Chapter 4

Episode I

Developing Theory to Understand Experiment

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RAFT in Emulsion Polymerization: What Makes It Different.
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> *If there is a 50/50 chance of something going wrong,*
> *nine times out of ten it will.*
>
> – Mathematical Version of Murphy's Law

4.1 RAFT/Emulsion Can Work

In previous chapters, it was noted that the pioneering studies of RAFT polymerization in emulsion systems had suffered from one or more significant drawbacks, making it impossible to obtain meaningful kinetic parameters from the experimental results. In particular, the studies reported:

- poor colloidal stability (phase separation or coagulation),[1,2]
- poor control of $\overline{M}_n$, the number-average molecular weight,[1-3] or
- poor control of the polydispersity.[2-6]

It was shown in Chapter 3 that these three main problems that have beset previous studies were avoided by the use of the acetone transport technique, suggesting that all three are attributable to poor transport of the RAFT agent.

In summary, the acetone transport technique was shown to permit colloidal stability to be maintained throughout the course of the reaction with neither coagulum nor viscous layers being observed. Control of $\overline{M}_n$ was achieved over the range 1×10^4 to 6×10^4, with good agreement between the predicted and observed molecular weight. Low polydispersity polymer was produced, with values of $\overline{M}_w/\overline{M}_n$ ranging from 1.2 to 1.4. While this value of $\overline{M}_w/\overline{M}_n$ is greater than the value that may be expected under similar conditions in a homogeneous reaction,[7] it still indicates good control of the reaction; moreover, the molecular weights of the polymer produced in the experiments reported in Chapter 3 are generally larger than those that can be produced in homogeneous systems while maintaining narrow polydispersity.

The difference in the experimental conditions between those of previous workers (*e.g.* Monteiro *et al.*[2]) and those described in Chapter 3 is that the RAFT agent was initially located in the particles rather than in the droplets. The outcomes of these experimental conditions are seen to be quite different, with the improved experimental conditions reported in Chapter 3 avoiding the three problems outlined above. These results are consistent with the postulate that the problems besetting simple attempts to make RAFT work in emulsion arise from poor nucleation, low water stability of the RAFT agent, and/or droplet polymerization, as outlined in Chapters 1 and 2.

4.2 Remaining Difficulties

While RAFT-mediated polymerizations can now be successfully carried out using the acetone transport technique described in the previous chapter, understanding of the mechanistic aspects of the RAFT process in a compartmentalized system is still limited; the RAFT/emulsion systems studied so far (including the one shown in Chapter 3) have exhibited considerably slower rates of polymerization than their non-RAFT analogues, and have displayed significantly greater inhibition periods.

An additional difficulty is found in interpreting experiments designed to yield the rate coefficients for radical entry into and exit from latex particles, as will be discussed below in section 4.3.

4.2.1 Inhibition and Retardation

While RAFT techniques in solution polymerization are known to sometimes produce a small inhibition period and a reduction in the polymerization rate (depending on the RAFT agent used),[4,7-9] the inhibition periods and retardation seen in emulsion systems are more significant, such as those shown in Chapter 3, and also those reported by other workers.[2,10]

RAFT/emulsion systems typically show quite long inhibition periods.[1] During this time, there is no observable conversion. Depending on the initiator concentration, the inhibition periods seen vary from 20 to 180 minutes, as shown in the dilatometric data in Chapter 3.

None of the mechanisms that have been proposed so far for the retardation of RAFT-mediated polymerizations adequately explain the inhibition and retardation effects reported in Chapter 3. For the purposes of this discussion, it is convenient to distinguish between chemical and physical processes that may lead to the retardation.

4.2.2 Chemical Causes of Inhibition and Retardation

The effect of the RAFT mechanism itself on the rate of polymerization is an effect that is not peculiar to RAFT/emulsion systems and is due purely to the chemical processes involved. In the case of bulk and solution polymerization reactions, a reduction in the rate of polymerization is sometimes observed,[4,7-9] although it has been suggested previously that such a reduction is often the result of sub-optimal choice of RAFT agents or the suppression of the gel-effect due to the production of shorter chains.[4,8] It has become apparent that experimental data, such as the rate of conversion and the molecular weight distribution, are insufficient to discriminate between the available models, although this has not prevented much lively debate.[11,12]

4.2.2.1 Slow Fragmentation

It has been suggested that long half-lives of the intermediate, bipolymeric radical species in the RAFT process may lead to retardation.[7,9] While long half-lives certainly would lead to such retardation, this mechanism requires the radical species in question to be quite stable with half-lives of up to 30 s (depending on the RAFT agent used).[7,9]

ESR experiments probing the intermediate radical found its concentration to be a factor of ~10^5 lower than that required by the slow fragmentation model. The discrepancies between the slow fragmentation model and these ESR data have since received considerable attention, with subsequent ESR studies being performed;[12-14] based upon the modeling of Wang and Zhu,[15] it would appear that these ESR data are consistent with the irreversible termination model (below). However, the additional information provided by the ESR data has been largely discounted in subsequent discussions by Barner-Kowollik *et al.*[11] Consistent with the slow-fragmentation model are conversion and molecular weight data, but these results are also consistent with the irreversible termination model, hence cannot be used to discriminate between the two models. Numerous modeling efforts have also been undertaken in an attempt to understand these data;[11,16] however, these numerical models have yet to permit the fate of the intermediate radical to be determined.

