Chapter 7

Compartmentalization in RAFT/Emulsion

Velilind’s Laws of Experimentation:

(1) *If reproducibility may be a problem, conduct the test only once.*
(2) *If a straight line fit is required, obtain only two data points.*

7.1 Abstract

The γ-initiated emulsion polymerization of styrene is reported, showing good control over the molecular weight of the products and a retardation dependent on the concentration of RAFT agent. Examination of the relaxation behavior after the reactor vessel is removed from the γ-source provides direct measurement of radical loss processes. Dormant *z*-meric chains in the particles are postulated to lead to an increase in the rate of radical exit from the particles, with the reactivation of these species generating a *z*-meric radical that is able to desorb from the particle surface in a RAFT-induced exit mechanism, leading to the rapid exchange of radicals between particles. Both γ-relaxation experiments and the semi-quantitative treatment of a previously reported Monte Carlo model show that the relaxations are dependent on the length of the dormant chains. Kinetic parameters are obtained from the γ-relaxation experiments, using pseudo-bulk kinetics to describe the systems. Values of $\langle k_t \rangle$ (the termination rate coefficient averaged over the chain-length distribution of radicals) as a function of the average dormant chain length at high weight-fractions of polymer may thus be determined from these experiments.

7.2 Introduction

The development of techniques for living free-radical polymerization has provided control over molecular architecture for a variety of monomers, allowing the easy synthesis of block copolymers and polymers with well-defined molecular weight distributions, as well as more exotic architectures, such as combs and stars.[1-4] The recently developed living free-radical techniques include nitroxide-mediated polymerization,[5] atom-transfer radical polymerization,[6,7] alkyl halide mediated polymerization[8,9] and reversible addition-fragmentation chain transfer (RAFT) polymerization.[2,10]

Living polymerization techniques have been successfully applied to many solution and bulk polymerization systems; however, application of living polymerization to emulsion polymerization has encountered numerous difficulties. Emulsion polymerization should, in principle, make it possible to obtain higher molecular weights and faster rates of polymerization compared to homogenous systems, as well as presenting other technical and environmental benefits (such as minimal changes in viscosity for high polymer loadings).[11,12] The main difficulties that have been experienced have been in maintaining colloidal stability, achieving reasonable reaction rates and controlling molecular weight polydispersity. It has previously been noted that the loss of deactivating species (such as the transition metal complexes used in ATRP or the stable nitroxide radical) through desorption from the particles may be problematic,[13] a difficulty that is easily prevented in systems mediated by reversible transfer kinetics, such as RAFT/emulsion polymerizations.

Significant advances have been made with low transfer constant xanthates[14] and high transfer constant dithioester RAFT agents,[15,16] with the seeded emulsion polymerization by Prescott *et al.*[16] and *ab initio* polymerizations of Ferguson *et al.*[17] illustrating the first implementations of RAFT in emulsion polymerization to avoid the abovementioned difficulties. These systems were developed by explicitly designing systems in which transport of the RAFT agent through the continuous phase is not required during polymerization.

While RAFT-mediated polymerizations can now be carried out in both heterogeneous and homogeneous systems, a reduction in the rate of polymerization is seen in many reactions in which good molecular weight control is achieved. Theories for the reduction in the rate of polymerization due to the addition of the RAFT agents have included the slow fragmentation of the intermediate bipolymeric radical,[18-20] irreversible[21] and reversible[3,22] termination of the intermediate radical and, most recently, the influence of chain-length dependent (CLD) termination.[23] Interestingly, there is a factor of ~10^6 difference in the expected concentration of the intermediate radical species between these models, a point that has widened the debate rather than resolved it.[24-26]

Retardation due to reactions of the intermediate bipolymeric radical are dependent on the nature of the RAFT agent being used, in particular the stability of the intermediate radical through the action of the stabilizing group of the RAFT agent, Z. In the case of a benzyl activated RAFT agent, such as the one used by Prescott *et al.*[16] and the trithiocarbonates used by Ferguson *et al.*,[17] the intermediate radical is much less stable than that of a phenyl activated RAFT agent.[20] Retardation due to CLD termination, however, is intrinsic to all living polymerizations.[23]

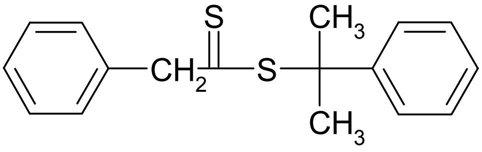
Monte Carlo modeling suggests that there is significant retardation due to CLD termination in RAFT-mediated polymerizations.[23] The effects of reversible transfer agents, such as RAFT agents, are expected to be seen in both homogeneous and heterogeneous polymerization systems, the rate coefficients for termination being greater for short chains than for long chains due to their different diffusion rates. The rate of polymerization is reduced by the RAFT agent as it changes the length of the radicals in the polymerization.[23] The essence of the inferences from this work is that RAFT systems differ from conventional free-radical polymerizations because the dominant mode of termination is the reaction between chains of equal length in RAFT-mediated systems, but between short and long chains in conventional systems. In summary, at low conversion, the dormant chains are short and the propagating radicals are on short chains, hence termination is a short-short reaction with high rate coefficient; conversely, at high conversion, the radicals and dormant chains are predominantly long, making termination proceed on the time scale of a long-long reaction with a much-reduced rate coefficient.

Based on these CLD termination arguments, it was deduced that RAFT/emulsion systems with high-activity RAFT agents were unlikely to follow the same simple kinetic models for emulsion polymerization (*viz.*, “zero-one” and “pseudo-bulk”) as the equivalent non-RAFT systems.[23] Moreover, it was concluded that the kinetics of polymerization for RAFT/emulsion systems would change throughout the reaction as the length of the propagating radicals change throughout the course of the reaction. While it was deduced by Prescott[23] that the “zero-one” limit[12,27] of the Smith–Ewart equations was inappropriate for RAFT/emulsion systems studied (styrene at 50°C) except at quite low conversion and with small particles, the applicability of other simplified kinetic schemes remains unclear. In particular, the applicability of pseudo-bulk kinetics is of interest, as this limit of the Smith–Ewart equations provides a simple conceptual understanding of emulsion polymerization and permits kinetic parameters to be determined with a minimum of model-based assumptions.[12,28] The role of these limits and their applicability to RAFT/emulsion systems is discussed below.

The usefulness of γ-radiolysis in understanding mechanisms in emulsion polymerization is in the study of the changes in polymerization rate after the reactor vessel is removed from the γ-source; this provides direct information about radical loss processes, separate from radical creation. These loss processes are termination ones, occurring either entirely within the particles (which is the same process as termination in bulk or solution free-radical polymerization) or termination following exit of a radical from a particle (which is a process peculiar to radical polymerization in dispersed media, such as emulsion polymerization). Here, the results of γ-radiolysis experiments are presented, establishing that RAFT-mediated emulsion polymerization may be successfully undertaken with γ-initiation and providing additional kinetic data about the RAFT/emulsion systems from relaxation experiments. A semi-quantitative treatment of the previously presented Monte Carlo model[23] is also used, with particular emphasis on understanding the γ-radiolysis experiments. The role of compartmentalization of the radicals in RAFT-mediated emulsion polymerization is also investigated, focusing on the possible desorption of oligomeric radicals and the consequences for the kinetic schemes applicable to RAFT/emulsion systems.

7.2.1 RAFT in Seeded Emulsion Polymerization

In a previous study of the kinetics of RAFT/emulsion systems, the seeded emulsion polymerization of styrene with persulfate initiator and mediated by the benzyl-activated RAFT agent PPPDTA (Scheme 7.1) was followed by dilatometry.[16] In that initial study, it was reported that the rate of polymerization was reduced by the addition of the RAFT agent and that the degree to which the rate of polymerization was reduced was dependent on the ratio of initiator to RAFT agent used. The system showed good control of molecular weight, no formation of colored, oily layers and no loss of colloidal stability.



(1)

Scheme 7.1: The benzyl-activated RAFT agent 2-phenylprop-2-yl phenyldithioacetate (PPPDTA).

While measuring the conversion as a function of time allows the rate of polymerization and the average number of radicals per particle, $\bar{n}$, to be determined, it is not possible to obtain unambiguous mechanistic information on the emulsion polymerization process accurately with the information available from such chemically-initiated studies alone. A useful technique for obtaining unambiguous kinetic parameters is the γ-relaxation experiment, which has been extensively used with various monomers including styrene,[29-31] methyl methacrylate,[32] and vinyl acetate,[33] as well as the RAFT-mediated polymerization of styrene using xanthates.[14] The strength of the γ-relaxation experiment is that the external source of radicals (*i.e.* the γ-induced decomposition of water into various radical species[34,35]) may be turned on or off at will, simply by introducing or removing the sample from the γ-source; thus, γ-relaxation provides two steady-state values of $\bar{n}$ (in-source and out-of-source), as well as the approach to the new steady state. While the initiating radicals in γ-radiolysis are a mixture of species including $H^\bullet$ and $OH^\bullet$, the relaxation behavior of non-RAFT emulsion polymerizations is expected to be independent of these initiating radicals and so the inferences about radical loss processes are more generally applicable.

7.2.2 Chain-Length Dependent Termination

The termination reaction in free-radical polymerizations has been shown experimentally[36,37] and through theoretical arguments[38,39] to be controlled by the diffusion of the radical chain ends towards each other; in systems in which the polymer fraction is above *c** (the concentration at which chain overlap occurs), this process seems to be controlled by the center-of-mass diffusion of the parent chains, except at very high polymer fraction, when reaction-diffusion, caused by chain propagation, may take over.[39] A direct consequence of this is that the kinetics of the termination reaction are chain-length dependent (CLD) as the diffusion of the polymeric radicals is slowed as the length of the polymer chain increases. Indeed, various experimental results have shown that CLD termination is necessary for the adequate interpretation of experimental data[30,36] and that termination in a classical emulsion polymerization (indeed, any conventional free-radical polymerization) is predominantly a short-long reaction between short radicals entering particles from the aqueous phase or generated by transfer to monomer reactions.[30] It has been previously shown by Prescott[23] that the CLD termination reaction has a profound influence on the kinetics of RAFT-mediated polymerizations, in particular RAFT/emulsion systems.

Including CLD termination in models of emulsion polymerization is difficult for two reasons.[23] First, termination rate coefficients that are valid at both high weight fractions of polymer, w_p, and for chains of polymeric (not oligomeric) length are required. At present, the available models are either for quite short chain-lengths, but high w_p,[40] or for polymeric chain-lengths at vanishingly low w_p.[36,37,41] For qualitative treatments, such as that presented previously,[23] this was not particularly problematic as the important feature of the modeling was that termination had *some* chain-length dependence, not the specific details of the dependence.

Second, the evolution equations describing the rate and molecular weight distribution, incorporating the compartmentalization of radicals into discrete particles, become extraordinarily complex except in the two limiting cases of zero-one and pseudo-bulk kinetics.[12] Thus, the "zero-one-two" evolution equations,[42] which should provide a quantitative description for systems not satisfying the conditions of either the zero-one and pseudo-bulk limits, involve coupled non-linear partial integrodifferential equations in three independent variables and have, so far, only been solved in the manner recently described.[43] This situation becomes even more complex in a RAFT system because of the need to account for the chain-length distribution of dormant chains. While the two limits, zero-one and pseudo-bulk, are widely applicable in conventional emulsion polymerizations, this is not the case for RAFT systems,[23] and at present, it appears that one is forced to use Monte Carlo simulations. Apart from the very long computational times that this involves, such simulations do not provide simple means of extracting information such as rate coefficients through comparison to experiments (*cf.* the "slope-intercept" method,[12,27] which enables the rate coefficients for radical entry and exit to be extracted from the time evolution of conversion in conventional zero-one systems, with minimal model-based assumptions). However, the Monte Carlo simulations give the means of determining the probability of a radical terminating in a particle as a function of its chain length, as discussed for non-RAFT systems previously,[43] and this opens the way to prediction and interpretation of relaxation data.

