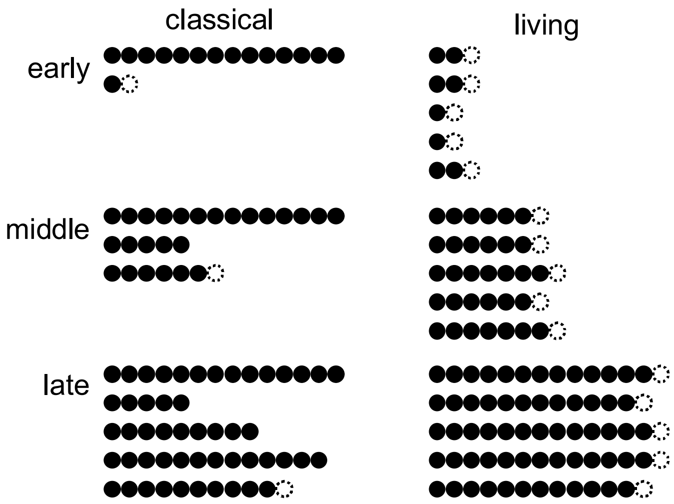


Figure 1.1: A comparison of classical and living polymerizations illustrating the chain length and number of growing centers (shown with dotted ends) at three stages during the reaction.

- *Block copolymers:* It is generally impossible to produce block copolymers by free-radical polymerization. The simple semi-batch approach of first polymerizing until one monomer is consumed and then adding a second monomer does not work in conventional free-radical polymerization: most of the chains are “dead” by the time the first monomer has been consumed, and thus cannot add the second monomer, as illustrated in Fig. 1.2. On the other hand, after the original monomer has been consumed in a controlled radical polymerization, most chains are in a “dormant” form capable of regaining radical activity, and will thus add on a second monomer when it is fed in, leading to a block copolymer.

- *Gradient copolymers:* As shown in Fig. 1.3, in a classical free-radical copolymerization, the composition of any one chain is the same along its length, although chains made at the start of the reaction may differ significantly in composition to those made at the end. By way of contrast, each chain produced in a living polymerization may have a varying composition along its length (a gradient copolymer), but each chain will have a similar composition.

- *Control of polydispersity:* Since all chains are initiated near the start of the reaction and grow through the same set of reaction conditions (with radical activity being briefly shared between each of them) the breadth of the molecular weight distribution (polydispersity) of the product is reduced.[6]

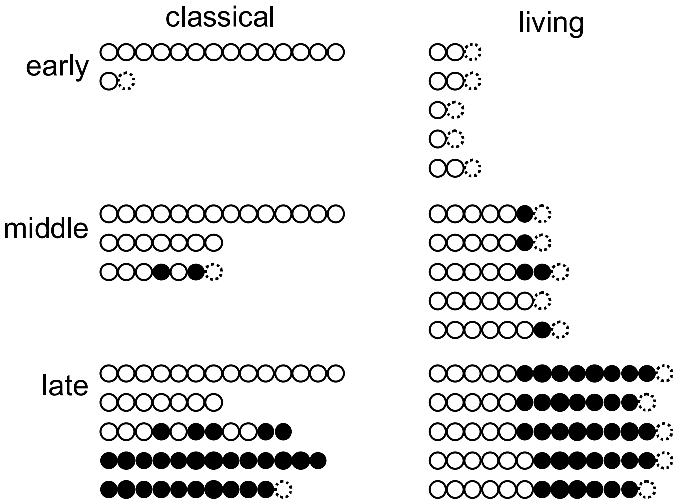


Figure 1.2: Illustration of how block copolymers are easily made with living polymerizations, but the same reaction would produce a heterogeneous mix of copolymers with a classical polymerization. Closed circles represent one monomer, open circles a second monomer and dotted ends growing centers. Three stages during the reaction are shown.

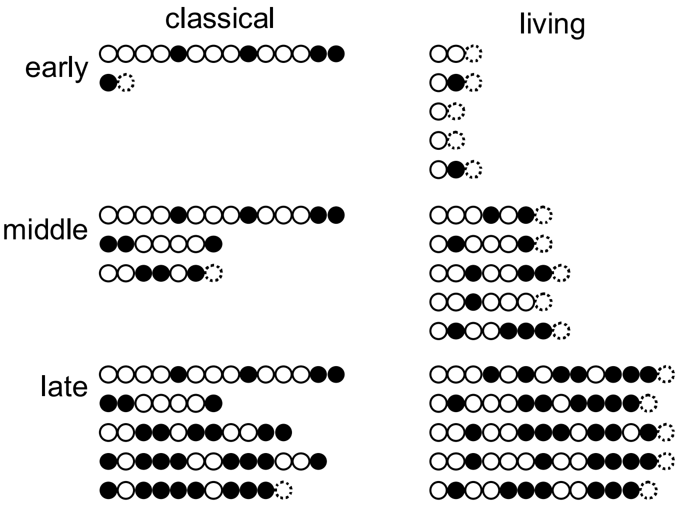


Figure 1.3: Illustrating how gradient copolymers are easily made with living polymerizations, but the same reaction would produce a heterogeneous mix of copolymers with a classical polymerization. Symbols as per Fig. 1.2.

