Chapter 2

Codetta

Developing RAFT/Emulsion Systems that Work

Adapted from:

RAFT in Emulsion Polymerization: What Makes It Different.
Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G.
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> *I have not failed. I've just found 10,000 ways that won't work.*
>
> – Thomas Edison (1847–1931)

2.1 In Search of Successful Experiments

In Chapter 1, the importance of developing RAFT/emulsion systems that do not show significant problems was highlighted. Of particular interest was the development of at least one system that does not exhibit any of the following difficulties that have been seen in previous studies:

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

Even if retardation and inhibition are still observed in the system that is developed to meet these criteria, it will still be an important step forward; once a system produces the correct products, it is then often possible to optimize the system to improve the remaining faults.

2.2 The Problem with Droplets

Using the postulate (outlined in Chapter 1) that the transport of the RAFT agent to the locus of polymerization is of paramount importance to the efficacy of the RAFT system and is implicated in the three difficulties listed above, it is possible to design successful RAFT/emulsion experiments. Consider first the accepted mechanism for aqueous-phase chemistry seeded emulsion polymerization,[7] shown in Fig. 2.1.

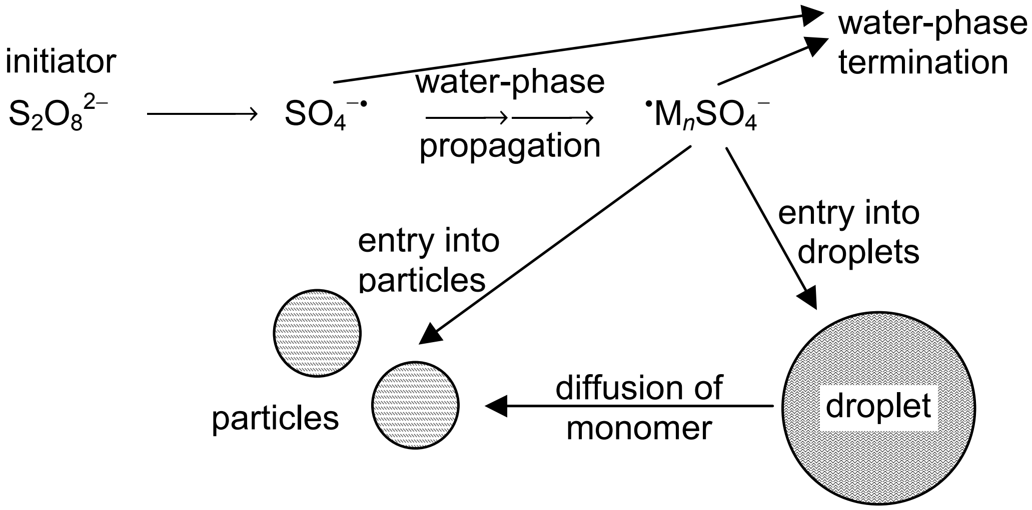


Figure 2.1: A schematic representation of the aqueous-phase chemistry as it occurs in a seeded emulsion polymerization in the absence of RAFT.

With the exception of a few monomers (*e.g.* neoprene[8]), the role of the monomer droplets in the emulsion polymerization is only to provide a reservoir of monomer to the propagating radicals that are located in the particles;[7] this occurs by the diffusion of monomer across the aqueous phase, as shown in Fig. 2.1. As noted in Chapter 1, small amounts of droplet polymerization are normally insignificant to the kinetics of the polymerization.[7] It has previously been argued that the diffusion of monomer from the droplets to the particles should not be rate determining in most situations, *i.e.* monomer should be able to diffuse from the droplets to the particles at a rate faster than it can be consumed through propagation in the particles.[7] Moreover, using similar arguments, it has been suggested that the transport of the RAFT agent from the droplets to particles should not be rate determining.[2]

The difficulty arises when the thermodynamics of the situation are compared to the kinetics. While it has been established that the initial RAFT agent is *kinetically* able to move between the monomer droplets and the particles there is no *thermodynamic* reason for it to do so once there are approximately equal concentrations of RAFT agent in both the particles and the droplets. As the initial RAFT agent is consumed in the particles, more RAFT agent may move across from the droplets to the particles. However, there is no reason to suppose that consumption of the initial RAFT agent would not be as fast in the monomer droplets as it is in the particles; indeed, it is proposed in Chapter 9 that the rate of consumption of RAFT agent is faster in the droplets than in the particles.

