Chapter 10

Cadenza

Conclusions on the Nature of RAFT in Emulsion Polymerization

The best way to have a good idea is to have lots of ideas.

– Linus Pauling (1901–1994)

10.1   Conclusions from Experiments

10.1.1   RAFT/Emulsion is Possible

The important initial result of this work is that there is nothing inherently incompatible between RAFT-mediated polymerizations and emulsion polymerization. It was seen in Chapter 3 that RAFT techniques can be successfully applied to seeded emulsion polymerization systems. Good control of the final molecular weight and molecular weight polydispersity was maintained throughout the polymerization. The γ-initiated polymerization of styrene with PPPDTA was demonstrated in Chapter 7, showing good control over the molecular weight of the products in both bulk and emulsion systems.

10.1.2   Droplets, Colloidal Stability and Molecular Weight Control

The three problems hitherto seen when attempts have been made to use RAFT in emulsion polymerization, *viz.* colored layers, problems with colloidal stability in RAFT-containing emulsion polymerizations and poor molecular weight control, were ascribed in Chapters 2 and 3 to problems with the transport of the RAFT agent to the locus of polymerization. When the RAFT agent is located in monomer droplets and not in the latex particles, the RAFT agent is unable to mediate the polymerization effectively and molecular weight control is poor. The formation of oligomeric adducts to the RAFT agent in the droplets leads to a species that cannot transport across the aqueous-phase to the particles, thus creating two separate polymerization environments with different [RAFT]/[monomer] and, hence, different $\overline{M}_n$. Such oligomeric adducts are also unable to form solid, stable particles, leading to significant coagulation and the spontaneous appearance of a viscous, highly-colored layer in the polymerization at about the point where the droplets should vanish.

10.1.3   Difficulties with RAFT/Emulsion

While RAFT/emulsion was seen to be possible, it was also seen that there were some detrimental effects of the use of RAFT agents in emulsion polymerization. Significant inhibition periods and a reduction in the rate of polymerization were observed both in the chemically initiated systems described in Chapter 3 and the γ-initiated systems in Chapter 7. Retardation of the rate of polymerization was observed with an increase in [RAFT]/[initiator], leading to a decrease in the rate of polymerization. This same trend was seen for the inhibition period.

The γ-relaxation experiments reported in Chapter 7 also showed that the RAFT/emulsion systems had significantly faster relaxations than the equivalent non-RAFT system, suggesting a faster radical loss process.

10.2   Conclusions from Theory

10.2.1   Chain-Length Dependent Reactions

The Monte Carlo model presented in Chapter 5 provided valuable insights into the relative importance of the different processes (propagation, transfer to dormant species and termination). The conclusions drawn from this work are general across all polymerizations mediated by reversible transfer kinetics (including RAFT); however, the implications for emulsion polymerization systems are of most interest here.

For a high-activity RAFT-agent such as PPPDTA, the kinetic behavior of the system changes markedly as a function of conversion. The lifetime of the radical at low conversion, when short chain lengths dominate the system, is much shorter than at higher conversion, when longer dormant chains are present. This was demonstrated through the use of a sophisticated Monte Carlo simulation and it may also be seen qualitatively by considering the length of both the dormant chains and the radicals in the system and the chain-length dependent nature of the termination reaction:

- high transfer constant RAFT agents at low conversion have short dormant chains and, hence, exhibit significantly shorter radical lifetimes due to the increased termination rate coefficient, $\langle k_t \rangle \sim k_t^{\text{short-short}}$

- long dormant chains lead to an extension of radical lifetimes, due to the reduced termination rate coefficient, $\langle k_t \rangle \sim k_t^{\text{long-long}}$