Prior to interpreting the relaxation experiments, the key qualitative results from the modeling work of Prescott[23] for RAFT/emulsion with a high-activity RAFT agent will be summarized. At low conversion, all dormant chains and the propagating radicals are short. Thus, termination in this system is a short-short reaction ($k_\mathrm{t}^{\text{short-short}}$) and is faster than would be expected in the absence of the RAFT agent ($k_\mathrm{t}^{\text{short-long}}$). It is noted that these termination rate coefficients are in fact averages over the chain-length distribution of the growing radicals of the microscopic values of the termination rate coefficients (*i.e.* averages of k_t^{ij}, where i and j denote individual degrees of polymerization but there are distributions of the lengths i and j) . As a consequence, the lifetime of the radical is reduced by the addition of the RAFT agent. Thus, if zero-one kinetics were applicable in the non-RAFT system, then they are also applicable in the RAFT-mediated system at low conversion.

At higher conversion, the dormant chains (and the propagating radicals) are longer; hence, radical lifetimes are increased by the addition of the RAFT agent. This is because the entering radical transfers rapidly to one of the longer dormant chains, creating a short dormant chain. Termination then requires either a long-long reaction, $k_{\mathrm{t}}^{\text{long-long}}$, or transfer of radical activity back to the short dormant chain followed by short-long termination. Both long-long termination and transfer back to one specific dormant chain are less likely to occur than propagation and, so, the termination reaction is suppressed. The transfer of radical activity back to the shortest dormant chain (the dormant species resulting from the transfer of the entering *z*-mer), though only present in relatively low concentrations, is an important route to termination, occurring frequently in the case of high-activity RAFT agents.

A significant outcome of the Monte Carlo modeling of Prescott[23] is that low-activity RAFT agents have little effect on the kinetics of emulsion polymerization as the probability of transfer is so low as to not alter whether a system will follow zero-one kinetics. The previously noted effects of low-activity RAFT agents on emulsion polymerizations have been explained in terms of the surface activity of the RAFT agents used and the "frustrated entry" of oligomeric radicals.[14]

In discussing the CLD kinetics in RAFT-mediated polymerizations, the molecular weight control of the RAFT agent is considered, the molecular weight (or the length of the dormant chains in the system) being the parameter of primary concern. In a system that is under good RAFT control (*i.e.* a system where polymerization is mediated by a high-activity RAFT agent such as PPPDTA), the number-average molecular weight is given by:

$$\overline{M}_{\mathrm{n}} = x \frac{m_{\mathrm{mon}}}{n_{\mathrm{RAFT}}} \tag{7.1}$$

where x is the fractional conversion, m_{mon} is the mass of monomer initially added to the system and n_{RAFT} is the amount of RAFT agent added. The average length (degree of polymerization) of the dormant chains, $\bar{X}_{\mathrm{n,d}}$, is used as a measure of the progress of the reaction (in many instances, $\bar{X}_{\mathrm{n,d}}$ may be used as a measure of conversion normalized for the amount of RAFT agent initially added). For an Interval III emulsion polymerization (*i.e.* in the absence of monomer droplets[12]) in the presence of a high-activity RAFT agent with an initial monomer concentration $[\mathrm{M}]_0$, $\bar{X}_{\mathrm{n,d}}$ is given by:

$$\bar{X}_{\mathrm{n,d}} = \frac{x[\mathrm{M}]_0}{[\mathrm{RAFT}]} \tag{7.2}$$

7.2.3 The Nature of Compartmentalization

Compartmentalization in emulsion polymerization is the primary reason that the kinetics of polymerization are often substantially different from those of homogeneous systems.[12] In an emulsion polymerization, the radicals in one particle generally cannot react with the radicals in another particle, as they are physically separated by the particle/water boundaries and the aqueous phase between them (in general, the propagating radicals in emulsion polymerizations are quite hydrophobic). This isolation of radicals in one particle from radicals in other particles is referred to as the compartmentalization of radicals and often leads to an increase in the rate of polymerization, as the rate of termination may be reduced by this effect.[12]

Whether compartmentalization affects a system may be determined by considering the Smith–Ewart equations[44] (or more precisely using a more complete system where explicit account is taken of the distributions of the lengths of both radical and dormant chain in each particle: an extremely complex set of hierarchical equations[42]). The original Smith–Ewart equations[44] consider the populations of particles with i radicals, N_i, in terms of the pseudo-first-order rate coefficient for radical entry into the particles, ρ, the first-order rate coefficient for the exit of a radical from a particle, k, and the pseudo-first-order rate coefficient for the annihilation of two radicals, c. As described previously,[43] the value of c used in the Smith–Ewart equations may be related to an appropriate average of the contributing termination rate coefficients.

7.2.4 Particle Growth Kinetics

The various kinetic models for the growth of emulsion polymerization particles have permitted many rate coefficients to be reliably obtained from experimental data for a variety of systems.[12] The applicability of these kinetic models to RAFT in emulsion polymerization has been the subject of previous discussion.[14,15,23] The results of Prescott[23] showed that the zero-one model is often inappropriate for RAFT/emulsion systems, in particular in systems with both long dormant chains (*i.e.* $\overline{M}_n \gtrsim 1000$) and high-activity RAFT agents. The applicability of other kinetic schemes such as pseudo-bulk kinetics will be considered in this work.

Ballard *et al.*[28] demonstrated two methods of solving the Smith–Ewart equations (in the absence of CLD termination), using different closure relations to reduce the infinite set of equations described by Smith and Ewart[44] to a tractable problem. A general recursion approach to solving the Smith–Ewart equations (in the absence of CLD termination) was presented by Ballard *et al.*,[28] allowing the populations of each of the N_i and, hence, $\bar{n}$ to be estimated. This method is used here to estimate the accuracy of various limits of the Smith–Ewart equations.

The most widely used solution to the Smith–Ewart equations presented by Ballard *et al.*[28] has become known as the "pseudo-bulk equation", as it represents the emulsion polymerization in terms of an equivalent bulk system (complete re-entry of desorbing species is required for this pseudo-bulk approximation).[28]

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho_1 - 2c\bar{n}^2 \tag{7.3}$$

However, the formulation of the Eq. 7.3 relies on the moment transformation $\overline{n^2} - \bar{n} \approx \bar{n}^2$, a relation that is only appropriate if $\bar{n}$ is sufficiently large. Comparison of the exact solutions to the Smith–Ewart equations and Eq. 7.3 shows that $\bar{n} \gtrsim 0.7$ is sufficient for Eq. 7.3 to be a reasonable approximation (*i.e.* $c < \rho_1$); Eq. 7.3 is also applicable when the system is highly uncompartmentalized (*i.e.* $c < k$, which also implies low $\bar{n}$ unless $c < \rho_1$).

To adequately describe the kinetics of the RAFT/emulsion systems, values of ρ, c, and k are required, and appropriate account needs to be taken of the fate of exited free radicals. Values of ρ can be successfully estimated from the Maxwell–Morrison theory for entry of oligomeric radicals into particles.[31,45] Values of c may be estimated from diffusion-controlled models for termination[39,46] (to within the limits noted for existing diffusion models), and values for k may be estimated using the RAFT-induced exit model presented here.

7.2.5 Relaxations and Radical Exit

In a γ-relaxation experiment, the system is initially subjected to γ-radiation until a steady state of polymerization is reached. The sample is then removed from all external initiation sources and the system relaxes from one steady state to another. In the experiments described here, this is done by means of a lead-encased lift mechanism that is capable of moving the autodilatometer and sample into the irradiation chamber.[11] When out of the γ-source, the system is not necessarily without radical sources, however, as the auto-initiation or spontaneous generation of radicals is still seen with monomers such as styrene[47] and chlorobutadiene.[48]

The relaxation is dependent not only on the entry of new radicals to lead to termination but also on the movement of radicals between particles. Relaxations of the emulsion polymerization of styrene have been described as follows.[29,30,47] Transfer to monomer reactions generate small, mobile radicals that have the ability to exit from a particle, and move from one particle to another. Upon re-entry, the monomeric radical may either terminate with a radical, should there be a pre-existing radical in the particle, or commence propagation. This process is illustrated in Fig. 7.1.

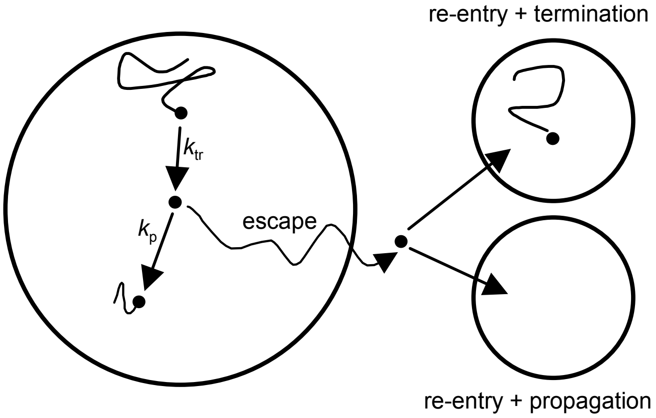


Figure 7.1: A schematic representation of the process by which the reduction in radical numbers occurs during a relaxation experiment.

The frequency of radical exit thus determines the timescale of the relaxation. Generalizing from this, a system that is highly uncompartmentalized due to the rapid exchange of radicals between particles (*i.e.* when k is quite large and there is complete re-entry of exited radicals) will have faster relaxations than a system that has a slower exchange of radicals (*i.e.* a lower value of k). The slow relaxation limit is described by a system in which monomeric radicals never desorb, because either $k_{tr} = 0$ or $k_{dM} = 0$ (where k_{tr} is the second-order rate coefficient for transfer to monomer and k_{dM} is the first-order rate coefficient for desorption of a monomeric radical from a particle).[12]

It may be noted that the rate coefficient for transfer to monomer should not be altered by the presence of a RAFT agent. Thus, a RAFT-mediated system that still follows zero-one kinetics (*e.g.* at low conversion with short dormant chains) would not be expected to show relaxation kinetics different from those of the equivalent non-RAFT system given the present level of understanding of RAFT/emulsion systems.

7.2.6 Adsorption and Desorption of Radicals

The processes involved in the entry of radicals into particles were first described by Maxwell *et al.*[45] The Maxwell–Morrison model for radical entry has been shown to agree with a large range of data (see the work of van Berkel *et al.*[31] and references therein). It identifies the rate-determining step in the entry process as the propagation of the aqueous phase radicals to a length at which they may be considered to be surface active. This critical degree of polymerization for the radical to enter a particle is denoted z and, for reasonably hydrophobic monomers such as styrene with a water-soluble persulfate initiator, $z = 2–3$. This model has been successfully used to account for the entry efficiency in emulsion polymerization,[31,45,49,50] the homogeneous nucleation of new particles,[51-53] and the formation of core-shell particles.[53,54]

As a conceptual simplification, Maxwell *et al.*[45] suggested that a reasonable picture of the entry process was that a surface-active radical would enter the first particle with which it collided although, in Appendix B of their paper, Maxwell *et al.*[45] demonstrated that this assumption could be successfully relaxed with only minor quantitative effects. It was estimated that a z-meric styryl radical was much more likely to desorb from a particle than to enter it during an encounter; a z-mer would interact with the surface of many particles (of order 10^2, on average) before a propagation event occurred within one of these particles, making the radical sufficiently water-insoluble as to be quite unlikely to desorb once more.

That the immediate and irreversible entry approximations are appropriate in many systems was demonstrated by comparing the frequency of desorption from a particle to the frequency of other fates for the radical, in particular aqueous phase propagation, aqueous phase termination and particle-phase propagation.[45] However, the ability for a surface-active z-meric radical to desorb from one particle and move to another is quite significant for living polymerization systems in which the entering z-mer does not necessarily have to propagate to a (z+1)-mer in order for radical activity to enter the particle; radical entry is thus reversible. This “RAFT-induced exit” mechanism is further developed here, with an attempt made to quantify the effect and its influence on the Smith–Ewart kinetics evaluated.