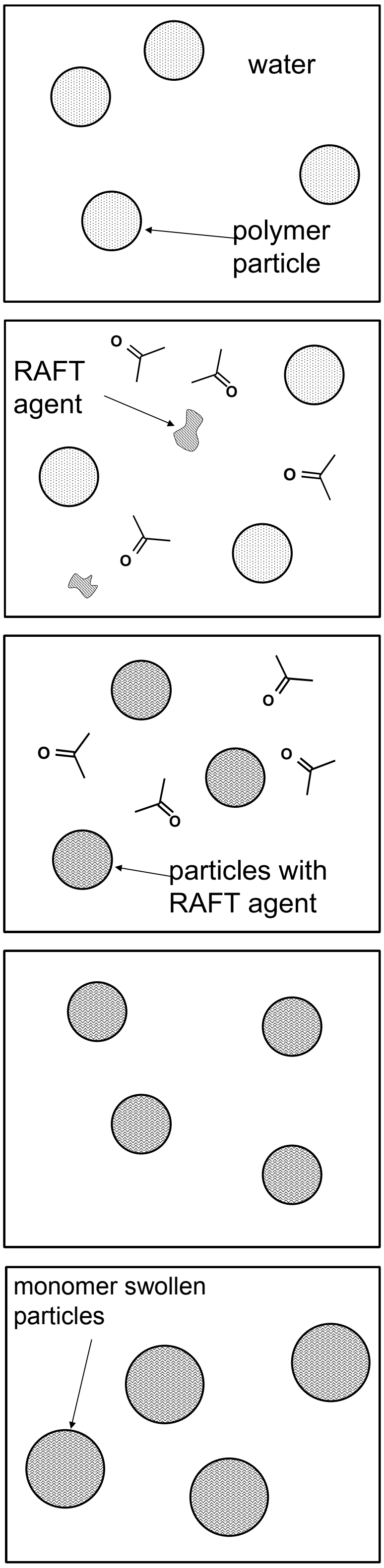
Once the initial RAFT agent has been consumed, forming an oligomeric adduct to the RAFT agent, the water solubility of the species drops significantly, even compared to its original relative water-insolubility. This will reduce the rate at which transport of the RAFT moiety from the droplet to the particle can occur, effectively locking the RAFT agent and the oligomeric species attached to it into the droplets.

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 losing colloidal stability at about the point where the monomer droplets would normally have evaporated. This is catastrophic failure of the RAFT/emulsion system.

It may be noted that the use of xanthates in emulsion polymerization systems has been less problematic.[6,9] This may be related back to the low value of the transfer constant for the xanthates, C_{tr}, which is often so low as to mean that the RAFT equilibration reaction may only occur once or twice in the lifetime of the chain. Instead of vast amounts of short oligomeric species being formed, relatively few long chains are produced; this situation is more like the non-RAFT case of droplet polymerization and is thus negligible.

2.3 Successful RAFT/Emulsion

Using the postulate that the transport of the RAFT agent to the locus of polymerization is of paramount importance to the efficacy of the RAFT system, it is possible to design successful RAFT/emulsion experiments as will be shown in Chapter 3. The basic steps in this “acetone transport technique” are shown in Fig. 2.2.



A seed latex is prepared and diluted as required. In this work, typically $N_c = 10^{17}$ dm^{-3} with $r_u = 35$ nm ($r_s = 50$ nm, final latex around 10% solids).

Acetone (25% w/w on the latex) and the water-insoluble RAFT agent (0.035% w/w on latex) are added to the latex with stirring.

Over time, the RAFT agent migrates to the particles (thermodynamically favored).

The acetone may then be removed from the latex using a rotary evaporator, leaving RAFT-containing particles suitable for further polymerization.

The RAFT-containing particles may be swollen with additional monomer. Surfactant (if needed) and initiator are added to commence polymerization.

Figure 2.2: A typical recipe for the acetone transport technique as used in the first successful implementation of RAFT in emulsion polymerization, described in Chapter 3.

In short, the addition of acetone (as a cosolvent) to the water phase to assist the transport of the RAFT agent into pre-formed particles of a seed latex before the onset of polymerization obviates the need to consider particle formation and droplet–particle transport of the RAFT agent. The acetone is effectively completely removed from the seed by rotary evaporation before the addition of monomer. While it is recognized that this procedure is unsuitable for many industrial processes (unless a mix of living and non-living polymer can be tolerated and the product is indeed high value-added), it does provide a highly effective method of producing RAFT/emulsion polymer, as shown in Chapter 3.

As will be seen in particular in Chapters 3 and 7, this technique allows the kinetics of the RAFT mechanism to be studied with reference to the kinetics of particle growth, uncomplicated by particle formation events.

2.4 References

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