Chapter 9

Improving Performance of RAFT/Emulsion

*It is the mark of an educated mind to be able to entertain a thought without accepting it.*

– Aristotle (384–322 B.C.)
9.1 Abstract

The use of a zero-one kinetic model accounting for the RAFT-induced exit of radicals, the desorption of the RAFT re-initiating radical from the particles and the specificity of the re-initiating radical for the RAFT agent is shown to successfully describe the inhibition period in the RAFT/emulsion polymerization of styrene. Strategies for reducing the inhibition period, such as using a more hydrophobic re-initiating radical, are tested using this zero-one model and predict a significant improvement. The time-dependent behavior of the dormant z-meric species in the RAFT-induced exit of radicals from particles is modeled, predicting that the rate coefficient for radical exit may be reduced by using a RAFT agent with a lower transfer constant. Alterations to the reaction conditions (such as using an oligomeric adduct to the RAFT agent and a less-active RAFT agent) are modeled using a generalized method of accounting for chain-length dependent kinetics.

9.2 Introduction

While reversible addition-fragmentation chain transfer (RAFT)\textsuperscript{1,2} is a well-established technique for living radical polymerization in bulk and solution, its adoption in heterogeneous polymerization systems has been somewhat slower, due to significant technical obstacles.\textsuperscript{3-6} In homogeneous systems, RAFT techniques have provided control over the molecular weight distribution and molecular architecture,\textsuperscript{7-10} with some retardation to the rate of polymerization.\textsuperscript{3,11,12} The causes of the retardation have been the subject of much speculation, centered primarily on the bipolymeric intermediate radical species in the RAFT mechanism. Several theories regarding retardation have been suggested, including the slow fragmentation of the intermediate radical,\textsuperscript{11,13,14} irreversible\textsuperscript{3} and reversible\textsuperscript{8,15} termination of the intermediate radical; ESR experiments to measure the concentration of the intermediate radical\textsuperscript{16-19} have further widened the debate.\textsuperscript{20,21}
RAFT-mediated polymerizations in heterogeneous systems have encountered many technical difficulties beyond those related to the RAFT equilibrium reaction. As a result, relatively few examples of living polymerization in emulsion polymerization have been reported where good colloidal stability and reasonable reaction rates were maintained throughout the reaction and molecular weight and molecular weight polydispersity were adequately controlled.\(^4,6\) The transport of the RAFT agent to the locus of polymerization was seen to be a significant difficulty in the seeded emulsion polymerizations of Monteiro et al.,\(^22\) a problem that was overcome by Prescott et al.\(^23\) through the use of a water-phase co-solvent to increase the solubility of the RAFT agent in the water phase.

Despite the previously reported difficulties, emulsion polymerization offers significant benefits to living polymerization systems.\(^6\) Based on the behavior of non-living systems, emulsion polymerization should offer good temperature control and negligible change in viscosity with conversion; additionally, emulsion polymerizations generally have various environmental advantages compared to solution systems.\(^24\)

Once successful RAFT/emulsion systems were reported,\(^23,25\) it became evident that such reactions were able to give good molecular weight control over a wide range of molecular weights, although the polydispersity was frequently slightly higher in the heterogeneous systems than in solution systems. Moreover, the RAFT/emulsion systems exhibited significant inhibition periods,\(^23\) retardation of the rate of polymerization dependent on the amount of RAFT agent\(^26\) and the amount of initiator,\(^23\) and an acceleration in the rate of polymerization during the course of the reaction.\(^23,26,27\)

### 9.2.1 Chain-Length Dependence in RAFT/Emulsion

While much has been made of the behavior of the intermediate radical in RAFT-mediated polymerizations, the importance of the chain-length distribution of the dormant chains and the polymeric radicals has only recently been recognized.\(^27\) In particular, the nature
of the termination reaction should be changed by the addition of the RAFT agent.\textsuperscript{27,28} In a classical emulsion polymerization, termination reactions typically involve the reaction between a short chain and a long chain; however, in RAFT-mediated polymerizations all propagating radicals are of approximately the same length and become longer as the polymerization progresses, so termination of two long chains should become important.

The termination reaction has been shown experimentally\textsuperscript{29,30} and through theoretical arguments\textsuperscript{31,32} to be controlled by the diffusion of the radicals towards each other. The termination rate coefficient, $k_{ij}$, is thus chain-length dependent (CLD) because the diffusion of the polymeric radicals is slowed as the length of the polymer chain increases. This phenomenon has been observed through pulsed laser polymerization (PLP) experiments.\textsuperscript{29,30} Recent RAFT-mediated polymerizations at low polymer concentrations have shown the same chain-length dependence for $k_t$ as found in conventional free-radical polymerizations;\textsuperscript{28} however, none of the experiments provide data for the termination rate coefficient at significant polymer concentrations.

The consistent treatment of experimental data in classical emulsion polymerization requires the use of CLD termination.\textsuperscript{29,33} In the RAFT/emulsion case, Monte Carlo modeling of radicals in particles\textsuperscript{27} and kinetically discriminating $\gamma$-relaxation experiments\textsuperscript{26} have shown that the CLD termination reaction has a profound influence on the kinetics of the system. At low conversions, the propagating radicals are short, hence termination is more rapid than in the absence of RAFT; moreover, zero-one kinetics are appropriate for the system. At high conversion, the propagating radicals are much longer, the termination rates much slower and pseudo-bulk kinetics becomes appropriate\textsuperscript{27} (to within 20–30\% error in the rate of polymerization\textsuperscript{26}).

CLD termination manifests itself in RAFT/emulsion systems (both chemically- and $\gamma$-initiated) as an increase in the average number of radicals per particle, $\bar{n}$, during the progress of the reaction. In kinetically discriminating $\gamma$-relaxation experiments, where the polymerization system is removed from the proximity of the $\gamma$-source, thus providing two
steady-states as well as the dynamic transition between them, relaxations were faster in the presence of shorter dormant chains than longer dormant chains in the region in which pseudo-bulk kinetics are valid.

The incorporation of CLD termination into the kinetic scheme of RAFT/emulsion (and indeed homogeneous RAFT-mediated polymerizations) is important, as the proposed mechanisms for retardation that rely on the behavior of the intermediate radical are inapplicable to compartmentalized systems and RAFT agents with unstable intermediate radicals. It has been noted\(^\text{14}\) that benzyl activated RAFT agents as used by Prescott \textit{et al.}\(^\text{23,26}\) and the trithiocarbonates used by Ferguson \textit{et al.}\(^\text{25}\) have a much less stable intermediate radical. It would be expected that the intermediate radicals formed by these RAFT agents would have lesser problems with slow fragmentation and would not undergo significant amounts of intermediate radical termination, as the intermediate radical concentration is much lower.

### 9.2.2 Particle Growth Kinetics

The kinetics of classical emulsion polymerizations were described by Smith and Ewart in terms of a set of population balance equations.\(^\text{34}\) From this scheme, various limiting solutions applicable in certain circumstances can be derived,\(^\text{24}\) the most useful being the zero-one\(^\text{35,36}\) and pseudo-bulk\(^\text{37}\) limits, the latter having now been generalized to account for CLD termination.\(^\text{38}\)

The zero-one limit is characterized by the pseudo-instantaneous termination of two radicals in a particle, limiting the system to either zero or one radical per particle.\(^\text{35,36}\) The zero-one model has been shown to describe the kinetics of styrene emulsion polymerization with small particle sizes\(^\text{35,39}\) and the xanthate-mediated emulsion polymerization of styrene.\(^\text{40}\) The Monte Carlo modeling of RAFT/emulsion particles has shown zero-one kinetics to be appropriate for high-activity RAFT agents at short dormant chain lengths.\(^\text{27}\) Since the inhibition period is at the beginning of the reaction, where the
dormant chains are short, the zero-one model is an appropriate tool to model the inhibition period.

In particles where significant amounts of polymer may be produced in a two-radical environment, the zero-one assumption of pseudo-instantaneous termination breaks down and the system becomes uncompartmentalized. In the case where all exiting radical species re-enter other particles, the reaction may be thought of as mimicking an "equivalent" bulk system, following pseudo-bulk kinetics. The Monte Carlo modeling of RAFT/emulsion particles showed that CLD termination results in significant amounts of polymer being made in a two-radical environment.