7.2.7 RAFT Polymerization with γ-Initiation

Diothioester-mediated polymerizations using γ-initiation were recently investigated by Hong *et al.*,[55] the “iniferter” process being proposed as the mechanism by which polymerization was mediated. Quinn *et al.*[56,57] subsequently demonstrated that these polymerizations were mediated by the conventional RAFT process, showing the successful RAFT-mediated polymerization of several monomers with various dithioesters in bulk and solution polymerization systems. In addition, there have recently been reports of the successful γ-initiated emulsion polymerization of styrene mediated by xanthates.[14]

The RAFT agent used in this study is the phenyl stabilized 2-phenylprop-2-yl phenyldithioacetate (PPPDTA), the use of which has been reported in the successful emulsion polymerization of styrene[16] and also in the γ-initiated polymerization of styrene.[58] It is thus expected that the γ-initiated emulsion polymerization of styrene mediated by PPPDTA should proceed via the RAFT mechanism without additional complications. NMR analyses of the products of the γ-initiated polymerization of styrene in the presence of PPPDTA were performed to verify that the appropriate products were obtained (including intermediate radical termination products), as described below.

7.3 *Theoretical Section*

7.3.1 Treatment of Dilatometry Data

Dilatometry data for γ-relaxation experiments can be designed to provide extensive data: numerous relaxations, approaches to steady states, as well as both the in-source and out-of-source steady states may be observed. Without reference to any models of the system, it is possible to determine conversion *vs* time and $\bar{n}$ *vs* time from these data, as shown previously for the seeded emulsion polymerization of styrene with PPPDTA.[16] To obtain further information from the data requires the application of an appropriate model for the evolution of $\bar{n}$ as a function of time. The use of zero-one or pseudo-bulk kinetics provides a method of extracting uniquely determined kinetic parameters, whereas treatment using a full chain-length dependent zero-one-two system[42] involves great numerical difficulty, even if one were to adopt a simple functional form for the chain-length distribution dependent rate coefficients, making the unique assignment of the parameters questionable.[12]

At the simplest level, radical loss may be treated as being a process that is either first- or second-order in $\bar{n}$. However, it has been shown that, in the presence of significant spontaneous radical generation (as is the case with styrene, for example), it is not usually possible from rate data alone to differentiate between first-order and second-order processes due to experimental uncertainties.[12]

On occasion, such as for the xanthate-mediated emulsion polymerization of styrene,[14] modeling by analogy to well-understood systems can adequately describe the kinetic behavior of the system and provide meaningful kinetic parameters. In the case of the RAFT/emulsion systems considered here, it has previously been shown that the zero-one limit may be applicable at low conversions, but is inappropriate for most of the reaction.[23] Cautiously drawing analogy to the equivalent non-RAFT system, it is likely that all exited radicals would re-enter another particle and propagate in that particle rather than re-exiting.[12] When zero-one kinetics are appropriate, this is described by "Limit 2a",[12,59] giving a relaxation process that contains both first- and second-order dependence on $\bar{n}$. On the other hand, should pseudo-bulk kinetics be appropriate, the kinetics will be purely second-order in $\bar{n}$.

In the alternative case of a system in which intra-particle termination is rate determining for annihilation of the radicals (*e.g,* a pseudo-bulk system) and all exiting radicals re-enter, the relaxation is a radical loss process that is second-order in $\bar{n}$:

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho - 2c\bar{n}^2 \tag{7.4}$$

which reduces to the following expression for a relaxation (*i.e.* final $\bar{n}$ < initial $\bar{n}$):

$$\bar{n}(t) = \frac{\bar{n}_{\mathrm{sp}}}{\tanh\left(2\bar{n}_{\mathrm{sp}}ct + \tanh^{-1}\left(\frac{\bar{n}_{\mathrm{sp}}}{\bar{n}_{\mathrm{i}}}\right)\right)} \tag{7.5}$$

where $\bar{n}_{\mathrm{sp}}$ is the experimentally determined $\bar{n}$ due only to spontaneous initiation and $\bar{n}(t=0) = \bar{n}_{\mathrm{i}}$.

The appropriate treatment of the experimental data is not only concerned with the choice of differential equations to use in the modeling; the data-processing procedures are also important. While plots of $\bar{n}$ *vs* time provide a useful pictorial view of the relaxation, the process of numerically differentiating experimental data introduces significant amounts of noise to the data as well creating interdependencies between points (*e.g.* if a three-point derivative method is used). Moreover, the naïve fitting of the $\bar{n}$ *vs* time data tends to place significantly more weight on the data points immediately following the removal from the source when any mechanical or temperature instabilities are at their worst. For these reasons, it is preferable to fit the conversion *vs* time data from the dilatometry experiment to the integrated form of the kinetics (*e.g.* Eq. 7.5). The use of a simplex algorithm to perform this curve fitting is quite appropriate.

7.3.2 Monte Carlo Simulation of RAFT/Emulsion

The previously reported Monte Carlo modeling of radicals in RAFT-mediated emulsion polymerization[23] is extended here with a semi-quantitative treatment of the previously reported results. It is useful to briefly review the significant features of the model (omitting the implementation details, as they are identical to those previously reported) before embarking on further development.

The physical system described by the Monte Carlo modeling consists of a particle with a pre-existing radical that has a new radical enter it from the aqueous phase. These two radicals may then undergo reactions, either propagating or terminating with each other (in a chain-length dependent manner). The inclusion of dormant chains from the RAFT process complicates this simple kinetic scheme considerably, as the additional reaction pathway of transfer to dormant chains provides a mechanism by which the length of the radical may change. It is this complication added to CLD termination that makes analytic solution impossible and Monte Carlo modeling attractive. The primary data obtained from the Monte Carlo model[23] are the probabilities P_j that j or more monomer units will be consumed in a two radical environment before termination occurs.

The number of propagation steps that takes place inside this test particle before termination occurs gives an indication of the validity of zero-one kinetics;[23,60] since the appropriateness of zero-one kinetics is inherently linked to the Smith–Ewart parameter c, it becomes a natural extension to the Monte Carlo model to attempt to link P_j, the probability of a radical consuming at least j monomer units, to c.

For the purpose of later quantitative comparison with experiment, it is noted that the termination model used in the Monte Carlo simulations[23] was the diffusion model of Russell *et al.*[39,46] combined with an empirical scaling law developed by Griffiths *et al.*,[40] as follows:

$$k_\mathrm{t}^{ij} = 4\pi(D_i+D_j)p^{ij}\sigma N_\mathrm{A} \tag{7.6}$$

with

$$\frac{D_i(w_\mathrm{p})}{D_1(w_\mathrm{p})} = i^{-(0.664\,+\,2.02\mathrm{w_p})} \tag{7.7}$$

where σ is the distance at which two radical centers undergo termination (the position of the transition state, closely approximated by the van der Waals radius of monomer[61]) and $D_1(w_\mathrm{p})$ is the center-of-mass diffusion coefficient of monomer at polymer weight fraction w_p (the full expression for this quantity given in the cited references has been simplified to take account of the conditions applicable to an emulsion polymerization). The diffusion coefficient and scaling "law" in this equation are taken from Griffiths *et al.*[40,62] It is noted that this scaling "law" was deduced only for oligomeric diffusion. While this is quite acceptable for conventional free-radical polymerization, where termination is dominated by the diffusion of short radicals, it may well not be applicable to controlled radical systems, where termination becomes dominated by termination between chains of approximately equal, and eventually non-oligomeric, degrees of polymerization. In the present work, additional Monte Carlo modeling results are included using an alternative scaling law (see Section 7.6.3).

7.3.3 Semi-Quantitative Treatment of Monte Carlo Results

The P_j *vs* j curves presented previously for the RAFT/emulsion polymerization of styrene provide a useful means of determining the appropriateness of zero-one kinetics.[23] By looking at the average number of monomer units consumed in a test-particle, $\overline{\Delta_\mathrm{m}}$, it is possible to obtain a value of c from the Monte Carlo simulation.[43] In short, c may be obtained from the P_j *vs* j curve for a test particle initially containing two radicals by first recognizing that:

$$\overline{\Delta_\mathrm{m}} = \sum_{j \geq 0} P_j \tag{7.8}$$

From this it follows that:

$$\overline{c}(t) = \frac{k_\mathrm{p} C_\mathrm{p}}{\overline{\Delta_\mathrm{m}}} \tag{7.9}$$

where $\overline{c}(t)$ is chain-length independent average of contributions of the termination rate coefficients with appropriate weighting for the lengths of the radicals involved. The time-dependence of $\overline{c}(t)$ is a dependence on the chain-length distribution, as described by Clay *et al.*,[42] which changes as the diffusion coefficients (hence termination rate coefficients) slow with increasing w_p. In the case where a system is zero-one but following kinetics with a second-order loss of radicals (such as "Limit 2a" kinetics[12]), the rate coefficient for second-order radical loss is not c and will not be described by this model.

While this would appear to provide a convenient method of interpreting the Monte Carlo results, evaluating $\overline{\Delta_{\mathrm{m}}}$ is fraught with difficulties. The Monte Carlo model uses a CLD termination model applicable to short chain lengths (as noted above), but is expected to be erroneous for longer chain lengths. Moreover, the model as originally presented does not include transfer to monomer, hence will over-estimate the length of the radical when c is low.

Additional complication comes from the need to consider the number of chains that terminated as a function of the amount of monomer consumed; in situations where c is small, exceedingly large numbers of test particles must be considered to achieve a reasonable number of terminated chains (*i.e.* to obtain suitable precision from the simulation). A final difficulty is that $\overline{\Delta_{\mathrm{m}}}$ is an integral with an infinite upper bound. In order to achieve good convergence for $\overline{\Delta_{\mathrm{m}}}$ by direct integration of the model output, the minimum j that must be considered is often far in excess of what may be feasibly simulated.

Recognizing the above caveats and making suitable approximations, the model provides a semi-quantitative measure of c, useful for understanding the effect of RAFT agents in changing the length of the propagating radicals.

7.3.4 Desorption of Oligomeric Radicals

In an emulsion polymerization initiated by an aqueous phase chemical initiation, a surface active oligomeric radical (a z-mer, in the terminology of Maxwell *et al.*[45]) may explore the surface of many particles before irreversibly entering a particle.[45] In many systems, it is sufficient to assume that the radical enters irreversibly into the first particle it encounters.[45] Maxwell *et al.*[45] showed this by comparing the frequency of desorption from a particle (typically[63] 10^4 to 10^6 s^{-1}) to the timescale of other fates for the radical, in particular aqueous phase propagation and aqueous phase termination. The frequency of aqueous propagation of the z-mer is $k_{\mathrm{p,aq}}^{z}C_{\mathrm{w}}$ (where C_{w} is the aqueous phase monomer concentration) and is typically of order 1 s^{-1}. Termination with other aqueous phase radicals (which typically have concentrations[52] of 10^{-9} M) also occurs with a frequency of order 1 s^{-1}.

However, in the case of a RAFT-mediated polymerization, the reaction that can cause the radical to enter the particle can be either propagation or transfer of radical activity to a dormant chain. This reaction leaves a *z*-meric-RAFT adduct $^{-}\mathrm{IM}_z\text{–S–C(Z)=S}$ on the surface of the particle that is then able to be reactivated later in the reaction. The probability of entry through formation of such a *z*-meric dormant species is high, with *P*(form adduct) being given by:

$$P(\text{form adduct}) = \frac{k_{\text{tr,RAFT}}[\text{RAFT}]}{k_\text{p}C_\text{p} + k_{\text{tr,RAFT}}[\text{RAFT}]} \tag{7.10}$$

For a high-activity RAFT agent with transfer constant $C_\text{tr} = 6000$ mediating the Interval II polymerization of styrene at 50 °C (propagation rate coefficient[64] $k_\text{p} = 237\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, monomer concentration in the particles[12] $C_\text{p} = 5.5$ M) and [RAFT] = 8.5 mM, *P*(form adduct) is 0.90. The formation of *z*-meric RAFT adducts is, thus, a significant process, not merely a marginal effect. For the purposes of this discussion, “*z*-meric RAFT adduct” refers only to the initiator-derived *z*-meric species, not $\mathrm{R}^{\bullet}$-derived chains (formed from the re-initiating group R) that have degree of polymerization *z*.

The *z*-meric RAFT adduct is water-insoluble to the extent that it is a surface-active species with a thiocabonylthio end-group; hence, it will remain dormant on the surface of the particle until such time as it is reactivated via a transfer reaction. At that stage, the short radical so generated will have four possible fates: it may transfer activity to another RAFT agent, propagate, terminate with another radical (should there be one present in the particle) or desorb from the particle. As the *z*-mer is identical to the surface-active oligomeric radical that first entered the particle (which may have previously explored the surface of many particles), it is now free to leave that particle and explore the surface of other particles before repeating the same process.

