

Chapter 8

Episode III

Using Theory to Develop Experiment

*A new scientific truth does not triumph by convincing its opponents
and making them see the light, but rather because its opponents eventually die,
and a new generation grows up that is familiar with it.*

– Max Planck (1858–1947)

8.1 Radical Exit in RAFT/Emulsion

The RAFT-induced exit of radicals from the RAFT/emulsion particles, as described in Chapter 7, highlighted the importance of exit in emulsion polymerization kinetics. The most-probable-path reaction scheme for the RAFT-induced exit mechanism is summarized as follows (for the specific example of styrene emulsion polymerization):

- An aqueous phase radical grows to length z .
- The z -meric radical explores the surface of many particles ($\sim 10^2$) before entering a particle due to a chemical reaction occurring, such that the radical is no longer free to move to another particle. In the absence of RAFT, this reaction is propagation; in the presence of a high-activity RAFT agent, it is transfer to a dormant chain.
- The entering radical transfers radical activity to a dormant chain within the particle, leaving a dormant z -meric chain ($\text{IM}_z\text{-S-C(Z)=S}$) in the particle.
- Propagation and transfer to dormant chain reactions occur within the particle following the RAFT mechanism.
- At some stage in the future, transfer to the z -meric dormant chain occurs; a z -meric radical (IM_z^*) is left in the particle.
- The z -meric radical desorbs to the aqueous phase.
- The radical re-enters another particle.

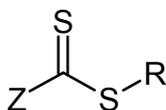
Based upon the calculations in Chapter 7, RAFT-induced exit is a rapid process for the systems under consideration, with $k > \rho, c$ when the dormant chains are not short. When the dormant chains are short, c is much greater, as shown in Chapter 7.

As will be seen in Chapter 9, exit also plays an important role in the behavior of the RAFT/emulsion system during the initiation period; both the exit of the RAFT

re-initiating group (R) and the RAFT-induced exit of z-meric radicals play significant roles in suppressing polymerization during the initial stages of the reaction.

8.2 Role of the RAFT Re-initiating Radical

The parts of the RAFT agent are commonly described according to their functionality within the RAFT reaction scheme (shown in Chapter 1). The canonical form of the RAFT agent is shown in Scheme 8.1, with the R and Z groups being the re-initiating and activating groups, respectively.



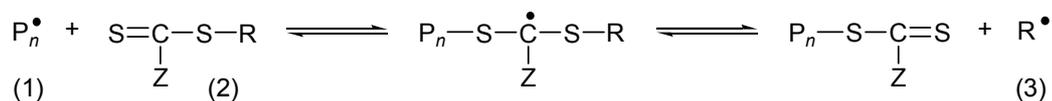
Scheme 8.1: The canonical structure of a RAFT agent, showing the activating group, Z, and the re-initiating group, R.

The role of the Z group (benzyl, in the case of PPPDTA) has received much attention, as it controls the stability of the intermediate radical and, hence, the concentration of the intermediate radical and whether or not it may be involved in termination reactions such as those suggested by Monteiro *et al.*¹ A detailed study of the influence of the Z group over various RAFT-mediated homogeneous polymerizations was recently published by Chiefari *et al.*,² showing that the LUMO energies of the RAFT agent may be used as a qualitative measure of the activity of the RAFT agent.

In the RAFT mechanism, the R group re-initiates polymerization, such that, through the initial fragmentation of the RAFT agents, most chains are initiated at the commencement of polymerization (although all but a few are dormant at any time). The R group is expected to have less effect on the kinetics of the reaction after initiation, as, after the addition of only one or two monomer units, the R group is chemically indistinguishable from a polymeric chain.