The conditions for compartmentalization may be conveniently expressed in terms of the Smith–Ewart rate coefficients for entry, $\rho$, exit, $k$, and bimolecular termination, $c$ (note that, in general, $c$ depends on the number of radicals within the particle); zero-one kinetics requires $\rho/c \ll 1$ and $k/c \ll 1$, while pseudo-bulk kinetics requires either $\rho/c \gg 1$ or $k/c \gg 1$. When the dormant chains are long, $k_pC_p \approx c$, where $k_p$ is the propagation rate coefficient and $C_p$ is the concentration of monomer in the particle. The $\gamma$-relaxation experiments using RAFT/emulsion systems with a high-activity RAFT agent showed that the conditions for pseudo-bulk kinetics are met, to a reasonable approximation, although an error in the calculation of the rate of polymerization of approximately 20–30% compared to the exact solution of the Smith–Ewart equations may be expected.

While pseudo-bulk models of the RAFT/emulsion systems were used for systems at higher conversions, here, zero-one kinetics are used to describe the inhibition period, when the dormant chains are quite small and radical-radical termination reactions occur with quite large rate coefficients.

### 9.2.3 Exit of Small Radicals

The exit of radicals from latex particles has been shown to reduce the rate of polymerization. An exited radical will either terminate in the aqueous phase or re-enter
another particle and, should it enter a particle already containing a radical, it leads to
termination. In the early studies of RAFT/emulsion systems, it was postulated that the R’
radical may exit the particles, leading to a reduction in the rate of polymerization. As
the RAFT agent should be consumed early in the reaction, it was concluded that, for a
high-activity RAFT agent, the exit of the R’ species should have little kinetic effect
throughout the main part of the reaction, although it may have a significant effect in the
early stages. It was subsequently calculated that the probability of a cumyl radical (the
R’ group on a number of common RAFT agents including PPPDTA) exiting a particle
was 0.098 (cf. 0.29 calculated using other estimates of the rate coefficient for the
re-initiation reaction). In the case of a low-activity RAFT agent (which is not consumed
as early in the polymerization), Smulders et al. postulated that the exit of the R’
radical occurred throughout the course of the reaction, leading to a decrease in the rate of
polymerization.

In comparison to homogeneous RAFT polymerizations, the heterogeneous
systems tend to exhibit longer inhibition periods for a given RAFT agent concentration.
The heterogeneous polymerization environment would thus appear to play an important
role in the retardation of these systems. The effect of the exit of the R’ radical is one
that is peculiar to emulsion polymerization; there is no equivalent effect in homogeneous
systems. Moreover, since the inhibition effects occur when the dormant chains are quite
short, the systems follow zero-one kinetics. Thus, mechanisms such as the termination
of intermediate radicals do not provide a suitable explanation for the reduction in the rate
of polymerization, as, under the zero-one assumption, two radicals in the particle are
already assumed to terminate very rapidly.

It will be shown that reducing the specificity of the R’ radical for the RAFT agent,
making the re-initiation process more efficient, significantly reduces the inhibition period,
as does increasing the hydrophobicity of the R’ radical, which decreases the probability of
R’ exiting.
At this early stage of the reaction, modeling predicts that the RAFT-induced exit\textsuperscript{26} of radicals through the formation of dormant $z$-meric species is of kinetic significance, with higher rates of radical exit through this mechanism leading to significantly longer inhibition periods.\textsuperscript{26} This mechanism was shown to lead to a 400-fold increase in the rate coefficient for radical exit in the simulated styrene system.\textsuperscript{26}

Inhibition mechanisms not specific to emulsion polymerization must also be considered. Moad \textit{et al.}\textsuperscript{2} summarized a number of chemical causes of inhibition based on the standard RAFT mechanism proposed by Chiefari \textit{et al.}\textsuperscript{1}. These have since been investigated by numerous workers. Perrier \textit{et al.}\textsuperscript{42} suggested that, in the case of the systems they studied, the inhibition period could be attributed to slow fragmentation of the intermediate radical formed during the consumption of the initial RAFT agent (Scheme 9.1). The slow addition of the $R^*$ radical to monomer was suggested to be the cause of inhibition by Moad \textit{et al.}\textsuperscript{2}, while Chong \textit{et al.}\textsuperscript{12} postulated that inhibition is caused by the $R^*$ radical having a very high addition rate coefficient to the RAFT agent, thus slowing the consumption of the initial RAFT agent.

\begin{equation}
P_n^* + SC\xrightarrow{Z} S\xrightarrow{\text{C-S-R}} P_n - SC\xrightarrow{Z} P_n - SC\xrightarrow{Z} P_n - SC\xrightarrow{Z} R^*
\end{equation}

 Scheme 9.1: The initial fragmentation of the RAFT agent.

### 9.2.4 Improving RAFT/Emulsion systems

Apart from reducing the inhibition period, it is also desirable to improve the rate of polymerization throughout the course of the reaction. Since modeling of styrene RAFT/emulsion has established that (a) CLD termination is important,\textsuperscript{27} (b) that pseudo-bulk kinetics applies at degrees of polymerization greater than $\sim$40,\textsuperscript{26} and (c) the inhibition period can be described by zero-one kinetics (below), there is now a theoretical basis on which to design further improvements to RAFT/emulsion systems.
Of particular interest are oligomeric adducts to the RAFT agent. Such adducts take the canonical form $M_i - S - C(Z) = S$, where the $R$ group of the RAFT agent is the oligomeric or polymeric species $M_i$. The use of these adducts has been described in homogeneous systems for various purposes\(^{17,43}\) and also in emulsion polymerization for the \textit{ab initio} emulsion polymerization of butyl acrylate.\(^{25}\) The oligomeric adducts used by Ferguson \textit{et al}.\(^{25}\) were amphipathic, being a diblock of acrylic acid and butyl acrylate, $(AA)_n-(BA)_m-S-C(Z)=S$. The oligomeric adduct to the RAFT agent, whether hydrophilic or hydrophobic, would be expected to reduce the termination rate coefficient at any given conversion, by increasing the length of the propagating radical. This is particularly true at low conversion, where the rate coefficient for termination is highest in RAFT/emulsion systems.\(^{27}\)

Another method for improving RAFT/emulsion systems that will be explored in further detail below is the use of a RAFT agent that is a \textit{less} effective chain transfer agent (a lower chain transfer constant $C_{tr}$). Highly active RAFT agents promote the RAFT-induced exit mechanism, thus reducing the overall rate of polymerization in RAFT/emulsion systems. In many cases, the activity of the RAFT agents used is considerably more than is required to maintain good molecular weight control,\(^{2,22}\) with the commonly used phenyl-activated RAFT agents having $C_{tr} \approx 6000$,\(^{43}\) and the benzyl-activated RAFT agents used in the experimental studies reported here certainly having $C_{tr} \gg 1$.

\section{9.3 Modeling RAFT Polymerization}

\subsection{9.3.1 Monte Carlo simulation of RAFT/Emulsion}

Some of the modeling presented here makes use of a previously described Monte Carlo model of RAFT/emulsion polymerization.\(^{27}\) The Monte Carlo model makes use of a particle with a pre-existing radical that has a new radical enter it from the aqueous phase. These two radicals may then either propagate, terminate or undergo transfer reactions.
with the dormant chains contained in the particle. As transfer to dormant species reactions occur, the length of the propagating radical and the rate coefficient for termination change. This model has now been used to determine the applicability of various kinetic schemes to RAFT/emulsion systems, obtain a semi-quantitative measure of the Smith–Ewart parameter for annihilation of two radicals, and will be used here to study how entry events change the chain-length distribution of radicals.

### 9.3.2 Chain-Length Distribution of Dormant Chains

In an ideal living polymerization proceeding by a reversible transfer mechanism, the molecular weight distribution of the dormant chains and radicals is given by the Poisson distribution. This is a single-parameter distribution in which the molecular weight polydispersity \( M_w/M_n \) is given by \( 1 + 1/X_n \), where \( X_n \) is the number average degree of polymerization. While RAFT polymerizations typically have a polydispersity that reduces throughout the course of the polymerization (as would be modeled qualitatively by the Poisson distribution), the Poisson distribution typically underestimates the polydispersity of the product.

For the purposes of assessing the robustness to a distribution of dormant chain lengths, the two-parameter Schulz–Zimm distribution may be used to give a physically reasonable distribution of dormant chain lengths for input into the of the Monte Carlo model of RAFT/emulsion particles. Given arbitrary \( X_n \) and polydispersity, this distribution provides a suitable population of chains that may then be used in the Monte Carlo model as the distribution of dormant chains within the initial particle; simulation is then carried out as previously described, with the lifetime of the radicals being expressed as a probability decay curve.
9.3.3 Concentration of Short Dormant Chains

The concentration of the \( z \)-meric dormant chains, \( \text{IM}_zX \) (from hereon denoted as \( ZX \)), in the particles may be estimated using the previously presented Monte Carlo model of RAFT/emulsion systems.\(^{27}\) The approach that is used here is as follows.