Turning briefly to terminology, "living" polymerizations are currently defined as being reactions in which termination reactions are absent.[8] With the advent of living radical polymerizations in which termination reactions are at best insignificant rather than absent, there has been considerable debate surrounding this definition.[12,13] The development of techniques such as RAFT (in which chains are *reversibly* terminated) has widened the debate further. For the purposes of this work, "living radical polymerization" or often simply "living polymerization" will be used to describe the application of ideal living polymerization to free-radical processes, with the associated non-idealities that must invariably be present (such as termination and transfer to monomer).

There are now many different mechanisms for living polymerizations; the three most important classes are:

- Reactions where the growing ends *cannot* react with each other to terminate, such as anionic polymerization.[14]
- Reactions where the growing ends are reversibly protected by an end cap that is removed through a unimolecular reaction for a short period of time (perhaps through being complexed with a metal catalyst) before an end cap is replaced, as illustrated in Fig. 1.4. Nitroxide-mediated polymerization (NMP) falls into this category.[11,15,16]
- Reactions where the ability to grow is reversibly exchanged for an end cap in a bimolecular reaction. This exchange may be between a small molecule and the polymeric chain (*e.g.* atom transfer radical polymerization, ATRP) or between two polymeric chains (*e.g.* RAFT). In such a scheme, the end cap is transferred amongst many different chains, as illustrated in Fig 1.5.

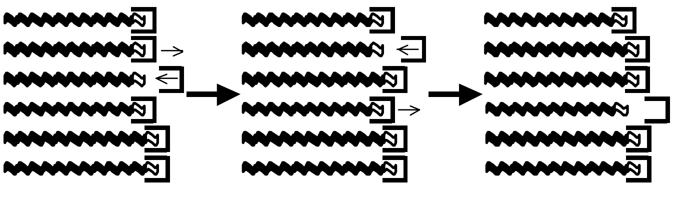


Figure 1.4: Illustrating a capping and uncapping style mechanism where each chain may briefly uncap itself, propagate and then re-cap itself. In this mechanism, the dormant to active reaction is unimolecular.

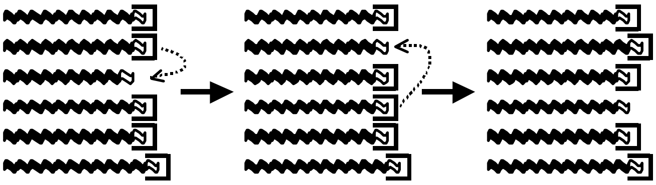


Figure 1.5: Illustrating a cap-swapping mechanism where the dormant species exchange their end-cap for the ability to grow. In the RAFT mechanism, the dithiocarbonyl functional group is the end-cap that is exchanged for radical activity. Here, the dormant to active reaction is bimolecular.

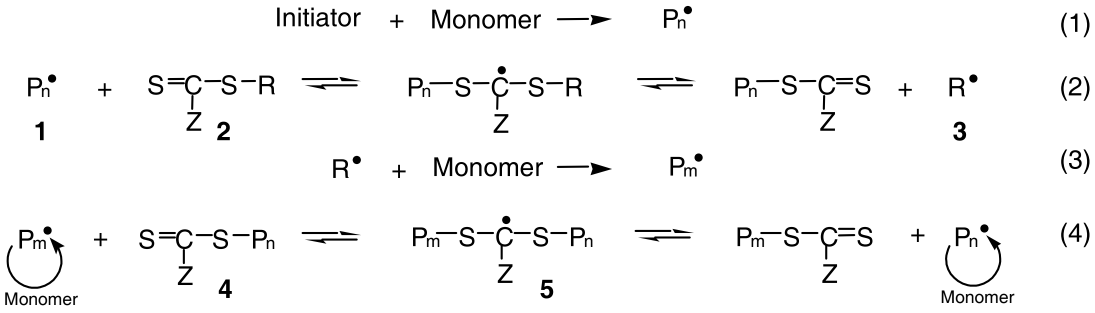
The living radical polymerization mechanisms detailed above have one important mechanistic feature in common: radical activity is reversibly transferred or added to a dormant species, making it reactive. The details of the equilibrium between the propagating and dormant species vary markedly, with each of the living radical polymerization techniques having its own complexities.