Goto *et al.*³ saw an increase in the rate of polymerization and the activity of the RAFT agent by changing the R group from a short radical to a polymeric chain. Using R groups of 1-phenyl-ethyl and cyanoisopropyl (both with benzyl-activated RAFT agents), Perrier *et al.*⁴ found a significant difference in the inhibition period, with the cyanoisopropyl-containing RAFT agent showing little inhibition. This difference was ascribed to differing fragmentation rates of the initial RAFT agents, with the intermediate radical formed by the 1-phenyl-ethyl-containing RAFT agent being more stable and fragmenting more slowly. The same retardation was seen with either RAFT agent (once polymerization commenced), as the fragmentation rate was the same beyond the edge-effect of the R group.

A wide-ranging study by Chong *et al.*⁵ instead proposed that the specificity of the R[•] radical to the initial RAFT agent was the dominant factor in determining the inhibition period. The equilibria between the initial RAFT agent and the R[•] radical is shown in Scheme 8.2 and was proposed by Chong *et al.*⁵ to lie to the left; thus, an R[•] radical was more likely to add to a RAFT agent than to add to monomer.



Scheme 8.2: The initial fragmentation of the RAFT agent, proposed by Chong *et al.*⁵ to lie to the left.

In the context of RAFT/emulsion systems, it was noted by Monteiro *et al.*⁶ that the exit of the R[•] radical from the latex particle would be a kinetically significant event. While the probability of exit is not necessarily high, as shown in Chapter 3 (being strongly influenced by the water-solubility of the R[•] species^{1,7}), the exit of the R[•] radical, the specificity of the R[•] radical to the RAFT agent *and* the RAFT-induced exit of *z*-meric radicals may be combined to study the inhibition period.

In Chapter 5, it was shown that the RAFT/emulsion particles follow zero-one kinetics when the dormant chains (hence, also, the propagating radicals) are quite short.

Moreover, this was the case even for quite large particle sizes that would normally be pseudo-bulk in the absence of RAFT. The combination of a zero-one model, which has been used to describe the behavior of exited radicals in other systems,⁸⁻¹¹ with the RAFT-specific effects listed above will be used to study the inhibition period in RAFT/emulsion systems in Chapter 9.

8.3 Designing New Experiments

The kinetics of polymerization in RAFT/emulsion reactions may now be successfully related to the Smith–Ewart equations: ρ from Maxwell–Morrison theory,¹² c from chain-length dependent termination (Chapters 5 and 7), and k from RAFT-induced exit (Chapter 7). An obvious omission from the work so far is a mathematical description of the inhibition periods, which will be outlined in Chapter 9. This allows the use of these models as a predictive tool to improve the performance of RAFT/emulsion systems. Of particular interest are reducing the inhibition period and the retardation of the rate of polymerization. An outline of methods for achieving these goals is as follows, with more detailed quantitative arguments presented in Chapter 9.

8.3.1 Reducing Inhibition

The inhibition period is of critical importance to the industrial usefulness of RAFT/emulsion. Inhibition periods of up to 3 hours (such as those shown in Chapter 3) are a serious weakness of RAFT/emulsion systems. Design of RAFT agents that are able to reduce these inhibition periods through either chemical or physical means is possible once the causes of inhibition are elucidated.

The use of lower-activity RAFT agents presents itself as a means of reducing the RAFT-induced exit of radicals from the particles, with a reduction in the desorption rate coefficient for the R^\bullet radical from the particles having a similar effect. Moreover, reducing the specificity of the R^\bullet radical to the RAFT agent improves the rate at which R^\bullet adds to monomer making it less likely to desorb.

8.3.2 Reducing Retardation

An improvement in the compartmentalization of the radicals in the RAFT/emulsion particles would be expected to increase the rate of polymerization. The abovementioned technique of using a lower-activity RAFT agent to reduce the rate of RAFT-induced exit would be expected to fulfill this criterion. The use of quite large R groups with slow diffusion coefficients (such as the oligomeric adducts to the RAFT agents of Ferguson *et al.*¹³) would reduce the rate coefficient for termination, thus reducing c and increasing the rate of polymerization.

8.4 References

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