First, consider the consumption of \( ZX \) species in a particle containing one radical (the population of \( N_1 \) particles). The rate of consumption of \( z \)-meric dormant chains may be equated to the rate of propagation of the \( z \)-meric radical species, as shown in Eq. 9.2. This assumes that the RAFT equilibrium reaction shown in Eq. 9.1 is sufficiently fast and lies towards the polymeric radicals; this is justified since \( C_{tr} = \frac{k_{tr,RAFT}}{k_p} \) is of order 6000 for phenyl-activated RAFT agents (and it is expected that \( C_{tr} \gg 1 \) for benzyl-activated RAFT agents),\(^{43}\) the equilibrium is suitably fast and \([PX] \gg [ZX]\). Note that Eq. 9.2 is dependent on the initial number of \( ZX \) species, \( n_{ZX}^i \).

\[
P^* + ZX \xrightleftharpoons[k_{tr,RAFT}]{k_{g,RAFT}} PX + Z^* \quad (9.1)
\]

\[
\frac{dn_{ZX}}{dt} \bigg|_{n_{ZX}=n_{ZX}^i, N_1} = -k_p C_p \frac{n_{ZX}}{n_D} \quad (9.2)
\]

The time-evolution of the \( ZX \) species can be estimated in a particle containing one radical from Eq. 9.2; however, in a particle containing two radicals, CLD termination reactions must also be included, making the system considerably more complex. Making use of the Monte Carlo model to simulate the behavior of \( ZX \) species in a particle with two radicals, \( N_2 \), a test particle of given swollen radius and monomer concentration is defined as before.\(^{27}\) Instead of using a single population of dormant chains of length, \( X_d \), in the particle as has been previously described, a bimodal distribution is used; a given number of \( ZX \), \( n_{ZX} \), are added to the particle with the balance of the dormant chain concentration being made up with chains of length \( X_d \). An entry event is then permitted to occur, with the number of propagation steps before termination occurs being taken into account as previously described.\(^{27}\) The fraction of termination reactions involving one
z-meric radical, \( f_{d} \), and the fraction of termination reactions involving no z-meric radicals, \( f_{ll} \), are counted. The rate of termination of z-meric species is related to the rate of entry, \( \rho \), and the fates of the z-meric radicals in termination, \( f_{d} \) and \( f_{ll} \):

\[
\frac{dn_{ZX}}{dt} \bigg|_{n_{ZX}=n_{1}, \, N_{2}} = -2k_{p}C_{p} \frac{n_{ZX}}{n_{D}} + \frac{\rho}{2}(f_{d} + 2f_{ll})
\]  

(9.3)

The time derivatives for the evolution of \( n_{ZX} \) shown in Eq. 9.2 and 9.3 may then be combined, taking account of the populations of \( N_{1} \) and \( N_{2} \) particles (here the \( N_{i} \) are normalized according to the Smith–Ewart convention where \( \sum N_{i} = 1 \)):

\[
\frac{dn_{ZX}}{dt} \bigg|_{n_{ZX}=n_{1}, \, N_{2}} = N_{1} \frac{dn_{ZX}}{dt} \bigg|_{n_{ZX}=n_{1}, \, N_{1}} + N_{2} \frac{dn_{ZX}}{dt} \bigg|_{n_{ZX}=n_{2}, \, N_{2}}
\]  

(9.4)

The population of the ZX species may then be evaluated using suitable values for \( k_{p}, C_{p} \) and \( \rho \); the sensitivity to these parameters may also be readily assessed. The steady-state values of \( n_{ZX} \) may then be assessed. As shown below, the time taken for a perturbed system to return to the steady state is of particular interest.

### 9.3.4 Exit of the RAFT Re-initiating Group

The exit of small RAFT-derived radicals (the R’ radical) from particles has previously been identified as a significant event in inhibition and retardation of RAFT/emulsion systems.\(^{22,40} \) The exit of such radicals has been proposed as a cause of retardation in xanthate-mediated polymerizations through a “frustrated entry” mechanism.\(^{40} \) Moreover, the exit of z-meric radicals has been shown to have the effect of reducing the compartmentalization of the system, reducing \( \bar{n} \) and making pseudo-bulk kinetics appropriate in the case of high-activity RAFT agents.\(^{26} \)

The Monte Carlo modeling of Prescott\(^{27} \) indicated that zero-one kinetics were inappropriate for RAFT-mediated emulsion polymerizations under many circumstances; however, at low conversion, when the dormant chains are also quite short, zero-one kinetics are appropriate.\(^{27} \) On that basis, it may be expected that a zero-one model of the
early stages of RAFT/emulsion systems would provide a suitable model for the emulsion polymerization-specific mechanisms that are involved in inhibition of the polymerization.

Exited radicals may be readily included in models of zero-one kinetics, as has been previously demonstrated in various studies seeking to explain such diverse phenomena as $\gamma$-relaxation data and the nucleation of new particles in a system with large pre-existing particles.\textsuperscript{36,47,48} While previous models were concerned with exiting monomeric radicals,\textsuperscript{36,47,48} here the exit of the RAFT re-initiating radical will be included; these models may be readily adapted to the study of inhibition in the RAFT/emulsion systems under consideration here.

The simplest model of a zero-one system simply accounts for the number of particles with one radical or without any radicals,\textsuperscript{24,49} while this is often sufficient, it is inadequate in circumstances where exit and re-entry of radicals becomes of kinetic interest. Here, three separate populations will be considered: the number concentration of particles with no radicals, $N_0$, the number concentration of particles with one polymeric radical, $N_1^P$, and the number concentration of particles with one R* species, $N_1^R$. This allows transfer to the unreacted RAFT species and the exit of R* radicals to be included in the model.

The population balances described in Figure 9.1 may be written as shown below (Eq. 9.6 to 9.11). In previous formulations of this model (e.g. Prescott et al.\textsuperscript{48}), it was assumed that the population of particles containing short radicals ($N_1^R$) and the concentration of exited radicals ($[R^*]_{aq}$) were both sufficiently small as to make entry of R* species into an $N_1^R$ particle insignificant. In this work, this assumption is relaxed, allowing for the pseudo-instantaneous termination of two R* species in a particle. The effect of the exit of other species (such as regenerated $z$-meric radicals) may be included in the model, denoted here as $k_{\text{exit}}$ ($k_{\text{exit}}$ does not include the exit of R* radicals, for which separately account is taken).
Figure 9.1: An illustration of the processes by which particles are converted between particle types in a zero-one system. The populations and rate coefficients for these processes are included.

In addition to the population balances of the particles, [RAFT] and [R’] are included in the kinetic scheme. As the rate coefficients for transfer to RAFT are different depending on both the leaving and attacking groups, the populations of the R-adduct and P\textsubscript{n}-adduct to the RAFT agent must be separately included, denoted here as dormant chain populations D\textsubscript{R} and D\textsubscript{P}. The rate coefficients for these transfer reactions are as follows:

\[
P^* + D_R \xrightarrow{k_{i,RAFT}} R^* + D_P
\]  

The population balances are thus described by:

\[
\frac{dN_0}{dt} = \left( \rho_i + k_c^{R}[R^*]_{aa} \right) \left( N_1^p + N_1^R - N_0 \right) + k_{dR}N_1^R + k_{exit}(N_0 + N_1^R) \tag{9.6}
\]

\[
\frac{dN_1^p}{dt} = \rho_i N_0 - \left( \rho_i + k_c^{R}[R^*]_{aa} \right) N_1^p - k_{exit}N_1^p + k_{i,RAFT}[D_P]N_1^R - k_{dR}N_1^R + k_{add}C_p N_1^R \tag{9.7}
\]

\[
\frac{dN_1^R}{dt} = -\frac{dN_0}{dt} - \frac{dN_1^p}{dt} \tag{9.8}
\]
\[
\frac{d[D_p]}{dt} = -k_{\text{tr,RAFT}}^1 \frac{N_p^1}{N_c} V_s - k_{\text{tr,RAFT}}^2 \frac{N_i^1}{N_c} + k_{\text{tr,RAFT}}^3 \frac{N_p^1}{N_c} \quad (9.9)
\]

\[
\frac{d[D_R]}{dt} = -\frac{d[D_p]}{dt} \quad (9.10)
\]

\[
\frac{d[R^*]_{\text{aq}}}{dt} = -k_{\text{e}}^R [R^*]_{\text{aq}} \frac{N_c}{N_A} + k_{\text{dR}}^R \frac{N_i^R}{N_A} - k_{\text{t,aq}} T_R [R^*]_{\text{aq}} \quad (9.11)
\]

where \( k_{\text{dR}} \) is the first-order rate coefficient for radical desorption, \( k_{\text{e}}^R \) is the rate coefficient for the entry of the \( R^* \) species into the particle, \( k_{\text{add}}^R \) is the second-order rate coefficient for the addition of the \( R^* \) species across the vinyl group of the monomer, \( \rho \) is the pseudo-first-order rate coefficient for the entry of initiator-derived radicals and \( V_s \) is the swollen volume of a particle with swollen radius \( r_s \). The termination reaction is expressed in terms of the average termination rate coefficient for the aqueous radicals, \( k_{\text{t,aq}} \), and the total aqueous radical concentration, \( T_R \). That particle formation does not occur in this system and that the RAFT moiety is conserved throughout are reflected in Eq. 9.8 and 9.10, respectively.