In the emulsion polymerization of styrene, an increase in $\bar{n}$ with conversion was seen in both chemically and γ-initiated systems, which is consistent with this model of chain-length dependent termination.
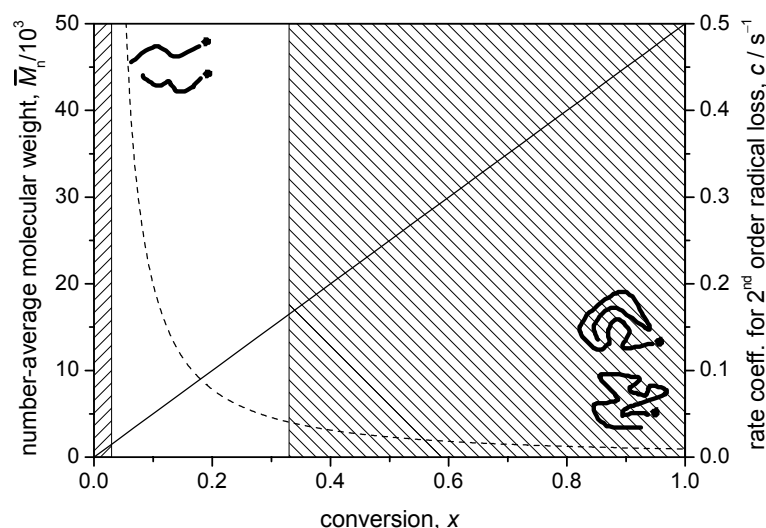

Figure 10.1: A stylized plot of molecular weight (—) and the rate coefficient for second-order radical loss, c, (– –) showing the transition from a region where zero-one kinetics are appropriate (marked ///) to a region where pseudo-bulk kinetics are appropriate (marked \\\\). The influence of short-short and long-long termination reactions is highlighted by this plot. Data is for $\bar{M}_n$ from theory using a target molecular weight of 5×10^4; data for c is derived from the experimental results of Chapter 7.

These effects are summarized using stylized plots shown in Fig. 10.1. The change in the pseudo-first-order rate coefficient for the second-order radical loss process, c, is shown as a function of conversion, highlighting the change in the kinetic behavior that occurs in the system. The region where zero-one kinetics should be applicable (ρ/c and

$k/c < 0.01$) at the beginning of the reaction is shaded, along with the region where pseudo-bulk kinetics should be appropriate ($k/c > 100$) in the latter part of the reaction.

10.2.2   Radical Compartmentalization

In Chapter 7, it was postulated that z-meric dormant chains in the particles could lead to an increase in the rate of radical exit from the particles, since z-meric radicals are able to desorb from the particle surface. The addition of a RAFT agent to the particles thus leads to an increase in exit though a "RAFT-induced exit" mechanism. This leads to a rapid exchange of radicals between particles, with the rate coefficient for radical desorption from a particle being increased by ~400-fold.

The z-meric dormant chains were shown in Chapter 9 to be present in low numbers in the steady state; however, it was also shown that numbers in individual particles may deviate significantly from the steady-state value. The movement of the system back to the steady state after such a perturbation occurs on a slower timescale than other processes such as RAFT-induced exit and, as such, these deviations have a significant impact on the kinetics of the system.

The lack of compartmentalization implied by the RAFT-induced exit mechanism leads to the quite fast relaxations shown by the system, with the abovementioned chain-length dependence of termination giving the characteristic relaxation time a chain-length dependence, as reported in Chapter 7. The semi-quantitative treatment of the Monte Carlo model presented in Chapter 7 (the theory for which was presented in Chapter 6) was seen to give a good description of the shape of the relationship between c and the length of the dormant chains; however, the magnitude was not correctly estimated by the Monte Carlo model due to limitations in the termination model used. These limitations probably arise in the scaling "law" used for the dependence of the termination rate coefficient on chain lengths for two relatively long chains.

10.2.3   Particle Growth Kinetics

10.2.3.1 Zero-One Kinetics

In Chapter 5, it was shown that, at short dormant chain lengths, termination was extremely rapid in the case where two radicals were in the same particle, and that zero-one kinetics were appropriate under these conditions. In Chapter 9, this was used to develop a model of the inhibition period. Taking account of the RAFT-induced exit mechanism and the exit of the R$^\bullet$ radicals from the RAFT/emulsion particles, this simple model was able to describe the inhibition period over a range of initiator concentrations. The exit of the R$^\bullet$ radical would thus appear to be a kinetically significant event, being an important contributor to the inhibition period observed in the RAFT/emulsion experiments described here, as shown in Chapter 9. This is qualitatively different from the exit process in conventional emulsion polymerizations.

10.2.3.2 Pseudo-Bulk Kinetics

It was shown in Chapter 5 that significant amounts of polymer could be produced in a two-radical environment when the dormant chains in a system were quite long. Moreover, the acceleration in $\bar{n}$ seen in both Intervals II and III in the experimental results of Chapters 3 and 7 illustrate that zero-one kinetics are inappropriate for these systems through most of the reaction. The measured value of c from the γ-radiolysis experiments of Chapter 7, along with the calculated values for ρ and k, showed that the system could be described by pseudo-bulk kinetics to 20–30% accuracy in $\bar{n}$; Chapter 6 illustrated that the region of (ρ/c, k/c)-space occupied by these systems is not particularly well described by either the zero-one or pseudo-bulk limits to the Smith–Ewart equations.

