

Review

## AQUEOUS STABLE FREE RADICAL POLYMERIZATION PROCESSES

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**Abstract** An overview of aqueous polymerizations, which include emulsion, miniemulsion and suspension polymerizations, under stable free radical polymerization (SFRP) conditions is presented. The success of miniemulsion and suspension SFRP polymerizations is contrasted with the difficulties associated with obtaining a stable emulsion polymerization. A recently developed unique microprecipitation technique is referenced as a means of making submicron sized particles that can be used to achieve a stable emulsion SFRP process.

**Keywords** Stable free radical polymerization, Living-radical polymerization, Aqueous polymerization, Miniemulsion polymerization, Emulsion polymerization, Suspension polymerization

### INTRODUCTION

A current area of significant research interest in our laboratory is aqueous stable free radical polymerization (SFRP); polymerizations that include emulsion, miniemulsion and suspension. These processes are highly sought after industrially since they lend themselves to large-scale material production.

Unlike conventional free radical polymerization, where the propagating free radical chains add monomer very rapidly and then quickly terminate, living-radical polymerization processes employ reagents that undergo reversible termination with the propagating radical chains to allow the polymer chains to grow in a predictable and continuous fashion. The popularity of living-radical polymerizations stem from their ability to deliver polymers with predictable molecular weights, narrow polydispersities and controlled architectures. To date, there are three major living-radical polymerization systems: SFRP<sup>[1]</sup>, Atom-Transfer Radical Polymerization (ATRP)<sup>[2]</sup>, and Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT)<sup>[3]</sup>. This paper will focus on the efforts in our laboratory to develop aqueous SFRP processes. Details on the work of other researchers in aqueous living-radical polymerizations can be found in two recent reviews<sup>[4]</sup>.

### RESULTS AND DISCUSSION

Our initial work in the area of emulsion polymerization was not particularly successful. It was, and to some extent, still is, very difficult to maintain stable emulsions under SFRP conditions. When these polymerizations do not go to high conversions, a common problem with SFRP emulsion polymerizations, a reaction mixture is obtained, which readily separates into two phases with a monomer layer on top. When the polymerizations are pushed to high conversion, millimeter sized polymer beads are obtained along with significant deposits of polymer (fouling) on the sides of the reactor and stirring shaft.

Emulsion polymerization systems are clearly very complex systems even under the best of conditions. Add nitroxides to the reaction mixture and perform the polymerizations at 135°C and the system becomes even more complicated. While some initial work has been performed to understand the partitioning of the nitroxides

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between the organic and aqueous phases<sup>[5]</sup>, there is still very little known about how the nitroxides affect the overall stability of the emulsion system. In a typical emulsion polymerization system, mixing initiator, monomer, water and surfactant together results in the surfactant molecules clustering together to form micelles that swell with monomer. These monomer-swollen micelles are typically between 5–15 nm in diameter<sup>[6]</sup>. However, the majority of the monomer is stored in large droplets (1–10  $\mu\text{m}$ ) that are relatively unstable. Herein may be one of the major reasons for the instability of the SFRP emulsion system. We suspect that these large monomer droplets, coupled with the relatively slow rate of polymer chain growth and the ever present autopolymerization of styrene at elevated temperatures, are all culprits to varying degrees in the failure of the living-radical emulsion polymerization reactions.

The initial lack of success with the emulsion prompted us to switch our attention to the miniemulsion polymerization process. The main physical difference between emulsion and miniemulsion systems is the size of the monomer droplets. Miniemulsions are typically formed by subjecting a mixture of initiator, monomer, water, surfactant and a costabilizer to a high shear process that breaks up the oil phase into submicron sized monomer droplets. The preformed droplets tend to be very stable because of the presence of the costabilizer. Whether this is the main reason for the stability of the miniemulsion SFRP processes remains to be seen but these polymerizations tend to be very successful. SFRP miniemulsions can currently be used to produce homopolymers of styrene and random and block copolymers of styrene and *n*-butyl acrylate to greater than 99% conversions with polydispersities in the 1.15 to 1.25 range<sup>[7]</sup>. Block copolymers were produced by first polymerizing styrene to high conversion, swelling the polystyrene particles with *n*-butyl acrylate and reheating the reaction mixture. The addition of a small amount of ascorbic acid to the aqueous phase facilitated the growth of the acrylate block. The speculation is that the ascorbic acid destroys excess nitroxide that migrates from the polymer particle into the aqueous phase. In doing so the concentration of nitroxide in the polymer particle is controlled to a level that enables the polymerization to proceed uninhibited. Using one of the newly introduced acyclic nitroxides<sup>[8]</sup>, miniemulsions of homopolymers of *n*-butyl acrylate was also accomplished<sup>[9, 10]</sup>. In all of these miniemulsion polymerizations a low molecular weight TEMPO-terminated oligomer is used both as an efficient initiator and as a costabilizer, eliminating the need to add hexadecane, which normally is used as a costabilizer.