The rate coefficients for adsorption and desorption of the \( R^* \) species may be estimated using Smoluchowski diffusion expressions as follows:\textsuperscript{24,36}

\[
k_{\text{dR}} \approx \frac{3D_R C_w}{r_s^2 C_p} \quad (9.12)
\]

\[
k_{\text{e}}^R = 4\pi D_R r_s N_A \quad (9.13)
\]

where \( D_R \) is the diffusion coefficient of the \( R^* \) radical. It must be noted that Eq. 9.12 is derived by assuming that the \( R^* \) radical is \textit{indistinguishable} from the monomeric radical and from monomer itself.\textsuperscript{6,23,24,36} That the cumyl radical (a common \( R^* \) species) is approximately the same as the styryl radical (and styrene) is plausible; however, as has been previously noted,\textsuperscript{23} this becomes more problematic in systems where \( R^* \) is (for example) an ethyl methacrylate radical in a styrene/polystyrene matrix. In such a situation, \( C_w \) must be interpreted as the solubility of ethyl methacrylate in water saturated by styrene and \( C_p \) as the solubility of ethyl methacrylate in styrene saturated polystyrene;
it might be reasonable to assume that the ratio of these solubilities $C_w/C_p$ remains approximately constant.\textsuperscript{23} The extension of this model for the inhibition period to systems where $R'$ is dissimilar to the monomer unit is a challenge that will not be addressed here.

The aqueous-phase chemistry for the emulsion polymerization of styrene is well described by the Maxwell–Morrison model for entry.\textsuperscript{50} In this model, the $z$-meric radical formed by aqueous phase propagation enters a particle before other reactions (such as propagation or termination) can occur; it is thus unnecessary to include aqueous propagation beyond $z$-meric species. Noting that the RAFT-induced exit mechanism included in this reaction scheme ($k_{\text{exit}}$) involves only initiator-derived species,\textsuperscript{26} exited radicals may be included in $\rho_i$, assuming that all exited radicals are re-entrant. The evolution equations for the initiator-derived radicals are, thus:

\[
\frac{d[\text{IM}^\bullet]}{dt} = 2k_d[1-I] - k_{p,aq}^1 C_w[\text{IM}^\bullet] - k_{t,aq} T_R[\text{IM}^\bullet] \quad (9.14)
\]

\[
\frac{d[\text{IM}^\bullet_i]}{dt} = k_{p,aq}^{i-1} C_w[\text{IM}_{i-1}^\bullet] - k_{p,aq}^i C_w[\text{IM}_i^\bullet] - k_{t,aq} T_R[\text{IM}_i^\bullet] \quad (2 \leq i \leq z-1) \quad (9.15)
\]

\[T_R = [R^*] + \sum_{i=1}^{z-1}[\text{IM}^\bullet_i] \quad (9.16)\]

\[\rho_i = k_p^{z-1} C_w[\text{IM}_{z-1}^\bullet] \frac{N_A}{N_c} + \frac{N_i^p}{N_c} + k_{\text{exit}} \quad (9.17)\]

The average number of radicals per particle, $\bar{n}$, determines the overall rate of conversion from monomer to polymer in the system. In a zero-one system it may be expressed as a function of the number concentration of particles described above:

\[\bar{n} = \frac{N_1^p + N_1^r}{N_1^p + N_0 + N_1^r} \quad (9.18)\]

The implementation of the model detailed above was undertaken using the numerical differential equation solving algorithm “NDsolve” within Mathematica 3.0 (Wolfram Research Inc.).\textsuperscript{51} The parameters used for the model of the emulsion polymerization of styrene with a persulfate initiator at 50 °C are given in Table 9.1, while
parameters used for the RAFT-mediated polymerization of styrene using a high-activity RAFT agent, such as 2-phenylprop-2-yl phenyldithioacetate (PPPDTA), are shown in Table 9.2. The use of the benzyl activated RAFT agent PPPDTA permits the behavior of the intermediate radical to be neglected in the model, as the fragmentation of the intermediate species formed by PPPDTA is expected to be sufficiently fast to be kinetically insignificant.  

Table 9.1: The parameters used for the modeling of styrene polymerization with a persulfate initiator at 50 °C.

<table>
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<th>parameter</th>
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<tbody>
<tr>
<td>$k_d$ / s$^{-1}$</td>
<td>$1.2 \times 10^{-6}$</td>
<td>52</td>
</tr>
<tr>
<td>$k_p^1$ / dm$^3$ mol$^{-1}$ s$^{-1}$</td>
<td>950</td>
<td>24</td>
</tr>
<tr>
<td>$k_p^i$, $i &gt; 1$ / dm$^3$ mol$^{-1}$ s$^{-1}$</td>
<td>237</td>
<td>53</td>
</tr>
<tr>
<td>$k_{t,aq}$ / dm$^3$ mol$^{-1}$ s$^{-1}$</td>
<td>$1.75 \times 10^{9}$</td>
<td>49</td>
</tr>
<tr>
<td>$C_w = C_w^{sat}$ / mol dm$^{-3}$</td>
<td>$4.3 \times 10^{-3}$</td>
<td>54</td>
</tr>
<tr>
<td>$C_p = C_p^{sat}$ / mol dm$^{-3}$</td>
<td>5.5</td>
<td>35</td>
</tr>
<tr>
<td>$z$</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>$D_w$ / cm$^2$ s$^{-1}$</td>
<td>$1.5 \times 10^{-5}$</td>
<td>55</td>
</tr>
</tbody>
</table>
Table 9.2: System-specific parameters used for the zero-one model of inhibition with a typical high-activity RAFT agent.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{tr}^{+} = \frac{k_{tr,RAFT}}{k_p}$</td>
<td>2000</td>
<td>12</td>
</tr>
<tr>
<td>$C_{tr} = \frac{k_{tr,RAFT}}{k_p}$</td>
<td>12000</td>
<td>12</td>
</tr>
<tr>
<td>$k_{add}^R / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$</td>
<td>$2.86 \times 10^3$</td>
<td>56,57</td>
</tr>
<tr>
<td>$k_{exit} / \text{s}^{-1}$</td>
<td>4</td>
<td>26</td>
</tr>
<tr>
<td>[RAFT] / mmol dm$^{-3}$</td>
<td>15</td>
<td>a</td>
</tr>
<tr>
<td>[I] / mmol dm$^{-3}$</td>
<td>0.114 – 1.32</td>
<td>a</td>
</tr>
<tr>
<td>$r_s / \text{nm}$</td>
<td>50</td>
<td>a</td>
</tr>
<tr>
<td>$N_c / \text{dm}^{-3}$</td>
<td>$1 \times 10^{17}$</td>
<td>a</td>
</tr>
</tbody>
</table>

*a* based on the experimental procedures of Prescott *et al.*$^{23}$

9.3.4.1 *Quantifying Inhibition Periods*

While it is often convenient to distinguish between an inhibition period and the retardation of the polymerization throughout the course of the reaction, it must be remembered that there is no sharp boundary between the inhibition period and the start of the approach to steady state. In this case, it is suggested that the mechanisms of inhibition are quite different from the mechanisms involved in retardation; hence, the distinction between retardation and inhibition is indeed a useful one, although the inherent difficulty in quantifying a time period with no sharp finish remains.