4.2.2.2 Intermediate Radical Termination

A mechanism involving the termination of the intermediate radical species has also been offered for discussion by Monteiro *et al.*[17] To this mechanism, Barner-Kowollik *et al.* have added reversibility of the intermediate radical termination reaction.[7,18] While these mechanisms have successfully been used to fit conversion-time data from a number of homogeneous polymerization experiments, firm experimental evidence to support them is still lacking. Shoulders in the molecular weight distribution at approximately three times the peak molecular weight have been interpreted as being 3-armed stars formed by the termination of a propagating radical with the bipolymeric intermediate.[12,16]

The application of both the postulated reversible and irreversible intermediate radical termination mechanisms[7,17,18] to emulsion polymerization is problematic due to the compartmentalization of the radicals. Typically, small-sized latex particles in an emulsion polymerization obey what is known as “zero-one” kinetics. In this model, the entry of a second radical into a particle already containing a growing radical leads to instantaneous termination (or, more precisely, very rapid termination on the timescale of other processes). Thus, a particle may only have either zero or one radicals in it.[19] Since, in a zero-one system, a latex particle containing one radical would have pseudo-instantaneous termination upon the entry of a second radical, the provision of an alternate termination mechanism, such as termination with intermediate radicals, does not offer a mechanism for retardation.

The system described in Chapter 3 has previously been shown to obey zero-one kinetics in the absence of a RAFT agent.[19,20] It must be noted that, despite previous attempts to determine whether zero-one kinetics will be obeyed by RAFT-containing particles,[2] it is not yet clear whether the zero-one criteria described by Maeder and Gilbert[21] can be applied to these systems. To this end, the applicability of zero-one kinetics will be investigated in detail in the following chapters.

4.2.2.3 Slow Re-initiation

Solution polymerization experiments indicate that the inhibition period may be linked, at least in part, to a failure in the re-initiation reaction.[4] It has been postulated that the cumyl radical (one of the common R groups used in many RAFT/emulsion studies such as this one and the work of Monteiro *et al.*[2]) may be quite slow at re-initiating.[4] However, previous radical addition studies do not support this conclusion;[22,23] the results of these studies indicate that the addition of the cumyl radical to styrene should be faster than a normal propagation step.

Interestingly, the retardation observed with cumyl-based RAFT agents is significantly greater than with cyanoisopropyl-based RAFT agents and the same activating group (Z).[4] Recent studies by Chong *et al.*[24] and Chiefari *et al.*[25] have illustrated that the effect of the R group may have a significant effect on the polymerization over and above the influence of the $R^\bullet$ radical on the re-initiation step. In particular, the affinity of the $R^\bullet$ radical towards the initial RAFT agent is quite high. One possible explanation that is consistent with these data is that the $R^\bullet$ radical generated by the fragmentation of one RAFT agent is more likely to add to another RAFT agent (ejecting an oligomeric radical, $P^\bullet$, or another $R^\bullet$ radical) rather than adding to monomer. This specificity may lead to inhibition as it causes a reduction in the concentration of propagating radicals. Moreover, in a heterogeneous polymerization environment, an $R^\bullet$ radical has a much higher probability of exiting from a particle than an oligomeric radical $P^\bullet$.

4.2.3 Physical Causes of Inhibition and Retardation

System properties, such as a high rate of radical exit from the latex particles, may be a cause of a reduction in the rate of an emulsion polymerization.[19,26] The kinetic effects of the exit of radicals from the particles is an artifact of the heterogeneous polymerization environment and will be described here as a physical cause of inhibition and retardation.

4.2.3.1 Exit of Radicals

Retardation due to the exit of radicals from particles is well known in other emulsion polymerization systems obeying zero-one kinetics.[26] Should the exited radical re-enter a particle that already contains another radical, instantaneous termination occurs. In the case where the radical re-enters a particle without a radical, it may either add to a monomer unit (starting a new polymer chain) or it may re-exit. Overall, the exit of radical species from latex particles in zero-one systems leads to a reduction in the rate of polymerization, as exit frequently leads to termination.

In the case of RAFT/emulsion systems, the first transfer reaction produces a small radical that could exit the particle. Note, however, that for a reactive RAFT agent (*i.e.* with a high C_{tr}) the exit of radicals only has the potential to explain retardation or inhibition in the first few percent of conversion, as, after that time, all the initial RAFT agent would have been converted to the dormant species on a chain end. The effects of the exit of small radicals from the particles will be further assessed in Chapters 8 and 9.

While it has been suggested that exit of the $\mathrm{R}^{\bullet}$ group from particles is likely,[2] the probability of exit for a cumyl-based RAFT agent in a styrene emulsion polymerization has since been recalculated to be much smaller (see Chapter 3). Since with most RAFT agents retardation can only be rationalized in terms of exit of the $\mathrm{R}^{\bullet}$ group for the first few percent of conversion and there is a small probability that it occurs, it may be surmised that this process is insignificant in terms of retardation. Its role in inhibition is investigated in detail in Chapter 9.