Suspension polymerization is another industrially useful heterogeneous aqueous polymerization technique, which can be applied to the SFRP process with good success. The major difference between emulsion/miniemulsion polymerizations and suspension polymerizations is that emulsion polymerizations occur in monomer-swollen micelles, whereas suspension polymerization reactions occur in monomer droplets. The suspension droplets act as small bulk reactors to produce small polymer beads. Droplet size is typically between 50–500  $\mu\text{m}$  and the monomer droplets are prevented from coalescing by using suspension stabilizers and/or surfactants and continuous stirring. In general, the amount of stabilizer used is less than in an emulsion polymerization, which accounts for the larger monomer droplet sizes. The suspension process used in our laboratory is based on a patent for a conventional polymerization in which tricalcium phosphate is used as the stabilizer in the presence of a small amount of Alkanol XC, an organosodium naphthalene sulfonate, which acts as a dispersant<sup>[11]</sup>. As in the case with the miniemulsion polymerizations, a TEMPO-terminated polystyrene prepolymer is used to initiate the polymerizations. 2-Fluoro-1-methylpyridinium *p*-toluenesulfonate is used to control excess free nitroxide<sup>[12]</sup>. Reactions are performed at 135 °C in a modified Parr reactor for 6 to 12 h. Yields of polystyrene and random copolymers of styrene and *n*-butyl acrylate are typically greater than 85% and polydispersities are in the 1.15 to 1.30 range, with the broader polydispersities being associated with the random copolymers<sup>[13]</sup>.

With the miniemulsion and suspension working well, our research focus has shifted back to the emulsion polymerization process. Since it is the most widely used of the conventional aqueous free radical polymerization systems it commands attention and the outstanding issues associated with it need to be resolved.

In recent months we have made substantial progress in stabilizing the emulsion system to the point where the system does not phase separate and there is minimal fouling on the walls of the reactor. This has been accomplished by adjusting the amount of surfactant and added nitroxide to the reaction mixture. In a typical

living-radical styrene emulsion polymerization, polymer samples taken from the reaction mixture over the course of the polymerization have very narrow polydispersities with expected increases in molecular weight with time and conversion (see Fig. 1, Table 1).

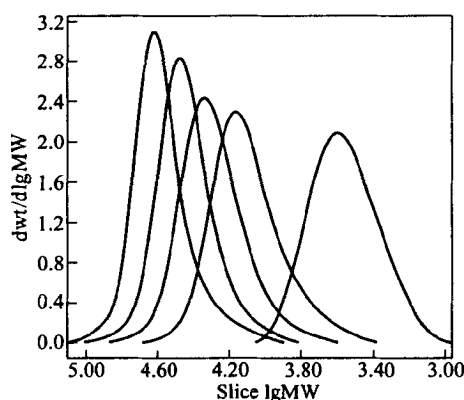


**Fig. 1** Gel permeation chromatography plot of polystyrene polymers prepared under emulsion conditions. Going from right to left, the distributions are for 1, 2, 3, 4 and 6 h samples.

**Table 1.** Molecular weights and polydispersities for the polystyrene samples shown in Fig. 1

| Time (h) | $M_n$ | PD   |
|----------|-------|------|
| 1        | 3300  | 1.19 |
| 2        | 11300 | 1.22 |
| 3        | 17900 | 1.18 |
| 4        | 25900 | 1.14 |
| 6        | 35200 | 1.15 |

However, there still remains one outstanding issue. Polymer particle sizes are still much larger than desired, typically in the 2 to 3  $\mu$  size range. As a consequence, the particles separate and settle out on standing for a few hours.

A number of approaches are being investigated to understand what factors control particle size. For example, one of the major differences between living and conventional polymerizations is the rate at which polymer chains grow. In a conventional polymerization, chains of high molecular weight are produced almost immediately and they act to stabilize the particles during propagation. However, in a living polymerization system chain growth is much slower and early in the polymerization only oligomeric chains are evident; chains too small to stabilize the polymer particles. Thus, we are looking at ways of speeding up the polymerization at the beginning of the reaction, as for example, by controlling the amount of excess nitroxide that is present. Earlier work in bulk has shown that lower amounts of free nitroxide can result in faster polymerization rates<sup>[14]</sup>.

The effect of the SFRP initiation process is also being studied to see how it affects particle size and stability. Under emulsion SFRP conditions, all polymer chains are initiated at the same time, unlike classical free radical polymerization where initiation takes place over a much longer time period. Initiating all the chains simultaneously generates large amounts of heat over a very short period that could be very disruptive to the reaction system. To avoid this problem, the use of a preformed water-soluble nitroxide-terminated initiator is being investigated. It has been shown in the case of the SFRP miniemulsion process that the use of TEMPO-terminated oligomers, which can act as initiators, give better results than when persulfate initiators are used<sup>[7]</sup>.

In summary, it has been shown that miniemulsion and suspension aqueous polymerization can readily be performed under SFRP conditions. While progress has been achieved with SFRP emulsion polymerization and

reactions can be performed without phase separation and fouling of the reactor, particle sizes are still too large to provide an emulsion in which polymer particles do settle out with time. Work continues in developing an understanding into what factors control particle size in the SFRP emulsion reactions<sup>[15]</sup>.

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