In comparing the experimental data and theoretical model, it must be remembered that the experimental data include not only the effect of exited radicals as described here, but also the effect of oxygen$^{58}$ and any other residual inhibitors common to all free radical polymerizations, and RAFT-specific effects observed in homogeneous media. On this basis it would be expected that the theoretically determined inhibition times would be an underestimate of the experimentally determined inhibition period.
For the purposes of quantifying the inhibition periods in the experimental data of Prescott et al.,\textsuperscript{23} the steady-state section of the conversion vs time plot has been extrapolated to zero conversion to give a measure of the inhibition period, as shown in Fig. 9.2.

\textbf{Figure 9.2:} Linear extrapolation (thick lines) of the initial steady state of polymerization back to zero conversion provides a measure of the inhibition period (time-intercept of thick lines). Data reprocessed from Prescott et al.;\textsuperscript{23} the apparent negative rate of conversion in the initial stages is due to thermal instability caused by the addition of the initiator and variations in the ambient temperature.

In the case of the data generated by the zero-one model described here, the approach to steady state is influenced by the value for $k_{\text{exit}}$ used in the modeling. Moreover, the extrapolation from steady-state approach outlined above for the treatment of the experimental data has an unphysical sensitivity to $k_{\text{exit}}$; the inhibition period is seen to counter-intuitively decrease as $k_{\text{exit}}$ increases, as an artifact of the extrapolation having a progressively gentler slope due to the use of zero-one kinetics for the take-off from inhibition.
An alternate method for determining the inhibition period must, therefore, be developed. Shown pictorially in Fig. 9.3, this method assumes that the inhibition period is approximately the period of time required for consumption of the initial RAFT agent. An arbitrary cut-off point of 99.9% consumption is defined as the end of the inhibition period. This method is not influenced by the approach to steady state in the same way as the linear extrapolation method; increasing $k_{\text{exit}}$ results in an increasing inhibition time, as would be intuitively expected from a simple treatment of zero-one kinetics (increasing $k_{\text{exit}}$ leads to reduced radical lifetimes, meaning that less of the initial RAFT agent may be consumed per radical). The inhibition time so calculated is not strongly dependent on the consumption threshold chosen (e.g. 99% or 99.99%), as may be deduced from Fig. 9.3.

![Figure 9.3: Populations of the different types of particles, $N_1^R$ (---), $N_1^P$ (—), $N_1^N$ (· —) (left axis), and the concentration of the initial RAFT agent, $[D_R]$ (right axis), as a function of time for $[I] = 1.32 \text{ mM}$. The inhibition period is taken to be the point at which 99.9% of the RAFT agent is consumed (circled).](image)

### 9.3.5 Modeling Altered Experimental Conditions

The alterations to the experimental conditions outlined above may be simulated using a combination of techniques including the previously described Monte Carlo model of RAFT/emulsion particles, the previously described transfer-exit model of desorbing
z-meric radicals, and the zero-one model of inhibition presented here. The methods by which the degree of improvement in the performance of RAFT/emulsion systems may be estimated will now be described for each of the suggested alterations.

9.3.5.1 Oligomeric Adducts to the RAFT Agent

The use of oligomeric RAFT agents is expected to give a reduction in the average pseudo-first-order termination rate coefficient, \( c \). The resulting improvement in the inhibition period may be estimated using the semi-quantitative measure of \( c \) provided by the Monte Carlo model of RAFT/emulsion particles. \(^{26,27}\) In terms of input parameters to the Monte Carlo model, the oligomeric adduct to the RAFT agent may be approximated as a slightly longer dormant chain for any given conversion. In the case of an oligomeric RAFT adduct, such as that described by Ferguson et al., \(^{25}\) the dormant chain is 10 to 20 units longer at any given conversion.

9.3.5.2 Less Active RAFT Agents

It has been previously shown that a reduction in the activity of the RAFT agent leads to an increase in \( c \), which would be expected to be detrimental to the rate of polymerization. \(^{27}\) However, a less active RAFT agent will also change the rate of accumulation of dormant z-meric species in the particles, thus reducing \( k \), and would also be expected to change the length of the inhibition period.

The accumulation of z-meric dormant species is readily studied using the adaptation to the Monte Carlo model presented here. Similarly, the effect of RAFT agent activity may be readily quantified using the zero-one model for the inhibition period reported here.
9.4   **Results**

9.4.1   **Distribution of Dormant Chain Lengths**

Since termination is a chain-length dependent reaction, it would be expected that addition of more short chains to the system would increase the rate coefficient for termination. The actual chain-length dependence of termination is not linear in chain length, so the Schulz–Zimm distributions used here lead to a decrease in the lifetime of the radicals with broadening dormant-chain length distribution, as shown in Fig. 9.4.

![Figure 9.4](image)

**Figure 9.4:** The probability of an incoming radical consuming at least $j$ monomer units, $P_j$, for a model styrene system with $r_s = 50$, dormant chains with $\bar{X}_n$ of 20 and 100, and polydispersity PD of 1, 1.1, and 1.3. Parameters for Monte Carlo modeling as previously described.\(^{27}\)

The lifetime of the radical is reduced, although not significantly, by broadening the distribution of the dormant chains to $\bar{M}_w/\bar{M}_n = 1.1$, with a further reduction in radical lifetime seen with $\bar{M}_w/\bar{M}_n = 1.3$. It may be noted that the previously reported RAFT/emulsion experiments showed $\bar{M}_w/\bar{M}_n$ in the region 1.1 to 1.3 for the final product\(^{23,27}\) and that the dormant chains should have a polydispersity somewhat less than the final product (which includes termination products). Simplifying the population of
dormant chains to a single degree of polymerization is thus a suitable approximation to a mono-modal distribution of dormant chains with a high-activity RAFT agent.

9.4.2 Fate of Short Dormant Chains

The steady-state number of short dormant chains per particle is shown in Fig. 9.5 to be quite low, being less than one per particle except for the large $r_s = 120$ nm particles at high [RAFT]. This may be understood qualitatively by recognizing that since $\bar{n}$ is low (and $\rho \approx c$), few particles contain two or more radicals (a necessary condition for ZX species to be generated). Since the steady-state number of ZX species in the particles is non-integral, a particle cannot be in the steady state and is perturbed from the steady state when an entering $z$-meric radical creates a ZX species. The response of a particle to a perturbation away from the steady state becomes quite important in estimating the importance of the RAFT-induced exit mechanism.\(^{26}\)

![Figure 9.5](image)

**Figure 9.5:** The steady-state of the number of $z$-meric dormant chains per particle with RAFT agents of various activity and dormant chain lengths. [RAFT] = 8.5 mM, $r_s = 50$ nm.

It was previously calculated that for the emulsion polymerization of styrene with a high-activity RAFT agent ($C_tr = 6000$, [RAFT] = 8.5 mM), an incoming $z$-meric radical
would transfer its radical activity and form a dormant z-meric radical in 90% of cases. Thus, a radical entering a particle is a large perturbation away from the steady-state number of dormant z-mers in the particle. The response to such a perturbation is shown in Fig 9.6. It is seen that a ZX species in excess of the steady-state concentration are consumed with a rate coefficient somewhat less than 0.4 s\(^{-1}\) and that as [RAFT] increases, the excess ZX species are consumed more slowly (radical activity being shared between more chains and, thus, the ZX species is activated less frequently).

\[ \frac{dn_{ZX}}{dt} = k_{react} \] $n_{ZX}$

\[ k_{react} = 0.4 \text{ s}^{-1} \]

Moreover, Fig. 9.6 shows that, in a particle where $n_{ZX} = 1$ (e.g. a particle which has recently had a z-mer enter), the frequency of consumption of ZX species is somewhat less than the frequency of exit calculated from the RAFT-induced exit mechanism (it was previously estimated that, for this system, $k = 4 \text{ s}^{-1}$). The most likely fate for the dormant z-mer in such a particle is thus reactivation followed by exit, re-entry into another particle, then transfer to a dormant chain forming another ZX species. It may be concluded from this most-probable path, that while the number of ZX species does not build up appreciably over the course of the reaction, particles containing a growing
radical are highly likely to contain a ZX chain and that the radicals are uncompartmentalized as a result.