This process is depicted pictorially in Fig. 7.2 and may be formalized in the following scheme:

$$^{-}\mathrm{IM}_z^{\bullet}(\mathrm{aq}) \underset{k_{\mathrm{d}z}}{\overset{k_{\mathrm{a}z}}{\rightleftharpoons}} {}^{-}\mathrm{IM}_z^{\bullet}(\mathrm{p}) \tag{7.11}$$

$$^{-}\mathrm{IM}_z^{\bullet}(\mathrm{p}) + \mathrm{P}_n\text{–}\mathrm{X} \underset{k_{\mathrm{tr,RAFT}}}{\overset{k_{\mathrm{tr,RAFT}}}{\rightleftharpoons}} {}^{-}\mathrm{IM}_z\text{–}\mathrm{X}(\mathrm{p}) + \mathrm{P}_n^{\bullet} \tag{7.12}$$

$$\mathrm{P}_n^{\bullet} + \mathrm{M} \xrightarrow{k_{\mathrm{p}}} \mathrm{P}_{n+1}^{\bullet} \tag{7.13}$$

where the state marking "(p)" denotes the particle phase, X denotes the thiocarbonylthio deactivating group, and $k_{\mathrm{a}z}$ and $k_{\mathrm{d}z}$ are the rate coefficients for the adsorption and desorption of the z-meric radical, respectively. Alternative pathways of propagation of the z-meric radical and termination with another radical are not shown in Fig. 7.2 for simplicity.

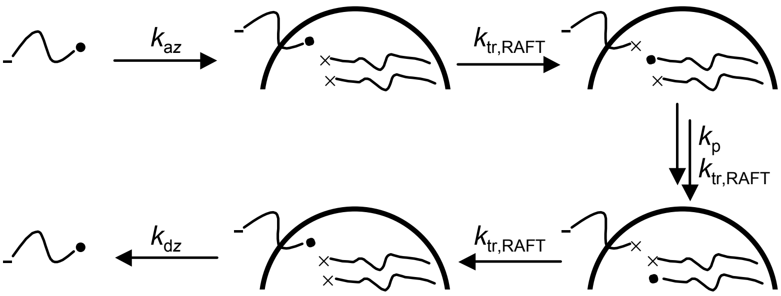


Figure 7.2: A schematic representation of the loss of compartmentalization through the regeneration of desorbing radicals from dormant z-meric RAFT-adducts. Symbols: radical •, dormant end group ×.

The sequence of events outlined in Fig. 7.2 is that the forward reactions of Eq. 7.11 and 7.12 proceed before propagation (Eq. 7.13) occurs. Somewhat later, the reverse reactions of Eq. 7.12 and then 7.11 lead to the loss of radical activity from the particle. In many ways, this process of transfer back to a dormant species followed by desorption is the same as transfer to monomer followed by exit of the monomeric radical. The overall effect of this is to decrease the compartmentalization of the system in the same way as addition of a highly active chain transfer agent, for example, can make a zero-one system progressively less compartmentalized until it becomes pseudo-bulk (k is increased until $k \gg c$). This phenomenon may be described as a "RAFT-induced exit" mechanism.

It may be noted that in a γ-initiated system, the z-meric species does not exist as there are no charged initiators present. However, initiation by γ-irradiation tends to produce an initiating radical flux that is predominantly $M^\bullet$ and $HOM^\bullet$ species (where $HOM^\bullet$ is the product of the addition of $HO^\bullet$ across the vinyl group).[35] These species have a water solubility similar to that of the monomer itself ($HOM^\bullet$ being somewhat more soluble that M) and would, thus, be able to enter and exit from the particles in a manner similar to that described by Casey *et al.*[65] for the desorption of monomeric radicals formed by transfer to monomer reactions. The kinetic scheme for RAFT-induced exit may be simply reworked in terms of entering and desorbing $M^\bullet$ and $HOM^\bullet$ species.

Estimating the rate coefficients for the adsorption and desorption processes in order to understand the importance of this effect is non-trivial. Maxwell *et al.*[45] supposed that entry to the particles was a diffusion-limited process, with the charges on the particle and entering oligomeric radical having little effect. This has since been seen experimentally in the work of van Berkel *et al.*,[31] where anionic and cationic surfactants were used with both anionic and cationic initiators. Using a Smoluchowski model for the adsorption rate coefficient, the following expression is obtained:

$$k_{\mathrm{a}z} = 4\pi D_z r_{\mathrm{s}} N_{\mathrm{A}} \tag{7.14}$$

where D_z is the diffusion coefficient for the z-mer and r_{s} is the swollen radius of the particle.

In assessing the influence of the repeated adsorption and desorption of oligomeric radicals from particles, Maxwell *et al.*[45] made use of the studies of Almgren *et al.*[63] on the adsorption and desorption of neutral arenes. Other studies of surfactant entry and exit with micelles corroborate this model.[66] While these data will be used for lack of more appropriate rate coefficients to describe these processes, it must be noted that they provide, at best, order of magnitude estimates for the desorption rate coefficients.

It may be seen from the data of Almgren *et al.*[63] that the exit rate coefficient for the neutral arenes was 10^4 to 10^6 s^{-1} for the variety of species studied. Moreover, the work of Aniansson *et al.*[66] showed exit rate coefficients for alkyl surfactants of similar molecular weight to the z-mer (for styrene monomer with persulfate initiator, $z = 2$ or 3) of 10^5 to 10^7 s^{-1}. As these two species are the natural analogs to consider for the desorption of surface-active oligomeric styrene, the precedent of Maxwell *et al.*[45] may be followed, adopting a value of $k_{dz} \sim 10^5\ s^{-1}$.

It is now possible to estimate the probability of the z-meric radical exiting a particle, $P(\text{exit-}z)$, once it is regenerated. An expression for $P(\text{exit-}z)$ may be developed in terms of the (pseudo-) first-order rate coefficients for the possible fates of the radical:

$$P(\text{exit-}z) = \frac{k_{dz}}{k_{dz} + k_p C_p + k_{\text{tr,RAFT}}[\text{RAFT}]} \tag{7.15}$$

The fate where the z-meric radical once again transfers is kinetically uninteresting (and there may be another opportunity for desorption at a later stage). In the case where another radical exists in the particle, termination may be trivially included in Eq. 7.15.

The Smith–Ewart parameter for loss of a radical by exit from a particle, k, may now be estimated from this model, by combining the effect of transfer to monomer, followed by desorption of the monomeric radical, with transfer to z-meric RAFT adduct followed by desorption of the z-meric radical.

$$k = k_{\text{tr,RAFT}} C_z P(\text{exit-}z) + k_{\text{tr}} C_p P(\text{exit-M}) \tag{7.16}$$

where C_z is the concentration of z-meric RAFT adduct in the particle and P(exit-M) is given by the usual expression:

$$P(\text{exit-M}) = \frac{k_{\text{dM}}}{k_{\text{dM}} + k_{\text{p}}^{1}C_{\text{p}}} \tag{7.17}$$

The first-order rate coefficient for the desorption of the monomeric radical, k_{dM}, is expressed in terms of the diffusion coefficient and solubility of the monomer (assumed to be the same as the radical) in water, D_{w} and C_{w}:[65]

$$k_{\text{dM}} = \frac{3D_{\text{w}}C_{\text{w}}}{r_{\text{s}}^{2}C_{\text{p}}} \tag{7.18}$$

It is shown below that the effect of exit of z-meric radicals is, by far, the dominant factor in terms of radical loss processes, with transfer to monomer making a negligible contribution to k from Eq. 7.16 in the presence of a high-activity RAFT agent.

Using the RAFT-induced exit model described here, the rate coefficient for the exit of one radical from the particle, k, may be estimated using Eq. 7.16 and the parameters shown in Tables 7.1 and 7.2. This in turn may be compared to the value of c obtained from the relaxation experiments to determine the applicability of various kinetic models to the system. By way of comparison, Table 7.3 shows calculated values for k for an $r_{\text{s}} = 50$ nm particle in the persulfate-initiated emulsion polymerization of styrene, methyl methacrylate (MMA) and butyl acrylate (BA) in the absence of RAFT as well as for a RAFT-containing system with a high-activity RAFT agent (both persulfate- and γ-initiated). In the RAFT-containing case, it is assumed that there is only one z-meric RAFT adduct present in the particle, although it is conceivable that more would be present.

Table 7.3 illustrates that the presence of only one z-meric RAFT adduct in the particle causes a 400-fold increase in the rate coefficient for radical loss from the particles in the case of a persulfate-initiated emulsion polymerization or a 40-fold increase in k for a γ-initiated polymerization. Moreover, k will scale linearly with the number of z-mer RAFT adducts in the particle, should more than one such adduct be present.

Given the uncertainty in k_{dz}, a sensitivity analysis over the range of feasible values may be performed. Increasing k_{dz} (*e.g.* to 10^6 s^{-1}) makes little difference to the calculated value of k, as $P(\text{exit-}z) \approx 1$ already; decreasing k_{dz} to 10^4 s^{-1} makes only a factor of 2 difference in k (insignificant in the context of a 400-fold increase in k induced by the RAFT agent).

Table 7.1. Parameters used in modeling the systems under consideration at 50 °C.

parameter	styrene	ref.	BA	ref.	MMA	ref.
C_p /mol dm^{-3}	5.5	12	5.7	60	6.6	67
C_w /mol dm^{-3}	4.3×10^{-3}	12	6.4×10^{-3}	68	0.15	67
k_p /dm^3 mol^{-1} s^{-1}	2.36×10^2	69	2.33×10^4	70	6.47×10^2	71
k_p^1 /dm^3 mol^{-1} s^{-1}	9.4×10^2	[a]	9.3×10^4	[a]	2.6×10^3	[a]
k_{tr} /dm^3 mol^{-1} s^{-1}	8.51×10^{-3}	72	1.55	60	7.53×10^{-3}	73
D_w /cm^2 s^{-1}	1.5×10^{-5}	74	1.5×10^{-5}	75	1.7×10^{-5}	74

[a] taking $k_p \approx 4k_p^1$.[12]

Table 7.2. Additional parameters used in the calculations presented here. C_z is the concentration of the z-mer RAFT adduct and k_{dz} is the desorption rate coefficient for the z-meric radical.

parameter	value
r_s /nm	50
$C_z = 1/N_A V_s$ /mol dm^{-3}	3.2×10^{-6}
k_{dz} /s^{-1}	10^5

Table 7.3. Comparison of the calculated Smith–Ewart rate coefficients for the exit of radicals from particles, *k*, using the parameters in Tables 7.1 and 7.2 in a persulfate-initiated emulsion polymerization and a $C_{tr} = 6000$ RAFT agent with [RAFT] = 8.5 mM where indicated.

system	k /s^{-1}
styrene	1.0×10^{-2}
BA	3.4×10^{-2}
MMA	3.6×10^{-2}
styrene + RAFT (γ-initiator)	4.4×10^{-1}
styrene + RAFT	4.0

7.4 Experimental Section

7.4.1 Materials

Inhibitors were removed from the styrene using a commercial inhibitor removal column (Aldrich), carbon disulfide was purified with several freeze-thaw cycles and α-methylstyrene was purified with a basic alumina column. Demineralized water was used throughout the experiments. All other materials were used as received from Aldrich. The RAFT agent PPPDTA was synthesized as previously reported.[16]

7.4.2 Radical Storage

PPPDTA was dissolved in styrene ([RAFT] = 12.9 mM) and thoroughly degassed through three freeze-thaw-evacuate cycles before being sealed under vacuum. Following the method of Barner-Kowollik *et al.*[22] for investigating radical storage in RAFT-mediated polymerizations, the ampules were subjected to γ-radiation for 18 h at ambient temperature using a 673 Gy h^{-1} ^{60}Co γ-cell. The samples were subsequently stored at room temperature for 20 to 60 min before being heated for 24 h at 50 °C in the absence of an external initiation source. Monomer conversion was determined by gravimetry and molecular weight distributions by GPC.