Of particular interest in recent years are ATRP and RAFT, with considerable effort being expended on both technologies. In terms of the outlined mechanism above, ATRP makes use of a bimolecular transfer reaction between the polymeric chain and a small molecule, typically a copper complex.[17-20] The RAFT process falls into the category of bimolecular activation requiring two polymeric species,[1,4] as do alkyl iodide mediated polymerizations.[11]

1.3.1 The RAFT Process

RAFT is now a well-established technique for living free-radical polymerization. It has been shown to be quite effective in solution and bulk polymerization systems[1,2,4,21] and has been applied with varying degrees of success to emulsion[1,4,22-24] and miniemulsion[25-28] systems. Its advantages include the robustness of free-radical polymerization and an ability to work over a wide variety of monomers and temperatures.[4,29]

The actual mechanism under which the RAFT process operates has received considerable attention lately, with numerous authors suggesting that additions to the "standard" mechanism (Scheme 1.1) are necessary in order to fully explain all available data.[30-33] This "standard" RAFT mechanism was proposed by Rizzardo *et al.*,[1,4,34,35] and will be discussed in detail before more recent proposed additions to it are described.



Scheme 1.1: The RAFT mechanism proposed by Rizzardo *et al.*[1,4,34,35] The crucial reaction for providing living character to the system is the equilibrium shown in reaction 4.

The key to the living nature of the RAFT process is the equilibrium, shown in Scheme 1.1 reaction 4, between the polymeric radicals (**1**), the dormant species (**4**) and the bipolymeric intermediate radical (**5**). This equilibrium was schematically represented in Fig. 1.5, where the end-cap is the dithiocarbonyl functionality. The position of this equilibrium (towards **1** and **4** or towards **5**) has been debated in recent studies,[4,30,31] although it is clear that there is no reason to suppose that all the different types of RAFT agents should exhibit the same generic behavior and that the nature of the Z group in the RAFT agent (**2**) is quite important in determining the rate of polymerization.

The re-initiation step of the RAFT process is also essential; it is due to the chain transfer events (Scheme 1.1 reaction 2) and re-initiation by the RAFT-agent fragment $R^\bullet$ (**3**, Scheme 1.1 reaction 3) that most chains are initiated quite early in the reaction. There is evidence that the R group of the RAFT agents (**2**) may have a significant effect on the reaction should re-initiation be poor.[4,36]

For a polymerization mediated by a RAFT agent with a transfer constant, C_{tr}, greater than about 2, the number-average molecular weight, $\overline{M}_n$, can be easily calculated from the initiation and re-initiation reactions (Scheme 1.1 reactions 1 and 2), since every chain that is produced must have either an initiator-derived group or the RAFT-agent fragment R on the end.[4,6] One can calculate the number-average molecular weight of the system from the mass of monomer, m_{mon}, the number of moles of RAFT agent n_{RAFT}, the number of moles of initiator present at the beginning, $n_{\mathrm{I}}^{\mathrm{i}}$, and the number of moles of initiator present at the end of the reaction, $n_{\mathrm{I}}^{\mathrm{f}}$:

$$\overline{M}_{\mathrm{n}}^{\mathrm{pred}} = \frac{x m_{\mathrm{mon}}}{n_{\mathrm{RAFT}} + 2(n_{\mathrm{I}}^{\mathrm{i}} - n_{\mathrm{I}}^{\mathrm{f}})} \tag{1.1}$$

where x is the final conversion and $\overline{M}_{\mathrm{n}}^{\mathrm{pred}}$ is the target $\overline{M}_{\mathrm{n}}$. In practice, the initiator-derived terms may often be ignored, as the proportion of initiator-derived chains is frequently quite low (typically ranging from below 1%, as used in this work, to around[1] 10%). The effectiveness of the equilibrium (Scheme 1.1 reaction 4) in mediating the polymerization is often measured by the molecular weight polydispersity, $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$.

Within this discussion of RAFT techniques, xanthates will be included within the family of RAFT agents, as the mechanism by which they are thought to operate is the same (RAFT using xanthates has frequently been described by a separate acronym, MADIX *e.g.* ref.[37]).

1.3.2 Non-ideal RAFT Kinetics

There have been many reports of RAFT-mediated polymerizations that do not appear to follow the kinetics that would be expected by the naïve implementation of Scheme 1.1. Specifically, there is sometimes an inhibition period at the beginning of the reaction during which little polymerization appears to occur,[36,38] and a reduction in the rate of polymerization (or retardation) once polymerization commences.[4,30,33,39-44] These effects have been seen in many reactions, including bulk, solution, emulsion and miniemulsion systems in which good molecular weight control is seen.