9.4.3 Fate of RAFT Re-initiating Group

Experimentally determined inhibition periods based on the work of Prescott et al.\textsuperscript{23} are shown in Fig. 9.7, together with the inhibition periods calculated using the zero-one model presented above. The values of $C_{\text{tr}}^1$ and $C_{\text{tr}}$ from Chong et al.\textsuperscript{12} used in this model have considerably uncertainty; however, the ratio $C_{\text{tr}}^1/C_{\text{tr}}$ is more reliable. For this reason, the predicted inhibition periods shown here include those derived from both the values reported by Chong et al.\textsuperscript{12} and half those values. While the length of the inhibition period reported here is relatively insensitive to $C_{\text{tr}}^1$ and $C_{\text{tr}}$ individually, the ratio $C_{\text{tr}}^1/C_{\text{tr}}$ will be shown to be quite significant.

![Figure 9.7](image)

**Figure 9.7:** The experimentally determined inhibition periods (from Fig. 9.2) along with those determined from the zero-one modeling using the RAFT consumption technique to measure the inhibition periods at representative $C_{\text{tr}}^1$ and $C_{\text{tr}}$ values. The dashed line is a $[I]^{-1/2}$ fit to the $C_{\text{tr}}^1 = 1000$ data (●).

It may be noted that the experimentally determined inhibition periods are highly variable, potentially due to factors such as variations in oxygen content, although the work of Calitz et al.\textsuperscript{18} indicates that some RAFT systems may be insensitive to oxygen
ingress. The correspondence between theory and experiment shown in Fig. 9.7 is encouraging given this caveat.

### 9.4.4 Altering Experimental Conditions

Those methods of improving the performance of RAFT/emulsion systems for which quantitative measures were described above are presented here. Considering first the use of oligomeric adducts to the RAFT agents, the lifetimes of the radicals are shown as probability decay curves in Fig. 9.8. The previously described integration method\(^2\) may then be used to obtain a semi-quantitative value of \(c\) from these probability curves, as shown in Fig. 9.9.

![Probability decay curves](image)

**Figure 9.8:** The probability \(P_j\) of an entering radical consuming \(j\) or more monomer units at various fractional conversions \(x\), showing the improvement offered by the use of an oligomeric RAFT adduct. Simulation parameters: \(X_d = 10, 100, \ C_r = 6000, \) [RAFT] = 8.5 mM, oligomeric adduct is \(M_{20} \cdot S(Z) = S\).
Chapter 9  Improving Performance of RAFT/Emulsion

Figure 9.9: The semi-quantitative value of $c$ determined by the Monte Carlo simulation of RAFT/emulsion particles,\textsuperscript{26,27} showing the improvement offered by the use of an oligomeric adduct to the initial RAFT agent. Simulation parameters: $X_d = 10, 100, C_t = 6000, [RAFT] = 8.5$ mM, oligomeric adduct is $M_{20-S(Z)}=S$.

It is seen in Fig. 9.8 and 9.9 that the use of an oligomeric adduct to the RAFT agent (in this case, $M_{20-S(Z)}=S$) gives a significant improvement in inhibition, particularly at low conversion. The chain-length dependent nature of the termination reaction makes the increase in chain-length due to the oligomeric adduct more important at low conversion than at higher conversion. The Monte Carlo-derived values of $c$ shown in Fig. 9.9 have previously been shown to provide a good semi-quantitative measure of the experimental values of $c$, with the shape of the relation being well described but the actual values of $c$ somewhat erroneous.\textsuperscript{26}

9.5 Discussion

9.5.1 Short Dormant Chains

While it was shown that the kinetics of RAFT polymerization in emulsion are relatively unchanged by a distribution of chain lengths of dormant species (Fig. 9.4), it was also seen that the presence of dormant $z$-meric species ($ZX$) has a profound influence on the kinetics of the system. In particular, it was seen that an entering $z$-meric radical was most
likely to transfer radical activity to a dormant chain creating a ZX species. Subsequently, the most probable reaction pathway is for the z-mer to be reactivated and for this radical to exit the particle.

The previously described RAFT-induced exit mechanism\textsuperscript{26} requires the formation of ZX species in the particle; thus, the ZX species is potentially detrimental to the performance of the system, as increasing $k$ decreases $\bar{n}$. A means of reducing the probability of forming ZX species when an entry event occurs is, thus, desirable. In Fig. 9.10, the probability of forming a ZX molecule when a z-mer enters a particle is shown as a function of $C_{tr}$ and with varying [RAFT] (as this depends only on the concentrations of monomer and RAFT in the particles, it is independent of $r_s$). As would be expected, higher [RAFT] leads to an increased probability of forming the dormant z-mer, as does increasing $C_{tr}$. A reasonable means of reducing $k$ and improving the performance of the system is, thus, to reduce $C_{tr}$.

It has been noted that the RAFT agents often used in polymerizations have a value of $C_{tr}$ somewhat higher than is required for the control of molecular weight;\textsuperscript{22} moreover, Fig. 9.10 indicates that reducing $C_{tr}$ to $\sim 10$ (or $10^2$) will lead to a significant reduction in the formation of ZX species. Compared with a system with a very high activity RAFT agent ($C_{tr} \approx 6000$), the adoption of a RAFT agent with $C_{tr} \sim 10$ would thus reduce the formation of ZX species by 20-fold, reducing $k$ by a similar amount. A RAFT agent with $C_{tr} \sim 10$ is still active enough to give good molecular weight control.\textsuperscript{2,22}
Figure 9.10: The probability of forming a dormant \( z \)-mer when an entry event occurs in a styrene system at 50°C (independent of \( r_s \)), shown as a function of the transfer constant of the RAFT agent, \( C_{tr} \).

### 9.5.2 Fate of Re-initiating Group

The role of the R* (or re-initiating) group of the RAFT agent in the inhibition period has been described by the zero-one model presented here. The experimental procedures of Monteiro et al.\textsuperscript{22} and the transport of the RAFT agent between the monomer droplets and the particles will now be reviewed in light of the zero-one model; moreover, this model will be used to predict how the inhibition period may be minimized.

Comparison of homogeneous polymerizations with emulsion polymerizations indicates that the inhibition periods in emulsion polymerizations are significantly longer than those experienced in bulk or solution.\textsuperscript{11,23,42} Therefore, the heterogeneous polymerization environment must play a significant role in the inhibition period. With the premise of the modeling presented here that the inhibition period ends once the initial RAFT agent is consumed, it may be concluded that the rate of consumption of the initial RAFT agent is slower in a small particle from which exit can occur than in bulk or, indeed, in a monomer droplet. This has further consequences for the transport of RAFT agents between droplets and particles.
The role of the monomer droplets in well-behaved emulsion polymerizations is (with a few exceptions\textsuperscript{59}) only to provide a reservoir of monomer to the propagating radicals that are located in the particles\textsuperscript{24} and small amounts of droplet polymerization are normally insignificant to the kinetics of the polymerization.\textsuperscript{24} It has previously been argued that the diffusion of monomer from the droplets to the particles should not be rate-determining in most situations.\textsuperscript{24} Using similar arguments, it has been suggested that there should be no kinetic barrier to the transport of the RAFT agent from the droplets to particles.\textsuperscript{22} On this basis, experimental procedures were developed that involved dissolving the RAFT agent in the monomer before adding the organic phase to seed latex and commencing polymerization, relying on the rapid transport of the RAFT agent across the aqueous-phase to transport the RAFT agent to the locus of polymerization in the particles.

While there may be little kinetic barrier to the initial movement of RAFT agent between the monomer droplets and the particles,\textsuperscript{22} it will partition between these phases in approximately equal concentrations.\textsuperscript{6,23} As the initial RAFT agent is consumed in the particles, more RAFT agent may move across from the droplets to the particles; however, if the rate of consumption of the RAFT agent is greater in the droplets than in the particles, movement of RAFT agent may actually be in the other direction, exacerbating the problem of having the RAFT agent in the monomer droplets.

Once the initial RAFT agent has been consumed, forming an oligomeric adduct to the RAFT agent, the water solubility of the species drops significantly. This reduces the rate at which transport of the RAFT moiety between the droplets and particles occurs, keeping the RAFT agent and the oligomeric species attached to it in the droplets.\textsuperscript{6,23}

\subsection{9.5.2.1 Reducing Inhibition Periods}

Based on the model presented here, it is suggested that the inhibition period of RAFT/emulsion systems is readily tunable based on the properties of the R’ radical.
Noting the relative insensitivity of the inhibition period to the values of $C_{1tr}$ and $C_{-tr}$ (at least for high-activity RAFT agents with $C_{1tr}/C_{-tr}$ constant), the particular property of most interest for reducing the inhibition period is the rate coefficient for the desorption of the R’ radical, $k_{dR}$, insofar as it influences $P(\text{exit-R'})$:

$$P(\text{exit-R'}) = \frac{k_{dR}}{k_{dR} + k_{add}C_p + k_{-tr,RAFT}[\text{RAFT}_p]}$$

(9.19)

In this expression for $P(\text{exit-R'})$, transfer to the initial RAFT agent does not need to be included as it does not change the probability of R’ exit, as previously shown by Prescott et al.23 A naïve treatment of Eq. 9.19 would tend to suggest that increasing $k_{-tr,RAFT}$ would also be of benefit; however, this acts to reduce the rate of consumption of the initial RAFT agent by ejecting a P’ radical and reforming the RAFT$_R$ species.