7.4.3 Seeded Emulsion Polymerization

A polystyrene latex was prepared following the method of Prescott *et al.*,[16] giving a 25% solids latex with average particle radius $\bar{r}_\mathrm{w}$ = 39 nm, $\bar{r}_\mathrm{w}/\bar{r}_\mathrm{n}$ = 1.18, particle number concentration $N_\mathrm{c} = 2.2 \times 10^{18}$ dm^{-3} (calculated from $\bar{r}_\mathrm{n}$), molecular weight $\overline{M}_\mathrm{n} = 7.4 \times 10^4$ and $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$= 3.4.

Styrene/polystyrene/PPPDTA seeds were prepared using the previously described acetone transport technique.[16] The mass of RAFT agent added was varied to give different RAFT agent concentrations in the fully swollen seed. The in-particle concentrations of RAFT agent (at $C_\mathrm{p} = C_\mathrm{p}^\mathrm{sat}$) as prepared were [RAFT] = 0, 3.7, 8.5, 20, 27 and 38 mM. For the control experiments with [RAFT] = 0, the seeds were still subjected to the acetone transport technique, but without the RAFT agent.

7.4.4 NMR Analyses

Ampules containing PPPDTA/styrene solution were prepared as described above with [RAFT] = 545 mM and irradiated for up to 32 h at 50°C using a 673 Gy h^{-1} ^{60}Co γ-cell. Samples were dissolved in chloroform-*d* to give a solution volume of ~0.7 mL. The solutions were placed into 5 mm NMR tubes (Wilmad 535 or New Era UL5). For quantitative ^{13}C measurements, ~3% Cr(acac)$_3$ was added to the solution as the relaxation agent. The NMR spectra were acquired on a Bruker DRX500 spectrometer equipped with a 5 mm inverse *z*-gradient ^{1}H–^{13}C–^{15}N (TXI) probe operating at 500.13 MHz for ^{1}H and 125.6 MHz for ^{13}C. The temperature was controlled to 305 K. All experiments were acquired with Bruker standard pulse sequences. The samples were analyzed with ^{1}H, quantitative-^{13}C, COSY, HSQC and HMBC experiments, the details of which are included in the Supporting Information (Section 7.9).

7.4.5 Dilatometry

The dilatometry experiments were carried out in a jacketed glass vessel, approximately 30 cm^3 in volume. The temperature was controlled using a water bath. Each of the seed latex, monomer and additional water were thoroughly degassed under vacuum, backfilling with argon. Monomer was added to the seed with stirring and allowed to swell the seed particles overnight under an argon blanket. The mixture was further degassed under vacuum and then brought to reaction temperature. Degassed water was added and the capillary topped up with decane. The particle number concentration, N_c, of the final latex was variously 1×10^{17} or 2×10^{17} dm^{-3}.

Once thermal equilibrium had been reached, the height of the meniscus in the capillary was followed using a computer-controlled tracking device. The dilatometer was lowered into a 151 Gy h^{-1} ^{60}Co γ-cell to initiate polymerization. Once the reaction appeared to have reached a constant rate of polymerization, the dilatometer was removed from the γ-source. Once the out-of-source steady state had been reached, the dilatometer was re-inserted into the γ-source and the relaxation procedure was repeated up to eight times.

Rate data were extracted from the meniscus height data using the densities for styrene and polystyrene from Hawkett *et al.*[27,47] Conversion of the final latex from each dilatometry experiment was determined by gravimetry and MWDs by gel permeation chromatography (GPC) using previously described signal subtraction techniques.[16]

7.4.6 Particle Sizing

For representative latexes, the particle size distribution was measured by a combination of Fraunhofer light-scattering and polarization intensity differential scattering techniques using a Coulter LS230 instrument.[76] This instrument has been previously used in studies of seeded emulsion polymerization with particle size distributions similar to those used here, showing good agreement with other techniques, including capillary hydrodynamic fractionation.[16] For each of the seeded experiments, the number average diameter of the particles (between 84 nm and 100 nm) agreed with the predicted size to within 4%. The shape and broadness of the distribution was unchanged and neither new nucleation nor coagulum was observed. There were no systematic differences between the particle sizes obtained in RAFT and non-RAFT experiments.

7.4.7 Molecular Weight Distribution

Molecular weight distributions were measured by GPC. Samples of dried latex were dissolved in THF (1 mg cm^{-3}) and filtered using a 0.2 μm PTFE filter. Analyses were carried out using 4 PLgel columns (3 Mixed-C columns and 1 Mixed-E column, Polymer Labs). Injection volumes of 100 μL were used with a Waters 410 differential refractive index detector and a flow rate of 1 $\text{cm}^3\,\text{min}^{-1}$. Cubic calibration curves were generated using 13 polystyrene standards (Polymer Labs) with molecular weights ranging from 264 to 2.56×10^6. GPC signal analyses were performed using the software *GPC for Windows* (Chemware).

7.5 Results

7.5.1 Radical Storage

Whereas the original radical storage experiments of Barner-Kowollik *et al.*[22] showed a significant difference in the conversion of the RAFT and non-RAFT samples both after irradiation and after heating to polymerization temperature, the same was not observed for the same experiments with PPPDTA. Specifically, Barner-Kowollik *et al.*[22] found that a phenyl-activated RAFT agent (cumyl diothiobenzoate, CDTB) led to a reduction in the conversion on irradiation at ambient temperature. The samples were then stored for some time (denoted in Fig. 7.3 as the “wait time”) at ambient temperature without further irradiation. After subsequent heating in the absence of an external initiation source, Barner-Kowollik *et al.*[22] found that the conversion in the RAFT-containing sample was greater than that of the non-RAFT sample. On this basis, it was concluded by Barner-

Kowollik *et al.*[22] that there was some form of radical storage mechanism in operation, such that radicals were released into the system upon heating.

In the same experiments performed here with PPPDTA, a benzyl activated RAFT agent, there were no significant differences between the conversion in the RAFT and non-RAFT samples, as illustrated in Fig. 7.3. In considering Fig. 7.3, it must be realized that the γ-source used in this study has a higher dose rate than that used by Barner-Kowollik *et al.*[22] The conversion of each sample is thus not directly comparable, but it is only the *difference* in conversion between the RAFT and non-RAFT samples that is of interest in analyzing these data.

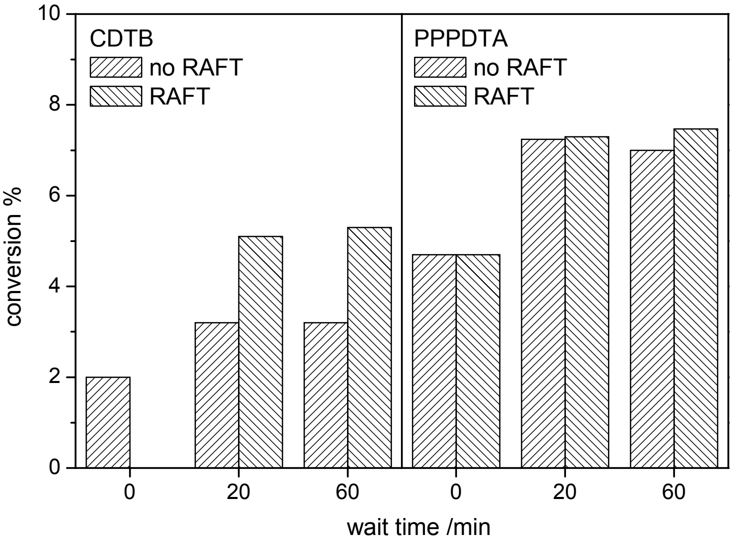


Figure 7.3: The conversion of different samples with the RAFT agent PPPDTA compared to the results for cumyl dithiobenzoate (CDTB) reprocessed from Barner-Kowollik *et al.*[22] The difference in conversion between the RAFT and non-RAFT samples that was observed by Barner-Kowollik *et al.*[22] for a phenyl-activated RAFT agent was not observed with a benzyl-activated RAFT agent.

This result is entirely consistent with the experiments of Barner-Kowollik *et al.*,[22] as the intermediate bipolymeric radical formed by phenyl-activated RAFT agents (*e.g.* CTDB) is much less stable than that formed by the benzyl-activated RAFT agent (PPPDTA). The less stable intermediate will have a shorter lifetime,[22] hence it will be present in lower concentrations and will be less able to take part in reactions, such as termination reactions, with other species.[21,77] The radical storage effects attributed by Barner-Kowollik *et al.*[22] to reactions of the intermediate radical are thus less likely to occur in PPPDTA-mediated polymerizations, as observed here.

In the NMR analyses performed in this study, the major products observed were the RAFT-containing chain formed from the cumyl re-initiating group with an average of 2.1 styrene units in the polymer backbone. No evidence of an intermediate radical termination product was observed in the spectra, with all signals in the region where the quaternary carbon of the coupling product is expected to be found being assigned to other groups (more details are in the Supporting Information). It is noted that formation of intermediate termination products at levels that could not be detected by these experiments may be kinetically significant; however, these experiments set an upper bound on the levels of termination products that can be observed in the case of an experiment that was designed to lead to the formation of such species.

Quinn *et al.*[56,57] demonstrated that various RAFT agents may be successfully used with γ-initiation;[56,57] moreover, their data were consistent with the hypothesis that the polymerization proceeds via the RAFT mechanism proposed by Rizzardo *et al.*[10,78,79] Thus, it may be concluded that PPPDTA may be successfully used with γ-initiation in the course of a relaxation experiment without adverse effects from the use of the γ-source.

7.5.2 Molecular Weight Control

The molecular weight of the polymer produced in a large number of reactions is shown in Fig. 7.4. In each case, γ-initiation was used, with the dose rate varying between 75 and 673 Gy h^{-1}. Samples from both bulk and emulsion polymerizations are included, with the emulsion polymer results covering a range of [RAFT] and final conversions. In each case, the theoretical value of $\overline{M}_\mathrm{n}$ is calculated using Eq. 7.1.

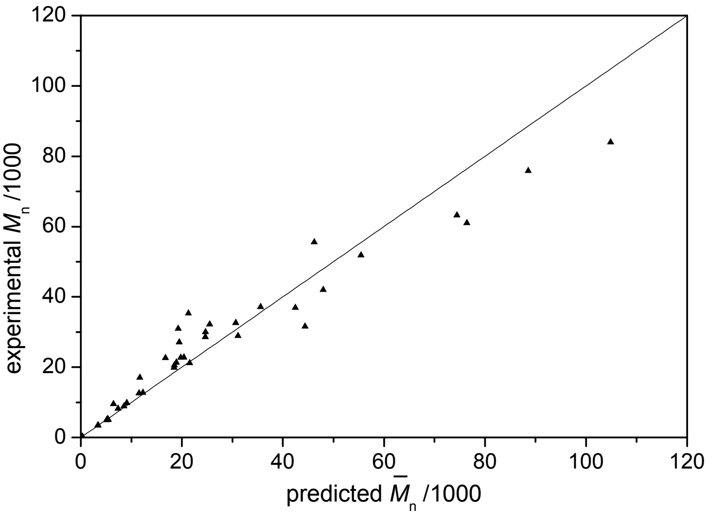


Figure 7.4: The calculated and experimentally determined value of $\overline{M}_n$ for a variety of γ-initiated experiments including sealed ampules and emulsion polymerization experiments, showing good control of molecular weight over the range $\overline{M}_n = 5 \times 10^2$ to 1×10^5. For all samples, $1.1 < \overline{M}_w/\overline{M}_n < 1.4$.

7.5.3 Rate of Polymerization

In RAFT-mediated polymerizations, a reduction in the rate of polymerization is often observed[18,78,79] and RAFT/emulsion systems are no exception.[14-16] In the case of RAFT/emulsion systems mediated by PPPDTA with a chemical initiator, it has previously been reported that the rate of polymerization was reduced by 30 to 50%, depending on the initiator concentration used.[16]

In the case of γ-initiated RAFT/emulsion with PPPDTA, the same is true. Fig. 7.5 shows the conversion *vs* time plots for three emulsion polymerizations, [RAFT] being the only difference between them. As previously seen in the chemically initiated studies, the rate of polymerization is reduced by the addition of the RAFT agent and the strength of this effect is dependent on how much RAFT agent is added.