The behavior of the RAFT equilibrium (Scheme 1.1 reaction 4) became the focus of study for many groups in recent years in an attempt to determine the concentration and fate of the intermediate radical species (**5**). The slow fragmentation of the intermediate radical was suggested by Barner-Kowollik *et al.*[30,31,45] to be the cause of retardation; however, this model requires high concentrations (~10^{-3} mol dm^{-3}) of the intermediate radical to be present in the system and for the intermediate radical to be particularly long-lived (~10^{2} s). Studies of the concentration of intermediate radicals by ESR have not supported this model as the intermediate radical has only been found in much lower concentrations ($\lesssim 10^{-6}$ mol dm^{-3}) than predicted using the slow-fragmentation model, indicating an extremely short lifetime for the intermediate radical (~10^{-4} s).[39-41,46]

The irreversible termination of the intermediate radical with other radicals (*e.g.* propagating radicals) was proposed by Monteiro and de Brouwer as a possible explanation for the observed retardation.[32] Experimental evidence in support of this model has been reported based on molecular weight data.[39,47]

Reversible termination of the intermediate radicals has also been suggested by Barner-Kowollik *et al.*;[33,42] data from the γ-initiated polymerization of styrene with the RAFT agent cumyl dithiobenzoate indicate that a radical storage mechanism is active in the RAFT-mediated reaction.[33]

The particular model chosen for the behavior of the intermediate radical profoundly changes the predicted kinetics of the fragmentation reaction; for example, the reversible termination model implies fragmentation rate coefficients for **5** around 10^{6}-fold faster than the slow-fragmentation model. The applicability of each of these mechanisms has been widely debated, with recent modeling efforts using the fast fragmentation model[48] generating replies from numerous groups.[43,44]

1.4 Emulsion Polymerization

Emulsion polymerization is a commonly used laboratory and industrial technique whereby a dispersion of polymer in water is formed. This dispersion (or latex) is produced through a complicated interplay between chemical and physical processes that have been well documented elsewhere.[49-52] Emulsion polymerization offers numerous technical advantages over solution and bulk polymerization (and also advantages for the scientific study of free-radical polymerization), including being solvent-free, maintaining a fairly low viscosity even to high polymer loadings (because the particles are colloidally suspended in water), fast rates of polymerization and good heat transfer.[50]

It is important to be aware that the term “emulsion polymerization” is a misnomer.[50,53] While the monomer/water system may form an oil-in-water emulsion, polymerization within these emulsion droplets is normally insignificant. The locus of polymerization is the latex particles (colloidal particles of polymer, swollen with monomer, typically 100 – 200 nm in diameter, with each particle containing many individual polymer chains). These particles are formed by two possible mechanisms, micellar and homogeneous nucleation, in both cases commencing with polymerization of the initiator with the small amount of monomer present in the water phase.[50] The droplets of monomer, when present, merely act as reservoirs for monomer to diffuse to the growing latex particles to maintain the polymer/monomer equilibrium ratio.

It is convenient to divide an emulsion polymerization into three Intervals. Interval I is the period of particle formation, Interval II is polymerization within particles in the presence of monomer droplets, and Interval III is after monomer droplets have been exhausted. It is common both in the laboratory and in industry to bypass Interval I by adding a pre-formed “seed” latex.

1.4.1 Radical Entry and Exit

The origin of the radicals in an emulsion polymerization has particular significance to this work. Typically, the radicals in an emulsion polymerization are formed in the aqueous phase from a water-soluble initiator. These radicals then add to successive monomer units (the millimolar solubility of many monomers in the aqueous phase is sufficient for this to occur) before becoming surface-active and entering a latex particle. This so-called "Maxwell-Morrison" model for the *entry* of oligomeric radicals into particles[54,55] has successfully formed the basis of models to predict particle formation[56,57] and particle growth,[51,52] and is shown pictorially in Fig. 1.6. Entry is usually quantified by the pseudo-first-order rate coefficient for radical entry into a particle, ρ, the average number of radicals entering a particle per unit time.

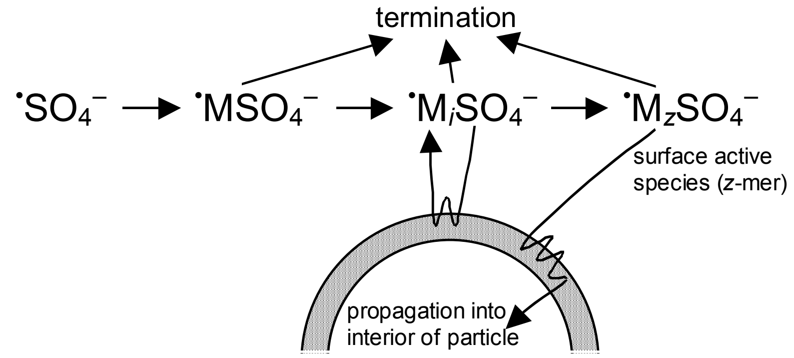


Figure 1.6: A schematic representation of the Maxwell–Morrison model[54,55] for the entry of oligomeric radicals into latex particles. In this model, the entering species is an initiator-derived oligomeric radical (a *z*-mer) that is surface-active; oligomers that are shorter than a *z*-mer tend to be too water soluble to enter due to the charged initiator fragment. The passage through the interface is not rate-determining.