Consideration of each of the terms in Eq. 9.19 indicates that the dominant process is transfer back to the polymeric RAFT agent, making $P(\text{exit-R'})$ approximately proportional to $k_{dR}$. A reduction in $k_{dR}$ would thus reduce the chance of R’ exiting, increasing the compartmentalization of the radicals and increasing the amount of RAFT agent that may be consumed per z-meric radial generated. The effect of a reduction in $k_{dR}$ by a factor of 10 is shown in Fig. 9.11, showing an improvement in the inhibition period of between 25 and 40%, depending on [I]. In practice, $k_{dR}$ may be reduced by making the R’ moiety less water-soluble or by reducing its diffusion coefficient; this is illustrated in part in Eq. 9.12, although once R’ is no longer chemically similar to the monomer the applicability of Eq. 9.12 becomes questionable. A styrene dimer radical as an R’ species would have a significantly reduced value of $k_{dR}$ (indeed, in the treatment of $\gamma$-relaxation data, it is usually assumed that only monomeric styrene radicals are capable of exit).
Figure 9.11: Comparison of different methods to reduce the inhibition period exhibited by RAFT/emulsion systems. Decreasing $k_{dR}$ or $k_{\text{exit}}$ both reduce the inhibition period, as does changing $R'$ so that it has the same transfer constant as the polymeric radical.

For the same reasons, a reduction in $k_{\text{exit}}$ (i.e. the desorption of other radicals, such as regenerated $z$-meric radicals) improves compartmentalization giving a similar decrease in the inhibition period, also illustrated in Fig. 9.11. Here, a 40-fold reduction in $k_{\text{exit}}$ is shown to reduce the inhibition period by a similar amount to the previously illustrated reduction in $k_{dR}$. A reduction in $k_{\text{exit}}$ may be achieved by reducing the number of dormant $z$-meric species formed, for example, by reducing $C_\text{tr}$ (and $C_{\text{tr}}^1$) or using an oil-phase initiator.

A final strategy for reducing the inhibition period is to make the addition of the $R'$ radical to the polymeric RAFT agent less favored. While, from Eq. 9.19, this would be expected to increase $P(\text{exit-}R')$, thus adversely affecting the system, it also serves to increase the rate of consumption of the initial RAFT agent, as shown in Eq. 9.9. In Fig. 9.11, the effect is shown of altering $R'$ such that $C_{\text{tr}}^1 = C_{\text{tr}} = 6000$. This would be the situation were both the forward and reverse transfer reactions to occur with the same transfer constant as that of the polymeric radical. With these values of $C_{\text{tr}}^1$ and $C_{\text{tr}}$, a reduction in the inhibition period by 40 to 50% is predicted (similarly, with
$C_r^1 = C_{-r} = 2000$, a 25 to 30% reduction in the inhibition period is predicted). The use of a styrene dimer radical as an $R^*$ species (as suggested above for reducing $k_{dR}$) would alter $C_r^1$ and $C_{-r}$ in this way.

In the event that all three methods detailed here for reducing the inhibition effects of RAFT/emulsion systems can be implemented in the same system, the calculated inhibition period is reduced by 85 to 90% (also illustrated in Fig. 9.11). Under such circumstances, the experimentally determined inhibition period would be dominated by features common to all RAFT polymerizations rather than intrinsic effects of the RAFT/emulsion system.

The modeling work of Chong et al.$^{12}$ illustrated that the efficiency of the re-initiation step in a homogeneous polymerization plays an important role in determining the molecular weight polydispersity of the system. It may be expected that this would also be the case in the RAFT/emulsion inhibition periods, with the strategies to reduce inhibition outlined here also reducing the molecular weight polydispersity of the system.

### 9.5.3 Understanding of RAFT/Emulsion

Credible explanations have been presented here of the inhibition periods in RAFT/emulsion systems. Significant work remains in quantifying and interpreting both the qualitative and quantitative aspects of the modeling work presented; additionally, experimental tests of the model must be devised and performed.

It is now possible to review each of the major features of the RAFT/emulsion polymerization in terms of the mechanistic models available. In particular, the following aspects will be discussed: inhibition periods, colloidal stability of the polymerization, effectiveness of molecular weight control, reduction in the rate of polymerization, acceleration throughout the reaction and the fast $\gamma$-relaxations.
9.5.3.1 **Inhibition period**

Starting from the commencement of the reaction, the inhibition period may be explained satisfactorily in terms of the fate of the R’ radical. In their early work on RAFT/emulsion systems, Monteiro *et al.*\(^{22}\) noted that the exit of the R’ species would be kinetically significant in the first few percent conversion for a high-activity RAFT agent (or throughout the polymerization in the case of the xanthates used by Smulders *et al.*\(^{40}\)). Meanwhile, the work of Chong *et al.*\(^{12}\) in homogeneous polymerizations showed that the typical R’ radical has a high affinity for transferring back to the RAFT agent, thus slowing down the consumption of the initial RAFT agent. Combining these two effects in a simple zero-one model of the inhibition period permits a quantitative explanation of the inhibition period.

9.5.3.2 **Colloidal Stability**

Several of the early reports of RAFT/emulsion experiments described many problems with colloidal stability.\(^{22,60}\) In particular, highly-colored, viscous layers were seen to appear spontaneously at about the time when the monomer droplets would disappear.\(^{22}\) While it had been shown that there should be little kinetic barrier to RAFT agent transport from the monomer droplets to the particles,\(^{22}\) the RAFT agent would still partition between the droplets and particles in approximately equal concentrations.\(^{23}\) Polymerization within the monomer droplets, while normally kinetically insignificant,\(^{24}\) could then lead to an oligomeric RAFT adduct that is unable to transport through the aqueous phase to the particles.\(^{23}\) Moreover, as inferred from the modeling work presented above, consumption of the initial RAFT agent may be faster in the droplets than in the particles, resulting in transport of the RAFT agent from the particles to the droplets, contrary to the desired outcome.

As monomer is consumed, the low molecular weight polymer produced by these RAFT agents will remain in the droplets. As the material contains the RAFT agent in relatively high concentration, it is seen to be highly colored and, given its low molecular
weight, it is quite “sticky”. While the shear of stirring is able to keep breaking up these droplets when monomer is plentiful, as the monomer is consumed these droplets of low-molecular weight polymer continue to coalesce, eventually causing loss of colloidal stability at about the point where the monomer droplets would normally have evaporated. This could be through coalescence of these droplets with true particles as well as with each other.

9.5.3.3 Molecular Weight Control

The previously reported problems with control over the molecular weight of the products of RAFT/emulsion experiments may be classified into problems with control of the molecular weight and problems within controlling the molecular weight polydispersity, $M_w/M_n$. The high polydispersity reported in some of these systems may be attributed to multiple polymerization environments, namely the particles and the monomer droplets, with different RAFT agent concentrations in each environment due to difficulties in transporting the RAFT moiety between them.

The sampling procedure used when collecting latex samples for drying and subsequent molecular weight analysis will have a significant effect on the molecular weight results when there are multiple polymerization environments that are quite different in nature (e.g. small particles that remain dispersed due to Brownian motion and large droplets that will cream and coalesce in the absence of stirring). In many cases, poor control of $M_n$ (as opposed to poor control of the molecular weight polydispersity) may be due to sampling artifacts.

Hydrolysis of the RAFT agent may also lead to deviations from the ideal $M_n$, with the various RAFT agents that have been considered having quite different susceptibility to hydrolysis. High initiator concentrations (leading to large numbers of initiator-derived radicals) may also lead to poor control of the molecular weight, particularly when extended polymerization times are used.
9.5.3.4 Retardation of Polymerization

The retardation of RAFT-mediated polymerizations has received considerable attention with numerous theories being proposed; it is possible that each of the proposed theories is quantitatively correct in a specific set of circumstances, whilst having little effect in others. Importantly, RAFT-mediated emulsion polymerizations have tended to show a greater degree of retardation than equivalent homogeneous systems, indicating that the heterogeneous polymerization environment plays an important role in the retardation of these systems.\textsuperscript{6,23,26}

It has now been shown that the compartmentalization of the radicals is vastly reduced in the RAFT/emulsion system due to the desorption of $z$-meric radicals. Consideration of this effect with respect to the Smith–Ewart equations\textsuperscript{34} indicates that the reduction in compartmentalization has the effect of reducing the number of radicals that may found in the system, thus reducing the rate of polymerization.