In the case of low-transfer constant RAFT agents (such as the xanthates of Smulders *et al.*[10]), the consumption of the initial RAFT agent occurs throughout course of the reaction, providing an exception to the above proposition regarding the insignificance of $R^\bullet$ exit in retardation. In such a system, $R^\bullet$ radicals will be continually generated leading to both an increase in the exit rate coefficient and a decrease in the number of true entry events, as many entering radicals simply exit immediately in a form of "frustrated entry" recently described by Smulders *et al.*[10]

4.2.3.2 Breakdown in Compartmentalization

It should be noted that compartmentalization (the separation of radicals into different particles) may be broken down in ways other than through the exit of radicals. Some systems, such as methyl methacrylate (MMA) and butyl acrylate (BA), do not obey zero-one kinetics for all except the smallest particles:[19,21,27] propagation is sufficiently rapid that an entering radical grows to a significant length before it terminates, even in the confines of a small particle. Thus an MMA or BA emulsion polymerization with the average number of radicals per particle, $\bar{n}$, less than 0.5 can contain a significant number of particles with more than one growing radical. The conditions necessary for a RAFT/emulsion polymerization to follow these "pseudo-bulk" kinetics will be discussed in Chapters 5 to 7.

4.3 Treatment of Kinetic Experiments

While it is possible to extract the rate of conversion *vs* time and hence $\bar{n}$ *vs* time from dilatometry data such as that presented in Chapter 3, further treatment of kinetic experiments (such as those described in Chapter 7) requires the assumption of a particular mechanistic model. Models such as pseudo-bulk[28] and zero-one[20] provide convenient methods of obtaining kinetic parameters from the experimental data with the minimum of model-based assumptions. As there are few kinetic parameters in these models, values can be assigned to them unambiguously.[19]

4.3.1 Zero-One or Pseudo-Bulk?

The previously noted difficulty in treating the dilatometry data generated by RAFT/emulsion experiments is that it is unclear from simple consideration of the system whether either of the zero-one or pseudo-bulk models are appropriate.[2,29] Since both models are mathematical limits of the Smith–Ewart equations[30] for describing emulsion polymerization (as will be discussed in detail in Chapter 6), it is possible to construct reaction conditions in which neither limit is applicable.

In general, the conditions for assessing the applicability of zero-one and pseudo-bulk kinetics are written in terms of the first-order rate coefficients for entry, ρ, exit of a radical from the particle, k, and mutual annihilation of two radicals, c. The conditions under which a system may be classed as either zero-one or pseudo-bulk have been previously reported,[28,31] but may be summarized as follows.

For a system to be zero-one, the conditions that are required are[19] $\rho/c \ll 1$ and $k/c \ll 1$. Within the mathematical framework developed by Casey *et al.*[31] and Gilbert,[19] a condition for the applicability of zero-one kinetics that is both sufficient and necessary is that $c^{\mathrm{SL}} \gg k_{\mathrm{p}}C_{\mathrm{p}}$, where c^{SL} is the pseudo-first-order rate coefficient for termination between a short chain and a long chain, k_{p} is the propagation rate coefficient and C_{p} is the monomer concentration in the particle. While this latter condition does not involve ρ or k, it still provides a measure of the likelihood of termination occurring before a significant amount of polymer is produced.

Conversely, for compartmentalization to break down, either of the requirements $\rho/c \gg 1$ or $k/c \gg 1$ must be satisfied.[28] For a particle to follow pseudo-bulk kinetics, there is an additional requirement that $\overline{n^2} - \bar{n} = \bar{n}^2$, a moment transform used as a closure relation for the Smith–Ewart equations. Formally, this condition is satisfied for sufficiently large $\bar{n}$ where the population of radicals across the particles conforms to a Poisson distribution;[19] in practice, $\bar{n} \gtrsim 0.7$ is sufficient for this condition to be met.[19] In the case where all exiting radicals re-enter particles without further re-escape, the system behaves as though it were like the “equivalent” bulk system (pseudo-bulk).[28]

This leaves the region of $(\rho/c, k/c)$-space where ($\rho/c \approx 1$ or $k/c \approx 1$) and ($\rho/c \not\gg 1$ and $k/c \not\gg 1$) as a kinetically difficult case (using “and”, “or” and the parentheses in the formal mathematical sense as Boolean operators and grouping symbols). In these systems neither zero-one nor pseudo-bulk kinetics are applicable; however, it may still be possible to use one of these theories to estimate the behavior of the system to a first approximation, as will be discussed further in Chapter 6.

4.4 Development of Understanding

In Chapter 5, the influence of chain-length dependent termination on RAFT-mediated polymerizations will be examined in detail, considering the conditions for applicability of both pseudo-bulk and zero-one kinetics to RAFT/emulsion systems.

Once a suitable mechanism has been found with which to interpret kinetic experiments on RAFT/emulsion systems, it will be possible to perform γ-relaxation experiments on representative systems and suggest a meaningful interpretation of the results, as will be shown in Chapter 7.

4.5 References

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