The generally accepted model for the *exit* of a radical from a particle uses chain-transfer to monomer events to generate a small radical that may diffuse out of the particle, should it not add to monomer and begin propagating a new chain,[50,58] as shown in Fig. 1.7. This event is the dominant reason for radical loss for all small particles except at high radical flux. The fate of the exited radical must also be taken into account; the significant possibilities are that the exited radical may re-enter another particle and start propagating (perhaps with termination if the re-entered particle already contains a growing radical), or re-enter and re-exit until it terminates with a radical in another particle.[50,58,59] Each fate requires different mathematical approaches, adding considerable difficulty to the interpretation of data to find the first-order rate coefficient for exit, *k*.

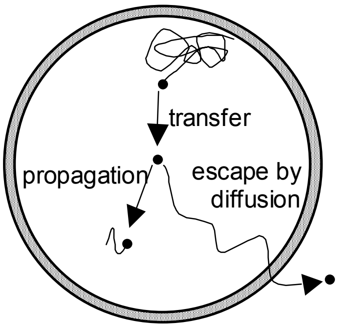


Figure 1.7: A schematic representation of the standard model for the exit of a monomeric radical from a latex particle. Once a chain-transfer to monomer event occurs, the monomeric radical can then either add to monomer (starting a new chain) or escape from the particle by diffusion. The passage through the interface is not rate-determining.

It is difficult to measure the rate coefficients for radical entry and exit directly.[50] Instead, the rate of polymerization is usually measured and values for ρ and k deduced from that data. If the conditions are such that that the rate is rapidly changing with time, independent values of ρ and k may be deduced under appropriate circumstances; however, if that rate is constant, the values obtained for ρ and k are not independent of the model used to fit the data.

Two of the tools available for obtaining these rate coefficients are dilatometry and γ-radiolysis, both of which are shown in Fig. 1.8. RAFT/emulsion systems are studied using dilatometry with a chemical initiator in Chapter 3, while dilatometry is combined with γ-radiolysis in Chapter 7.

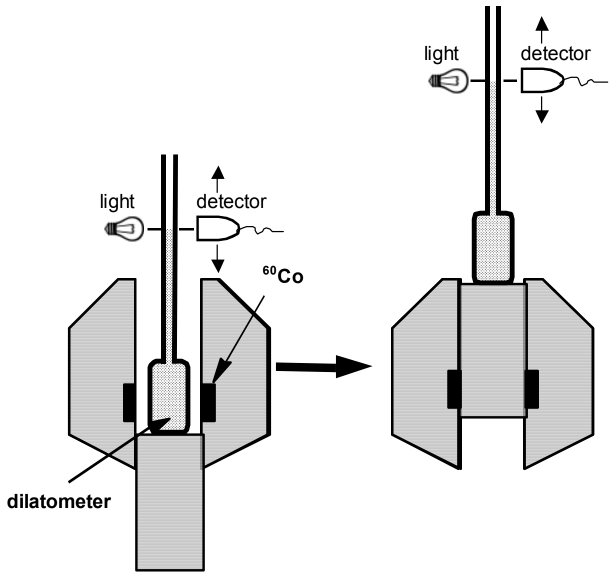


Figure 1.8: The techniques of dilatometry and γ-radiolysis provide useful tools for gaining mechanistic understanding of emulsion polymerization systems. The automated dilatometer measures the height of the meniscus within the capillary tube above the reactor as shown in the diagram. This may be coupled with a γ-radiolysis apparatus (the γ-source and lead shielding are pictured) to provide initiation, and to study radical loss processes after removal from the radiation source (shown in the figure on the right).