9.5.3.5 Gradual Acceleration of Polymerization

In many RAFT/emulsion reactions, $\bar{n}$ is seen to increase throughout most of the reaction (while remaining below what would be expected in the absence of RAFT). This is expected in a pseudo-bulk system in Interval II (when the particles are growing in size, hence the first-order rate coefficient for termination, $c$, is falling); however, this is seen in RAFT/emulsion reactions even if the system is in Interval III (when the particles remain approximately the same size). It was demonstrated through the Monte Carlo modeling of RAFT/emulsion particles that $c$ reduces throughout the course of the reaction due to the chain-length dependent termination reaction;\textsuperscript{27} once again, considering the Smith–Ewart equations, a reduction in $c$ leads to an increase in both $\bar{n}$ and the rate of polymerization.
9.5.3.6  Fast Relaxations

The previously reported $\gamma$-relaxation of RAFT/emulsion systems showed that the relaxation occurs faster than would be expected in the absence of RAFT.\textsuperscript{26} This phenomenon may be understood in terms of the lack of compartmentalization in the system, where the dormant $z$-meric species are reactivated and may then leave the particle, resulting in the exit of a radical from the particle. An increase in the rate of generation of desorbable radicals has been shown to lead to an increase in $k$,\textsuperscript{64} and as $k$ increases, radicals have more frequent opportunities to terminate, making the relaxation faster.

9.5.3.7  Remaining Difficulties

While there is now at least a qualitative (and, in many cases semi-quantitative or quantitative) explanation of most facets of RAFT/emulsion systems, there are still two significant aspects of these systems that are not well understood.

Firstly, the role of RAFT agents in the particle formation process is almost entirely unknown. The work presented here, along with that of various other workers, has been principally concerned with seeded or miniemulsion systems in which particle formation is of little consequence. While significant advances in the use of RAFT in the \textit{ab initio} polymerization have been made through the use of low-activity RAFT agents\textsuperscript{62} and amphipathic RAFT agents,\textsuperscript{25} this is still a relatively unexplored area.

A further curious observation noted by many workers is that polymerization in RAFT/emulsion systems often ceases before 100% conversion (as measured by various techniques including dilatometry and gravimetry). In reactions from which samples are removed, one may speculate about the oxygen sensitivity of the RAFT process; however, no experimental evidence has yet been presented and the studies of Calitz \textit{et al.}\textsuperscript{18} indicate that the RAFT systems are not significantly affected by the ingress of oxygen.
9.5.4 Improving RAFT/Emulsion

The models that have been presented recently for RAFT/emulsion systems\textsuperscript{26,27} suggest strategies for the optimization of such systems. Specifically, it has been suggested here that the use of an oligomeric adduct to the RAFT agent and a reduced activity (lower $C_t$) RAFT agent would lead to improvements.

The use of an oligomeric adduct to the RAFT agent was shown above to lead to a significant reduction in $c$, particularly at low conversions. This effect would not be restricted to amphipathic RAFT agents, such as those of Ferguson \textit{et al.},\textsuperscript{25} but would also be seen in hydrophobic adducts, such as those described by Goto \textit{et al.},\textsuperscript{43} and is general to both homogeneous and heterogeneous polymerizations. While the kinetics of RAFT/emulsion experiments with such agents are yet to be described in detail, the successful use of amphipathic RAFT agents in the \textit{ab initio} emulsion polymerization of butyl acrylate has been described by Ferguson \textit{et al.}\textsuperscript{25} In the work of Ferguson \textit{et al.},\textsuperscript{25} the oligomeric adduct to the RAFT agent is amphipathic, comprising an acrylic acid block and a butyl acrylate block.

It is also feasible to use such RAFT agents in miniemulsion systems,\textsuperscript{65} since the water solubility of the RAFT agent is less important. Indeed, such RAFT agents could be used as a replacement of the hydrophobe in the miniemulsion, thus replacing one component in the miniemulsion recipe, leading to simpler recipes and removing the detrimental effects frequently introduced by the hydrophobe.

The rate coefficient for the exit of radicals from the particles, $k$, has been postulated to be quite dependent on the ability of an entering $z$-meric radical to transfer radical activity to a dormant chain within the particle.\textsuperscript{26} It was shown above that the use of a less-active RAFT agent (e.g. $C_t$ of ~10 rather than ~6000) has a beneficial effect on the production of such dormant $z$-mers; molecular weight control should not be affected by such a change. Such a technique will improve the rate of polymerization by increasing $\bar{n}$. 
The inhibition period was modeled successfully by including in the simulation the preference for the R’ radical to add to the RAFT agent over monomer, the desorption of R’ radicals and the desorption of other radicals through the RAFT-induced exit mechanism. Making appropriate changes to parameters affecting each of these kinetic events led to a reduction in the calculated inhibition period, with the best results coming from a combination of improvements. Various methods for implementing these changes were suggested above, but notably the use of a less-water soluble R’ radical should make a significant improvement by reducing $k_{dR}$, as also suggested by the experiments with dithiobenzoates reported by Monteiro et al.\textsuperscript{22} and experiments with xanthates reported by Smulders et al.\textsuperscript{40} In the case of the xanthates, the effect of the R’ radical is seen throughout the reaction as a retardation in the rate of polymerization, because the consumption of the initial xanthat typically takes much longer than for a high-activity RAFT agent.\textsuperscript{41,61} The use of a quite hydrophobic RAFT agent in an emulsion polymerization would require the use of an assisted transport technique such as that previously described.\textsuperscript{23}

Finally, alternate systems may be constructed that also improve the performance of RAFT/emulsion systems based on these general principles. If, for example, one uses a small amount of a water-soluble co-monomer in the polymerization (say, 5% methyl acrylate in the styrene polymerization) the water-soluble monomer is principally found in the water phase and a significant proportion of the incoming $z$-meric species would have the radical functionality of this co-monomer. In the case of a methyl acrylate radical, the incoming radical will frequently have acrylate functionality, and will be sufficiently fast propagating as to reduce the probability of forming dormant $z$-meric species.

\textbf{9.6 Conclusions}

It has been seen here that the inhibition period of the RAFT/emulsion system may be successfully modeled using zero-one kinetics accounting for the RAFT-induced exit of radicals,\textsuperscript{26} the desorption of the R’ radical from the particles and the specificity of R’ for
RAFT over monomer. Additionally, the robustness of the Monte Carlo model (and the conclusions about RAFT/emulsion kinetics derived here and in previous publications\textsuperscript{26,27}) to a distribution of dormant chains was tested, with modest polydispersity in the dormant chain distribution having little effect on the kinetics.

The z-meric dormant chains involved in the RAFT-induced exit mechanism were shown to be in low numbers in the steady state. However, it was also shown that individual particles may deviate significantly from the steady-state position; moreover, such deviations have a significant impact on the kinetics of the system because other processes are likely to occur before the particle can tend back towards its steady-state position. In particular, it was shown that it is highly probable that a particle containing high-activity RAFT agents will form dormant z-meric species when a radical entry event occurs and that such dormant chains will then lead to the RAFT-induced exit of the radical from the particle.

Various approaches for improving the rate of polymerization of the RAFT/emulsion systems were suggested, with the use of lower-activity RAFT agents being a key route to improvement. Additional improvement may be obtained through the use of a highly hydrophobic R group on the RAFT agent to reduce the inhibition period and a slowly diffusing R group to reduce the termination rate coefficients at any given conversion.

Finally, a coherent description of RAFT/emulsion systems has been presented here, incorporating at least qualitative understanding of various facets of RAFT/emulsion experiments, including issues with colloidal stability and molecular weight control, the kinetics of the inhibition period, the retardation of polymerization and the acceleration of polymerization throughout the reaction. Importantly, the results of kinetically discriminating $\gamma$-relaxation experiments are shown to be consistent with the proposed mechanisms.
9.7 Acknowledgements

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9.8 References


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Chapter 9

Improving Performance of RAFT/Emulsion


(51) “NDSolve” makes use of the Gear algorithm when solving stiff differential equations.