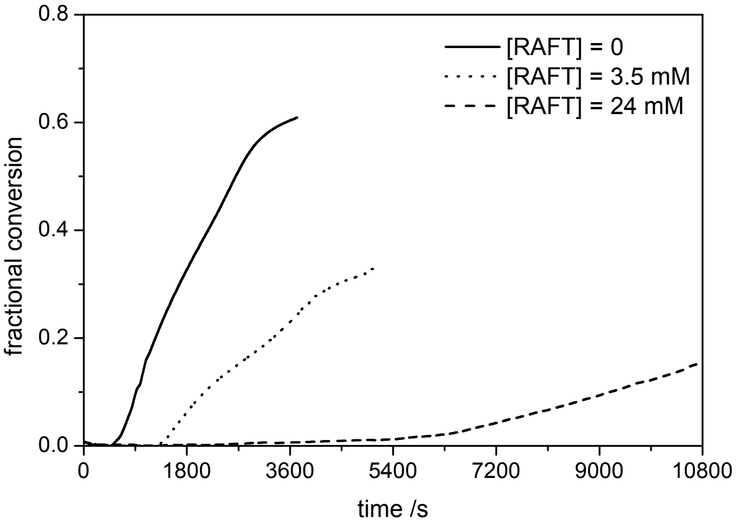


Figure 7.5: Conversion *vs* time for the emulsion polymerization of styrene at [RAFT] = 0, 3.5, 24 mM. Each system was started at the Interval II/III transition with $N_c = 2 \times 10^{17}$ dm^{-3}, $r_s = 48$ nm, 151 Gy h^{-1} γ-source.

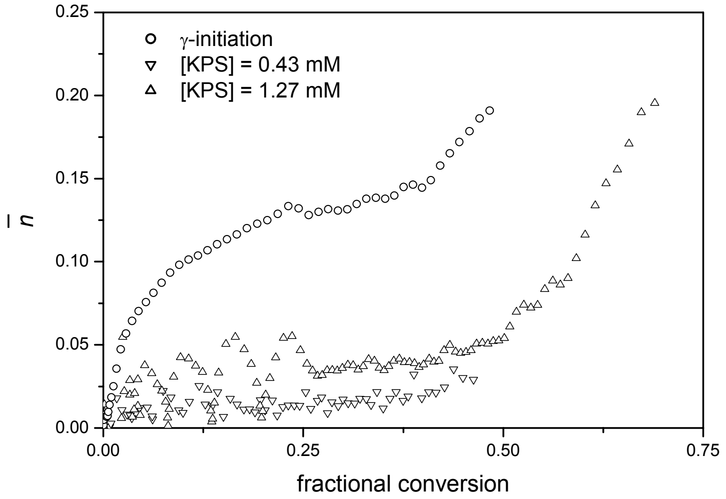


Figure 7.6: Experimental $\bar{n}$ as a function of time for RAFT/emulsion systems with various initiation systems and [RAFT]. For persulfate (KPS) initiation, [PPPDTA] = 60 mM and for γ-initiation, [PPPDTA] = 25 mM. These data, showing $\bar{n}$ increasing over time in Interval II and III are inconsistent with zero-one kinetics for the systems under consideration.

Noting that these experiments were conducted in Interval III (*i.e.* no monomer droplets present), C_p is monotonically decreasing throughout the course of the reaction. As a result, $\bar{n}$, the average number of radicals per particle, is increasing with conversion, as shown in Fig. 7.6. As $\bar{n}$ should remain constant throughout the polymerization in a zero-one system, this indicates that the systems are not behaving in a zero-one manner. This is consistent with the previously reported modeling results that indicated that RAFT/emulsion systems with high-activity RAFT agents would not be zero-one except when the dormant chains are quite short.

7.5.4 Relaxations

For the emulsion polymerization of styrene with PPPDTA, γ-radiolysis experiments showed that the cessation of initiation leads to a rapid decrease in the rate of polymerization, with polymerization ceasing 100 – 200 s after irradiation is stopped. Representative relaxation data ($\bar{n}$ *vs* time) are shown in Fig. 7.7; it is seen that both the in-source and out-of-source steady-state values for $\bar{n}$ are reduced by the addition of the RAFT agent, as well as the characteristic time-scale of the relaxation.

As discussed above, the chain-length dependence of termination is important in correctly describing RAFT/emulsion systems and the chain length of the radicals is determined by the (average) chain length of the dormant chains, $\bar{X}_{\mathrm{n,d}}$. The relaxation data for relaxations at various conversions, [RAFT], C_{p}, and N_{c} are shown in Fig. 7.8, with $\bar{X}_{\mathrm{n,d}}$ calculated from Eq. 7.2. In Fig. 7.8, the relaxations are characterized as a radical-loss process that is second-order in $\bar{n}$ (*i.e.* following Eq. 7.4 and 7.5). A similar figure showing the dependence of the relaxations on $\bar{X}_{\mathrm{n,d}}$ but as a process first-order in $\bar{n}$ may also be prepared, although it is not possible to distinguish between first- and second-order loss mechanisms (or, indeed, a combination) with these data.

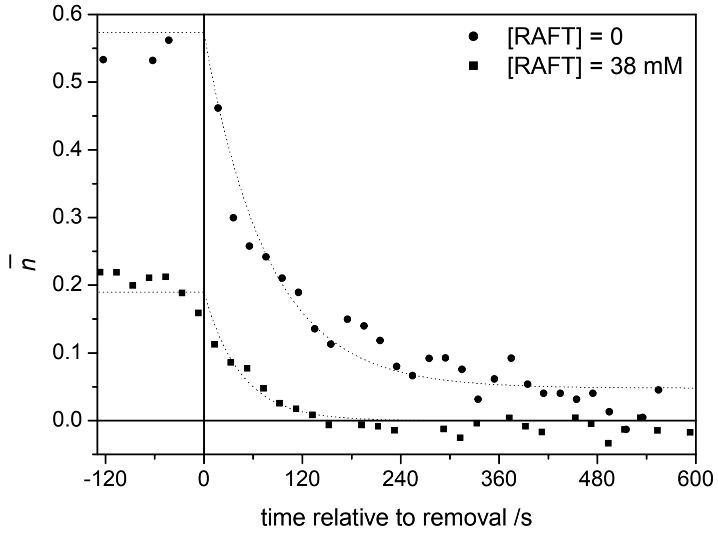


Figure 7.7: Sample relaxation data ($\bar{n}$ *vs* time) showing the effect of the RAFT agent. The average shown for the in-source $\bar{n}$ is the average over the previous 500 s, with the sample removed from the γ-source at time $t = 0$. Note that both the in-source and out-of source $\bar{n}$ are reduced by the addition of the RAFT agent.

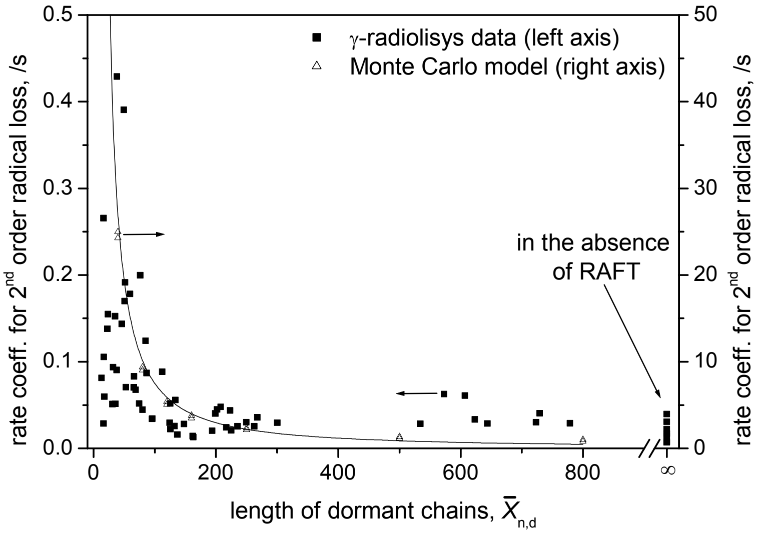


Figure 7.8: Summary of the relaxation data, treating the relaxations as a loss process that is second order in $\bar{n}$. The rate coefficient for second-order radical loss is shown here as a function of the dormant chain length, $\bar{X}_{n,d}$, and corresponds to the Smith–Ewart parameter c when the system is pseudo-bulk (*i.e.* $\bar{X}_{n,d} \gtrsim 40$). Modeling data for the semi-quantitative treatment of the Monte Carlo simulations is also shown (line). The assumption of infinite dormant chain lengths is a convenient representation of the situation in the absence of RAFT agent, using the limit of Eq. 7.2 at [RAFT] = 0.

The relaxation behavior shown in Fig. 7.8 is dependent on the length of the dormant chains in the system, over a wide range of experimental conditions. When the system is sufficiently uncompartmentalized that it may be treated as following pseudo-bulk kinetics, the rate coefficient for second-order radical loss shown in Fig. 7.8 is the Smith–Ewart parameter *c*; when the system is zero-one (Limit 2a), the second-order radical loss is given by[12,65] $k_{\mathrm{tr}}C_{\mathrm{p}}k_{\mathrm{dM}} / (k_{\mathrm{p}}^{1}C_{\mathrm{p}} + k_{\mathrm{dM}})$ and is not directly related to termination.[12,65] In this system, pseudo-bulk kinetics are appropriate for $\bar{X}_{\mathrm{n,d}} \gtrsim 40$, at which point termination is sufficiently slowed to allow significant amounts of polymer to be produced in a two-radical environment.[23] Thus, for the longer dormant chain lengths, the average value of the second-order termination rate coefficient, $\langle k_{\mathrm{t}} \rangle$, may be extracted from the data presented in Fig. 7.8 using the relation $c = \langle k_{\mathrm{t}} \rangle / N_{\mathrm{A}} V_{\mathrm{s}}$, as shown in Fig. 7.9.

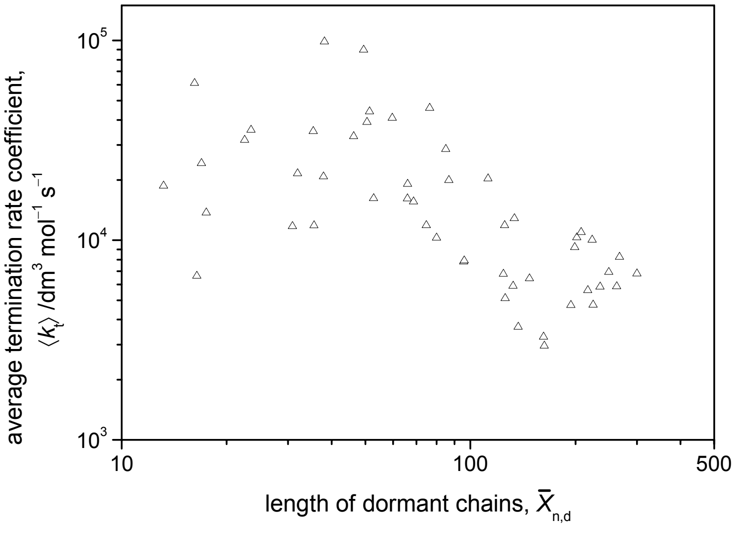


Figure 7.9: The value of $\langle k_{\mathrm{t}} \rangle$ as a function of the dormant chain length $\bar{X}_{\mathrm{n,d}}$. Note that, where the system is not described by pseudo-bulk kinetics (*i.e.* $\bar{X}_{\mathrm{n,d}} \lesssim 40$), the rate coefficient for second-order radical loss is not *c* and the value shown here is not $\langle k_{\mathrm{t}} \rangle$.

7.6 Discussion

The results presented here for the γ-relaxation experiments and the modeling of the desorption of the oligomeric radicals may now be interpreted together. The implications of the loss of compartmentalization are first examined in terms of Smith–Ewart kinetics to present a coherent picture of the effects of RAFT in emulsion polymerization systems, first developing a qualitative understanding of the relaxations, followed by a semi-quantitative treatment of the relaxation data.

7.6.1 Loss of Compartmentalization

The values of k presented above show a marked change as a result of the addition of the RAFT agent. In particular, the addition of the RAFT agent is firstly seen to lead to the presence of z-meric RAFT adducts that are capable of desorbing from the particles, transferring the radical activity from one particle to another. The values of k shown in Table 7.3 show that the addition of the RAFT agent causes a 400-fold increase in the rate coefficient for radical loss from the particles in a persulfate-initiated system and a 40-fold increase in k in the γ-initiated system.