Dilatometry measures the volume change of the reaction and relies on the density difference between monomer and polymer to give the conversion as a function of time, yielding the rate of polymerization.[50,60] Initiation for a dilatometry experiment can be either by a chemical initiator (*e.g.* potassium persulfate) or γ-radiation. The advantage of γ-radiation is that initiation may be stopped by removing the reaction vessel from the radiation and the resulting relaxation gives a rate of polymerization that varies with time. While UV radiation is sufficient to initiate bulk and solution polymerization experiments, the turbid nature of the latex formed in emulsion polymerizations prevents spatially uniform initiation by UV radiation throughout the latex. Hence γ-relaxation provides a way of directly studying the radical-loss processes in an emulsion polymerization. In a small particle, this radical loss process is exit. The way in which the rate of polymerization slows once initiation ceases allows the fate of the exited radicals to be determined along with k.[50]

1.5 Early Studies of RAFT in Emulsion Polymerizations

While RAFT has been quite successful in solution and bulk polymerizations, the use of RAFT in dispersed systems has not enjoyed the same successes. Problems such as loss of molecular weight control, coagulum formation and phase separation abound, perhaps arising from the additional physical events involved in an emulsion polymerization experiment.[22,24,32] Similarly, attempted use of RAFT in miniemulsion systems was also at first unsuccessful.[26,61]

Prior to the work included here, there were relatively few reports of successful RAFT/emulsion experiments (*i.e.* those that do not fall into the failure categories below) with the notable exception of the *ab initio* polymerization of butyl methacrylate with cumyl dithiobenzoate RAFT agent by Chiefari *et al.*[1] A survey of the early work in applying RAFT to emulsion polymerization shows that most experiments have exhibited one or more of the following problems:

- poor colloidal stability (phase separation or coagulation),[24,62]
- poor control of $\bar{M}_n$, the number-average molecular weight,[22,24,62] or
- poor control of the polydispersity.[4,22,23,37,62]

Additionally, a number of studies noted quite slow polymerization rates.[24,62] These results have even led to speculation that RAFT cannot be made to work in emulsion polymerization systems.[61]

The poor polydispersity in some studies was due to the use of xanthates as the RAFT agent. While it appears that xanthates may be easily included in emulsion polymerizations with no significant colloidal stability problems,[22,23,37,63] they are unable to produce polymers of low polydispersity for most monomers even in the most ideal conditions.

1.5.1 Water-Soluble or Not?

In a multi-phase system such as an emulsion polymerization, the choice of water- or oil-solubility for the RAFT agent becomes important. A general pattern is observed in the literature: all available data are consistent with the postulate that transport of the RAFT agent to the locus of polymerization is, at present, a major difficulty in RAFT/emulsion systems. The observed trends and possible mechanistic interpretations are discussed below.

1.5.1.1 Water-Soluble RAFT Agents

If the RAFT agent used is quite water soluble, considerable chain transfer will occur in the water phase, hence it will take quite some time for *z*-meric species (oligomeric radicals that are capable of entering a particle[50,54]) to be formed. In such a situation, the RAFT agent becomes an effective inhibitor, as seen by Uzulina *et al.*[24]

1.5.1.2 Water-Insoluble RAFT Agents

When a quite hydrophobic RAFT agent is used, an entirely different set of problems is created. The use of highly water-insoluble RAFT agents without facilitating RAFT agent transport has so far been unsuccessful.[24,62] In Chapter 3, it is postulated that one of the principle problems experienced in early studies was the transport of the RAFT agent to the locus of polymerization (*i.e.* from monomer droplets to particles). Once a water-insoluble RAFT agent has been dissolved in the monomer and then added to the water phase, the kinetic and thermodynamic barriers to the transport of the RAFT agent into the particles may be quite large. Put simply, if the RAFT agent is not at the locus of polymerization, it cannot mediate the polymerization reaction, and so molecular weight control will be poor.[4]

The nature of the barrier to transport has not been clearly elucidated. With analogy to styrene dimer, Monteiro *et al.*[62] estimated that for common thiocarbonylthio RAFT agents (such as cumyl diothiobenzoate and PPPDTA, the RAFT agent on which this work is focused), the rate of transport should be quite fast ($\sim 10^6\ \mathrm{s}^{-1}$). This would seem to indicate that the barrier to transport is unlikely to be kinetic, as this process is fast on the timescales of both propagation and the polymerization reaction.[61] However, if significant amounts of RAFT-mediated transfer were to occur within the monomer droplets, the RAFT agent would no longer be in the form of **2** but rather in the form of the dormant polymeric species **4**. Such a species would have a significantly slower diffusion coefficient and significantly lower water solubility, presenting a large barrier to transport.

Droplet polymerization is usually negligible in emulsion polymerization reactions (with a few notable exceptions such as in neoprene[64]). If droplet nucleation were to occur in a RAFT/emulsion polymerization, the oligomeric species (**4**) formed in the equivalent RAFT-containing reaction would be much smaller and will not form a hard particle as the monomer droplet evaporates. Instead, they will readily coagulate.