Using the pseudo-bulk model for particle growth, kinetic parameters were obtained from the γ-relaxation experiments of Chapter 7. The use of pseudo-bulk kinetics permitted the determination of $\langle k_t \rangle$ as a function of the dormant chain length. With

improved precision in these measurements of c, it is possible for k_t^{ii} to be determined at both high w_p and long chain lengths.

10.2.3.3 Zero-One-Two Kinetics and Beyond

In Chapter 6, a method was presented by which suitable average pseudo-first-order rate coefficients for the termination reaction could be obtained. Using the doubly distinguished population balance equations, the chain-length distribution of the radicals in the particles may be used to find an appropriate average value of the Smith–Ewart parameter for termination. In some cases, this may be calculated analytically, while in general numerical techniques may be employed to evaluate the average rate coefficient for termination. Depending on the complexity of the system, this may be done through simple numerical integration of the population of doubly distinguished particles or, alternatively, from the data generated by the Monte Carlo simulations described here. This method is applicable to the zero-one-two system (which permits analytic solutions in certain cases) or to any Smith–Ewart system (involving numerical eigenvalue solutions).

10.3   Drawing Together Theory and Experiment

Once the various features of the RAFT/emulsion system had been described by the collection of theories presented here, it was possible to use these models as a predictive tool to improve the performance of RAFT/emulsion systems. Of specific interest are methods for reducing the length of the inhibition period and the strength of the retardation.

Various approaches for improving the rate of polymerization of the RAFT/emulsion systems were suggested in Chapter 9, with the use of lower-activity RAFT agents being a key method by which improvements could be achieved. This approach has the effect of reducing the probability of formation of the dormant z-meric species required for the RAFT-induced exit mechanism, thus improving

compartmentalization of the system. This tends to reduce both the length of the inhibition period and increase $\bar{n}$ throughout the rest of the polymerization.

Additional improvement may be obtained through the use of a highly hydrophobic R group on the RAFT agent to reduce the inhibition period. An R group with a particularly slow aqueous diffusion coefficient reduces its desorption rate coefficient, thus reducing the inhibition period; similarly, a slow diffusion coefficient in the polymer reduces the termination rate coefficients at any given conversion, thus increasing $\bar{n}$.

10.4   *The Show's Not Over Till the Fat Lady Sings*

While the body of work presented here has interwoven theory and experiment in a manner similar to a fugue that must now conclude, there is still more to be discovered about the nature of RAFT in emulsion polymerization.

There is now at least a qualitative (and, in many cases, semi-quantitative or quantitative) explanation of most facets of a RAFT/emulsion system; with such descriptions of the key features of the polymerization, it is possible now to suggest methods for improving the performance of RAFT/emulsion systems. Obviously, more experimental work and refinement of the theory presented here is required to turn these qualitative theories into semi-quantitative theories and, similarly, the semi-quantitative theories into quantitative theories.

Two significant aspects of RAFT/emulsion systems that are not well understood were highlighted in Chapter 9: the role that RAFT agents play in particle formation, which determines how they can be used in *ab initio* emulsion polymerization, and the reason for failure of many RAFT/emulsion systems to proceed to 100% conversion. Addressing both of these issues will assist RAFT/emulsion to be successfully applied in various industrial contexts.

Of course, there are also the perennial questions about the behavior of the intermediate radical species in the RAFT-mediated polymerization. Much has already been made of this issue and, undoubtedly, research in this field will continue. It may be that the use of emulsion polymerization techniques will provide ready access to kinetically discriminating experiment, by making use of the compartmentalization of radicals into particles, from which these issues may be addressed.

The journey down the road to controlled, complex macromolecular architectures achieved with the safety and speed of emulsion polymerization has progressed considerably since the first reports of RAFT/emulsion experiments. Perhaps, one day it will be possible to begin an article:

> RAFT/emulsion polymerization is a commonly used laboratory and industrial technique, whereby a dispersion of polymer in water is formed through a complicated interplay between chemical and physical processes that have been well documented elsewhere….