In the previously presented Monte Carlo modeling of RAFT/emulsion systems,[23] it was established that once the dormant chains are no longer short, even a relatively small latex particle is able to support more than one radical within it; therefore, c is reduced. From the relaxation data (Fig. 7.8) and the estimate for k (Table 7.3) presented here, it would appear likely that $k/c \gg 1$ in the persulfate-initiated systems studied and $k/c \gtrsim 1$ in the γ-initiated systems. The rapid exchange of radicals between particles implied by this relation is a condition that would be expected to make pseudo-bulk kinetics applicable, at least in the chemically initiated system.[28]

In using the pseudo-bulk equation to model RAFT/emulsion systems, care must be taken to understand the role of the exiting RAFT fragment $R^{\bullet}$,[15] and it must be appreciated that the value of c changes throughout the course of the reaction. At low-conversion, when the radicals and dormant chains are quite short, the Monte Carlo modeling of Prescott[23] shows that termination is an extremely rapid event, such that $k/c \ll 1$ even with the vastly increased value of k shown here. Such systems are still zero-one, even though there is a rapid exchange of radicals between the particles (just as a zero-one system with a chain transfer agent is still zero-one, as in the work of Lichti *et al.*[80]).

7.6.2 Qualitative Treatment of Relaxations

The relaxation data presented in Fig. 7.7 and 7.8 show that the shorter the radical, the faster the relaxation and, conversely, the longer the dormant chains, the slower the relaxation. Since zero-one kinetics have previously been shown to be inapplicable at all but the shortest dormant chain lengths[23] and the loss of compartmentalization described here indicates that pseudo-bulk kinetics are applicable, it is possible to understand this trend in terms of the changing lengths of the radicals involved.

In a classical emulsion polymerization, the mechanism for radical loss in a γ-relaxation is a minor breakdown in the compartmentalization through transfer to monomer followed by exit of the radical species, as shown in Fig. 7.1. In the case of the RAFT-mediated polymerization, the kinetics of the relaxation are those of an uncompartmentalized system with the rapid exchange of radicals through the RAFT-induced exit mechanism. In Fig. 7.10, these mechanisms are illustrated; it is seen that at low conversion, termination is entirely a short-short reaction, hence the termination reaction is quite fast. It should be noted that the short-short termination is particularly fast compared to the transfer to monomer/exit/re-entry/termination sequence involved in non-RAFT emulsion polymerizations.

At higher conversion, the radicals and dormant chains are longer, with the exception of the initiator-derived radicals such as the z-meric RAFT adducts that lead to the breakdown in compartmentalization. As with the relaxations at low conversion, intra-particle termination is the chief mechanism for the relaxation process; in this case, however, the termination reactions involve longer chains as previously described by Prescott.[23] The actual termination reaction may either be long-long or be preceded by a transfer reaction to a short dormant chain, resulting in a termination reaction that is short-long. Following either route to termination, the termination reaction is much slower than the normal short-long reaction seen in emulsion polymerizations.

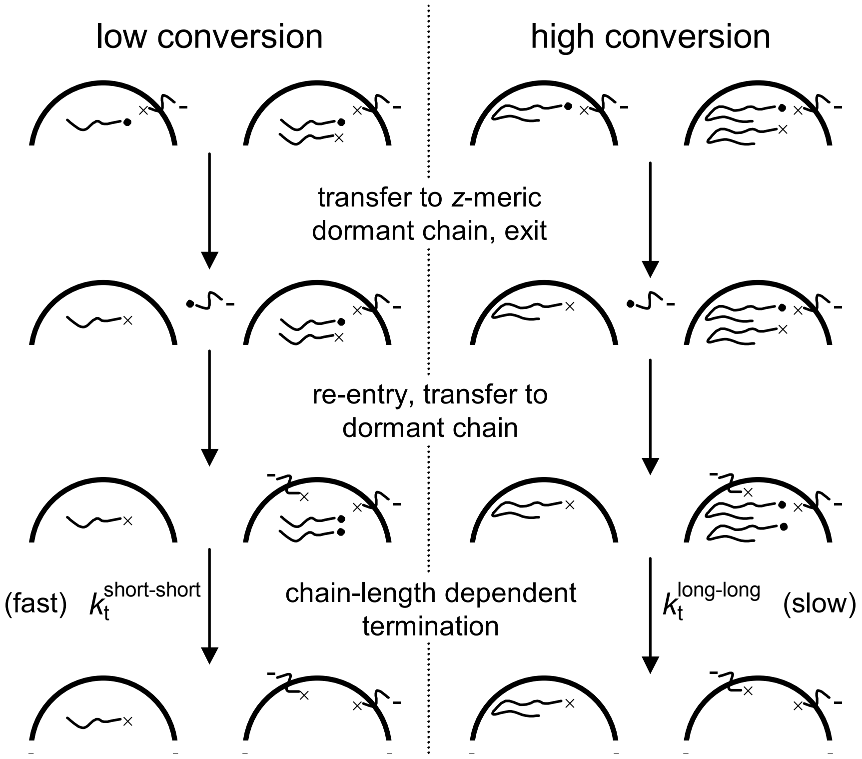


Figure 7.10: Relaxations in the uncompartmentalized RAFT-mediated emulsion polymerization are governed by short-short termination at low conversion and, later, by much slower termination reactions at higher conversion (most probable path shown). Symbols: radical •, dormant end group ×.

7.6.3 Semi-Quantitative Prediction of Relaxation Behavior

The integral technique previously described for the semi-quantitative treatment[43] of the Monte Carlo results may be used to calculate values of the rate coefficient for second-order loss of radicals, *c*. Calculated and experimental values for *c* at various dormant chain lengths, $\overline{X}_{\mathrm{n,d}}$, are shown in Fig. 7.8. In considering the correspondence between the experimentally determined values for *c* and those obtained from the semi-quantitative treatment of the Monte Carlo results, three important features are obvious. The first and perhaps the most important of these features is that the general shape of the experimental results is quite well-described by the shape of the model predictions. This provides strong evidence that the suggested mechanisms involving CLD termination have a significant influence on the kinetics of the system.

More detailed analysis of Fig. 7.8 shows that the actual numerical agreement between the experimentally- and theoretically-derived values for c is poor, with the value being in error by a factor of between 30 and 100 for the parameter values chosen for the Monte Carlo simulations. Given the inherent errors involved in extrapolating the P_j *vs* j curves so that the integration to evaluate c may be performed, and the extrapolated model for the diffusion of the polymeric radicals, it is unsurprising that there is considerable difference between the experimental and theoretical values of c.

While it is desirable to quantitatively calculate c without making use of adjustable parameters, it is useful to consider the range for c that may be obtained using physically reasonable values for the exponent for chain-length dependence (Eq. 7.7). Making use of a composite model for the diffusion of the polymeric species similar to that of Smith *et al.*,[41] it is possible to construct a model that is consistent with the data of Griffiths *et al.*[40] at short chain lengths and with the reptation model[81] at long chain lengths. Recalculating c using this composite model in the Monte Carlo simulations, it is found that at $\overline{X}_{\text{n,d}} = 160$, c is 0.01 s^{-1}; this result compares favorably with the calculation only making use of the empirical scaling law of Griffiths *et al.*[40] ($c \approx 3\ \text{s}^{-1}$, shown in Fig. 7.8) and the experimental data ($c \approx 0.03$–$0.06\ \text{s}^{-1}$). The method presented here for calculating c from the Monte Carlo model of RAFT/emulsion particles[23] is thus able to give a semi-quantitative value of c with the termination models currently available, but may be able to give a quantitative measure of c using improved composite models such as that suggested here.

Finally, the trend at low values of $\overline{X}_{\text{n,d}}$ does not appear to be well described. However, at low values of $\overline{X}_{\text{n,d}}$, the system follows zero-one kinetics rather than pseudo-bulk kinetics; the experimentally determined rate coefficient for second-order radical loss is not the Smith–Ewart parameter c, but, rather, is a kinetic parameter related to the generation and desorption of monomeric radicals as noted above. It would not be expected that the experimentally determined rate coefficient for second-order radical loss would match the theoretical value for c in such a situation and the divergence of the two data sets is to be expected at low $\bar{X}_{\mathrm{n,d}}$.

The agreement between the shapes of the two curves for c shown in Fig. 7.8 is a strong indicator of the importance of CLD termination in describing the system. The differences between the experimental dataset and the predicted values of c are to be expected given the difficulties in preparing theoretical values of c and the inapplicability of pseudo-bulk kinetics to the zero-one system at low $\bar{X}_{\mathrm{n,d}}$.

7.6.4 Simple Model of RAFT/Emulsion

While the Monte Carlo model of RAFT/emulsion systems has provided significant understanding of the important mechanistic pathways in these systems, its use as a predictive tool for the kinetics of the system is limited. It has been demonstrated here that a pseudo-bulk model may be appropriate to modeling these systems, at least for moderate to high conversion when the dormant chain lengths are sufficiently long so as to preclude the use of zero-one kinetics. However, this suggestion is made with two important caveats: (a) a value of c (or rather $\langle k_{\mathrm{t}} \rangle$) is required for the pseudo-bulk model, and (b) the error in the pseudo-bulk model compared to the exact solution of the Smith–Ewart equations must be recognized.

The data for $\langle k_{\mathrm{t}} \rangle$ shown in Fig. 7.9 could, in principle, be improved through more experiments to show the variation of $\langle k_{\mathrm{t}} \rangle$ with both w_{p} and $\bar{X}_{\mathrm{n,d}}$. Recent experiments by Vana *et al.*[82] used the control over the length of the propagating radicals imparted by RAFT (Eq. 7.2) to measure k_{t}^{ii} by assuming that termination reactions were dominated by the reaction of two i-meric radicals. In that study, it was shown that RAFT-based measurements[82] of k_{t}^{ii} were able to reproduce PLP measurements[37] at low w_{p}, even without agreed understanding of the intricacies of the behavior of the intermediate radicals in the RAFT process. It may thus be surmised that experiments, such as those described here, may likewise be able to measure the dependence of k_t^{ii} at much higher w_p. Once a model for k_t^{ii} at both high w_p and long chain lengths has been developed, it would be possible to use the pseudo-bulk equation for RAFT/emulsion systems subject only to caveat (b).

It must be recognized that the values of ρ, c and k reported here do not satisfy the necessary conditions of pseudo-bulk kinetics that $\rho/c \gg 1$ or $k/c \gg 1$; indeed, here it is suggested that $\rho/c \approx 0.5$ and $k/c \approx 4$ for the γ-initiated system. Using the recursive solution method for the Smith–Ewart equations presented by Ballard *et al.*,[28] it is possible to determine the accuracy of the pseudo-bulk equation in estimating $\bar{n}$ under these conditions. It is found that $\bar{n}$ may be estimated to an accuracy of 20–30% under such conditions, meaning that the pseudo-bulk model is a useful approximation to these RAFT/emulsion systems, but by no means an accurate model.

7.7 Conclusions

It has been shown here that the γ-initiated polymerization of styrene may be successfully mediated by the benzyl-activated RAFT agent PPPDTA. Good control over the molecular weight of the products was shown. NMR analyses of the products of γ-initiated polymerizations did not detect any intermediate radical coupling species. Retardation of the rate of polymerization was observed with an increase in [RAFT]. In the emulsion polymerization of styrene, an increase in $\bar{n}$ with conversion was seen, indicating that zero-one kinetics are inappropriate for these systems except, perhaps, at low conversions.

The presence of z-meric dormant chains in the particles was postulated to lead to an increase in the rate of radical exit from the particles, since z-meric radicals are able to desorb from the particle surface. This RAFT-induced exit mechanism leads to radical entry being a reversible process and a rapid exchange of radicals between particles, with the rate coefficient for radical desorption from a particle being increased by ~400-fold.

The time-dependent behavior of the number of *z*-meric dormant species is, thus, an important subject for further study.

The semi-quantitative treatment of the Monte Carlo model was seen to give a good description of the shape of the relationship between *c* and the length of the dormant chains. Using the established model for the chain-length dependence of short chain diffusion, the magnitude was not correctly estimated, but use of a model that was more applicable to the diffusion of longer chains in the Monte Carlo modeling suggests that the treatment is at least semi-quantitatively in accord with observation. This supports the applicability of the qualitative explanations given here for the origins of the strong effect of RAFT on γ-relaxations.