It is this process that is postulated to lead to the highly viscous, colored layer seen in many attempts at RAFT/emulsion polymerization (the color arising from that of the RAFT agent). This effect has been observed at the Interval II to Interval III transition,[24,62] at which monomer droplets disappear. Note that since the RAFT agent had been dissolved in the monomer for these studies, any breakdown of the emulsion (such as caused by cessation of stirring) would be expected to lead to a RAFT-colored layer forming above the latex. However, at the Interval II to Interval III transition, these systems spontaneously phase-separate, yielding a highly viscous, colored layer, and often produce large amounts of coagulum.

It is important to note that, even if the kinetic rate of transport is suitably fast (as believed in this case), it is still possible for thermodynamic barriers to prevent sufficient RAFT agent transport. As the RAFT agent will initially partition with approximately equal concentration between the monomer-droplet and particle phases, a significant amount of RAFT agent would be present in the monomer droplets. As this RAFT agent is not at the desired locus of polymerization, any transfer events (RAFT-mediated polymerization) within the monomer droplet would lead to coagulum, as described above.

1.5.1.3 Surface-Active RAFT Agents

If the RAFT agent used is surface active, it may have enough water solubility to transport across the aqueous phase from the droplets to the particles,[22,23,37,63] but its surface activity will minimize its participation in the aqueous phase chemistry. Thus, the inhibition seen for water-soluble RAFT agents by Uzulina *et al.*[24] would not be observed. Even still, partitioning of the RAFT agent between droplets and particles may lead to poor control of $\bar{M}_n$.[22]

Unfortunately, most of the RAFT agents believed to be surface-active that have been used so far are xanthates, which typically show poor results for molecular weight polydispersity.[22,23,37,63] The exception to this was the amide-functionalized RAFT agent of Uzulina *et al.*,[24] which, while successful in producing polymer, had only moderately good molecular weight and polydispersity control.

1.5.1.4 Assisting Transport

Considering the plethora of problems involving RAFT agent transport, an alternative approach to transporting the RAFT agent from monomer droplets to the particles becomes desirable. Addition of an organic cosolvent (such as acetone) is known to facilitate transport of hydrophobic species in the aqueous phase in emulsion polymerization reactions and would be expected to assist the implementation of RAFT in seeded emulsion polymerizations. While such a procedure would not be commercially viable (the example shown in Chapter 3 makes use of ~25% w/w acetone), it provides a RAFT system that should behave ideally: RAFT-mediated polymerization within the particles without transport problems, which should show good molecular weight control. The use of an assisted transport technique in performing RAFT/emulsion experiments is detailed in Chapter 3.

1.5.2 RAFT in Miniemulsion Polymerization

While the focus of this work is the development of understanding in the RAFT/emulsion field, it seems pertinent to briefly discuss some work that has been done in RAFT/miniemulsion systems. Recent studies of RAFT/miniemulsions have also reported significant problems,[26,65-67] including loss of colloidal stability with anionic and cationic surfactants,[26,65] and broad particle size distributions.[26]

The important difference between emulsion and miniemulsion polymerization is that the miniemulsion polymerization produces the particles as a 1:1 copy of the droplets. Ideally, each droplet is “stung” by an incoming radical and becomes a new particle as polymerization proceeds;[68] this permits the easy incorporation of quite hydrophobic entities into the particle,[69,70] including RAFT agents.[25,71,72] Generally, either high shear and/or sonication is used to produce an emulsion of ~100 nm diameter droplets with a narrow droplet size distribution. The combination of surfactants to maintain colloidal stability and a hydrophobe to prevent droplet evaporation (sometimes incorrectly called a cosurfactant) maintain the emulsion for at least long enough for polymerization to occur.

From studies of RAFT/miniemulsion systems, some authors concluded that there was an inherent incompatibility between RAFT and some stabilizers such as the anionic surfactant sodium dodecyl sulfate.[26,65] More recent results indicate that the reported difficulties in RAFT/miniemulsion polymerization are more likely related to the quality of the original miniemulsion than with an inherent incompatibility.[25,27,28,61]

Many of the reported failures can actually be more easily explained in terms of the collapse of the miniemulsion itself, the effects of which may be exacerbated by the highly water-insoluble RAFT agent. There is some evidence that many miniemulsion systems take on an emulsion polymerization mechanism once particle formation has occurred (*i.e.* droplets coalesce and feed monomer into the particles to allow continued polymerization).[26,27] In a non-RAFT miniemulsion system, this is not a problem as the large monomer droplets evaporate, leaving behind only a trace of the hydrophobe that may be adsorbed onto other particles and cause no problems. However, in the case of a RAFT/miniemulsion experiment, the presence of RAFT agents in the large monomer droplets leads to the production of oligomers just as in the emulsion polymerizations described above,[26] leaving the system prone to coagulation and broad particle size and molecular weight distributions.