Kinetic parameters were obtained from the γ-relaxation experiments, making use of both Monte Carlo modeling of RAFT/emulsion particles and the RAFT-induced exit mechanism for the rapid exchange of radicals between particles to justify the use of pseudo-bulk kinetics for these systems. The use of pseudo-bulk kinetics permitted the determination of $\langle k_t \rangle$ as a function of the dormant chain length, offering a method whereby k_t^{ii} may be determined at both high w_p and chain lengths.

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7.9 Supporting Information

7.9.1 Experimental Procedures

Additional details of the NMR analyses performed on the irradiated samples are as follows:

^{1}H An FID of 32K data points was collected over 7500 Hz (0.23 Hz/pt; acquisition time of 2.18 s) and summed over 32 scans using a 10° ^{1}H acquisition pulse, with a 2 s relaxation delay. Exponential multiplication of 0.1 Hz was applied to the FID and the line-broadened data were zero-filled and Fourier transformed to give a spectrum of 64K data points. Spectra were referenced to the residual solvent signal, $CHCl_3$, δ_H 7.26.

^{13}C An FID of 64K data points was collected over 32,700 Hz (0.50 Hz/pt; acquisition time of 1.00 s) using a 30° ^{13}C acquisition pulse, continuous bilevel-waltz-16 ^{1}H-decoupling, and a 2 s relaxation delay. Exponential multiplication of 1 Hz was applied to the FID and the line-broadened data were zero-filled and Fourier transformed to give a spectrum of 128K data points. Spectra were referenced to the solvent signal, $CDCl_3$, δ_C 77.03. Quantitative measurements were obtained using the previously defined conditions and inverse-gated bilevel-waltz-16 ^{1}H-decoupling, an 87° ^{13}C acquisition pulse, and a 3 s relaxation delay.

COSY Gradient selected; 2048 FID data points, 4000 Hz sweep width, 0.26 s acquisition time, 1.0 s relaxation delay, 8 scans, 512 experiments, sine-bell window function in both dimensions; zero-filled and Fourier transformed to 2048 × 2048 points.

HSQC Gradient selected, phase-sensitive using echo/antiecho–TPPI, garp ^{13}C-decoupling, 2048 FID data points, 4000 Hz sweep width, 0.26 s acquisition time, 1.0 s relaxation delay, $^{1}J_{CH}$ = 150 Hz, 16 scans, 1024 experiments, $^{\pi}/_{2}$-shifted sine-squared-bell window function in both dimensions, Fourier transformed to 2048 × 1024 points.

HMBC Gradient selected, 2048 FID data points, 4000 Hz sweep width, 0.26 s acquisition time, 1.0 s relaxation delay, $^{1}J_{CH}$ = 150 Hz, $^{n}J_{CH}$ = 8 Hz, 16 scans, 1024 experiments, $^{\pi}/_{2}$-shifted sine-bell window function in both dimensions, Fourier transformed to 2048 × 1024 points.

7.9.2 Analysis of NMR Results

The quantitative-^{13}C spectrum (Fig. 7.11) was used to estimate the average length of the polymeric chain attached to the RAFT moiety. The integral of the aromatic carbons in the range 120–145 ppm includes both the benzyl Z group and the cumyl re-initiating group and was referenced to the thiocarbonyl signal at 232 ppm.

The combination of the experimental procedures outlined provides no evidence of intermediate radical termination products, as follows. It was estimated that chemical shift of the quaternary carbon of the intermediate radical termination product (shown in Scheme 7.2) was 60 ppm, using the ^{13}C-NMR shifts function of ChemDraw 7.0.1 (CambridgeSoft). In the vicinity of 60 ppm, there is a peak at 68 ppm and a set of peaks in the range 56.5–58.0 ppm.

The HSQC spectrum shown in Fig. 7.12 indicates that the peak at 68 ppm is protonated. Similarly, the peaks between 56.5 and 58 ppm are all correlated to proton signals in the HSQC spectrum and are assigned to CH_2 in the Z group of the RAFT agent. Hence, there is no evidence for a quaternary carbon in that range. While it is recognized that the quaternary carbon of the intermediate radical termination product may be obscured by other peaks in the region of interest, no evidence of the radical-radical coupling product proposed by Monteiro *et al.*[21] could be found in the samples.

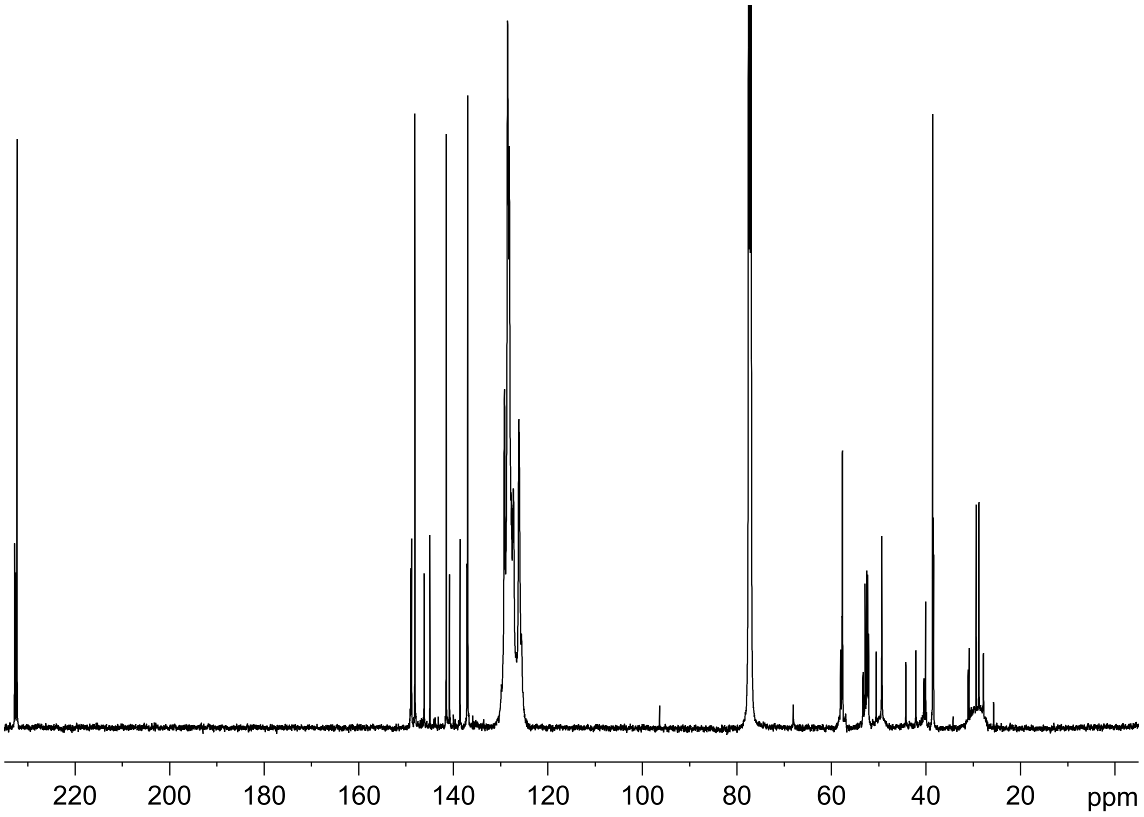
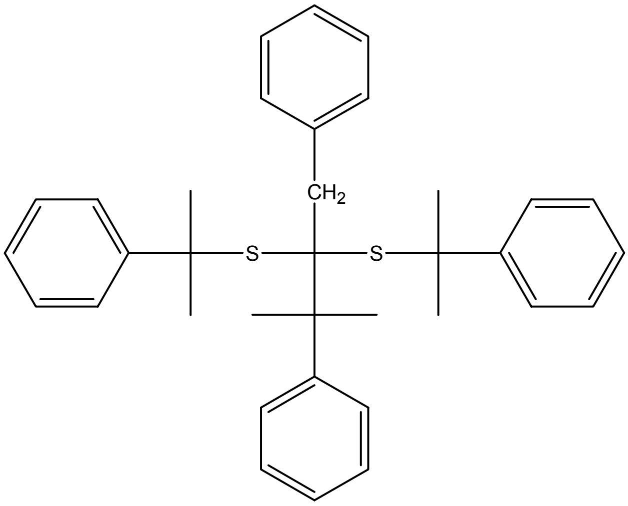


Figure 7.11: Quantitative ^{13}C spectrum from the PPPDTA/styrene irradiation at 50°C.



Scheme 7.2: The model intermediate radical termination compound.

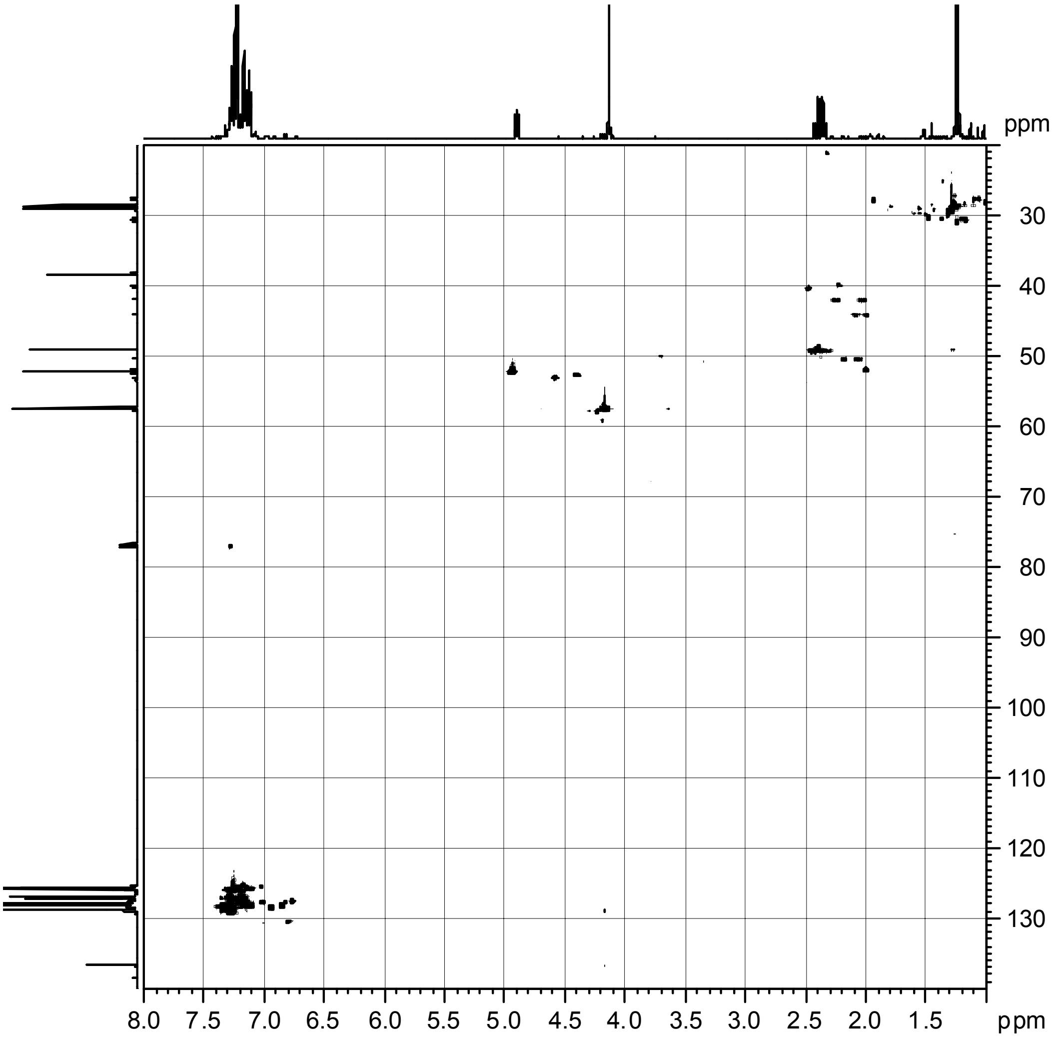


Figure 7.12: HSQC spectrum of the irradiated sample.

7.10 References

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