1.6 Unusual Behavior of RAFT/Emulsion

In Chapter 3, RAFT/emulsion systems are seen to exhibit unusual behavior including long inhibition periods and a reduction in the rate of polymerization. This behavior is not naïvely expected from consideration of the principles of emulsion polymerization and RAFT-mediated polymerization alone, and requires the removal of various simplifications regarding the physical processes involved that have been used in previous studies of emulsion polymerization.

Of particular interest in this study is the chain-length dependent termination reaction. One of the consequences of the RAFT-mediation of the polymerization process is that the lengths of the propagating radicals are different from those in classical polymerization reactions; moreover, the lengths of the radicals change throughout the polymerization. The kinetic models developed for this project show that much of this seemingly inexplicable behavior is readily understandable when chain-length dependent processes are considered.

1.7 On Theses and Fugues

Presented in this thesis is the story of the development of understanding of RAFT in emulsion polymerization. The work may be broken into the following categories, with the unraveling of the complex interactions between the different chemical and physical processes involved in both RAFT and emulsion polymerization occurring throughout the course of the story:

- development of protocols for successful use of RAFT in emulsion polymerization
- identification and quantification of RAFT-induced changes to the emulsion polymerization (*e.g.* inhibition, retardation, entry/exit rates)
- description of various methods by which RAFT/emulsion systems may be improved

The structure of the thesis reflects the musical form known as a *fugue*; the association between the fugue and science is described in great detail in a Pulitzer prize winning book by Hofstadter.[73] The fugue is a complex form based on the round or canon, and was mastered and brought to popular acclaim by the prolific baroque composer J.S. Bach. In short, a fugue starts with a single musical motif (the *subject*) presented by one of the performing voices. Each of the voices may then enter in turn, presenting the same theme, sometimes with embellishments, whilst the other voices move onto other musical ideas (*e.g.* the *counter-subject*). The initial presentation of ideas is called the *exposition*. At various places during the fugue, the composer may introduce new material (the *codetta* and *episodes*) as a break from the contrapuntal writing, providing respite from the polyphony (many voices) and allowing the listener to appreciate the complexity of the work. The *cadenza* is the traditional conclusion to the fugue in which the polyphony is often resolved to a majestic homophonic finale.

While it can in no way be claimed that this thesis is a work of beauty comparable to those of J.S. Bach, the way in which theory and experiment complement each other throughout this work bears more than a passing resemblance to fugal form. Throughout this thesis, the main ideas are presented in the odd-numbered chapters, alternating between experiment and theory. The even-numbered chapters are the codetta, episodes and cadenza. The codetta and episodes provide additional details about the methods used to investigate the RAFT/emulsion systems, critically placing the main chapters in the context of the field of RAFT/emulsion systems, while the cadenza provides the overall conclusions to this body of work.

1.7.1 Outline of this Thesis

Following the Exposition of the main ideas of RAFT in emulsion polymerization in this chapter, we move to the development and first reports of successful RAFT/emulsion systems.

An outline of the successful use of RAFT in the seeded polymerization of styrene is presented in the codetta, Chapter 2; the full details of how RAFT may be implemented in emulsion polymerization and the unusual behavior observed as a result are discussed in Chapter 3. Describing in more detail the unusual behavior that is seen in these RAFT/emulsion systems, Chapter 4 (the first episode) outlines the specific challenges that face the successful widespread use of RAFT in emulsion polymerization (namely the understanding and amelioration of the inhibition and retardation).

The start of physical understanding of RAFT/emulsion systems is presented in Chapter 5, focusing on the role of chain-length dependent termination in living radical polymerizations mediated by reversible transfer agents (the superset of RAFT and alkyl halide mediated systems). In Chapter 5, the groundwork for the explanation of inhibition, retardation and radical entry and exit rate coefficients is presented.

An introduction to the theory of radical population distributions in emulsion polymerization developed by Smith and Ewart[74] is presented in the second episode, Chapter 6, with a view to understanding what is meant by compartmentalization of radicals in an emulsion polymerization and, more importantly, the possible effects of RAFT on these processes. A method by which suitable average rate coefficients for termination may be calculated from the full chain-length dependent kinetics is presented in Chapter 6. These ideas are then explored with reference to the mechanisms by which radicals may desorb from a particle in Chapter 7. The results of γ-relaxation experiments performed on RAFT-containing seeded emulsion polymerizations are also presented in Chapter 7.

The third episode, Chapter 8, foreshadows the application of this physical understanding to predict various methods for improving the performance of RAFT/emulsion systems. The use of these methods in emulsion polymerization along with a model of the processes involved in inhibition are described in Chapter 9, along with the expected results of these models.

Finally, Chapter 10 is the cadenza; it draws together the different ideas that have allowed this work to progress from oily colored layers to mechanistic understanding from which recommendations for new experimental protocols may be derived.

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