Stable Free-Radical Emulsion Polymerization

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ABSTRACT: Polymerizations of styrene under emulsion stable free-radical polymerization conditions are reported. Precipitation of an acetone solution of a low molecular weight TEMPO-terminated polystyrene into an aqueous solution of poly(vinyl alcohol) enables the formation of emulsion particles that can be swollen with monomer and subsequently polymerized. The polymerizations proceed in a living manner, yielding polymers that show an incremental increase in molecular weight with time and have narrow molecular weight distributions. Plots of number-average molecular weight versus conversion are linear, indicating a controlled polymerization. The resulting latexes are colloidally stable, and particle size distributions are Gaussian with an average particle diameter of 450 nm. These results constitute the first successful example of an SFRP emulsion process in which the product is not contaminated with a conventionally produced broad molecular weight distribution polymer.

Introduction

Living-radical polymerizations have increased in popularity since their discovery just over 10 years ago. To date, three living radical polymerization processes exist: stable free radical polymerization (SFRP),[1] atom transfer radical polymerization (ATRP),[2] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[3] These polymerizations combine attributes of anionic polymerizations, such as the ability to produce narrow polydispersity polymers and block copolymers, with the ease and industrial usefulness of free-radical polymerizations. They also lend themselves to aqueous polymerization processes,[4] a distinct advantage over other living polymerization systems.

The technology behind SFRP was developed using bulk polymerization conditions and subsequently extended to miniemulsion.[5] While miniemulsion polymerizations have been relatively facile to perform, SFRP emulsion reactions have been very difficult,[6,7] a characteristic SFRP appears to share with ATRP and RAFT. Reminiscent of earlier reported results with RAFT,[8] SFRP emulsion systems phase separate into an upper foamy oily layer and a lower aqueous layer. Increasing the amount of stabilizer and/or allowing the polymerization to proceed for longer times provides latexes that contain very large particles (>2 μm) in combination with suspension beads (0.5−2 mm) that settle on standing. Significant amounts of reactor fouling also occur in most cases.[7] It has remained an elusive goal of our group to develop a living-radical emulsion polymerization system, although, as delineated in this paper, it is increasingly clear that a simple, straightforward living-radical emulsion polymerization system may not be attainable.

In an attempt to understand why SFRP emulsion systems are so unstable, we have gone back and contrasted them with living-radical miniemulsion and conventional radical emulsion polymerization systems.

The most obvious difference between an emulsion and a miniemulsion system is the presence or absence of large monomer droplets, respectively. The reaction mixture of a miniemulsion is subjected to a high shear device that breaks the monomer layer into 50−500 nm size droplets, which are stabilized by a surfactant and a co-stabilizer (usually a long-chain hydrocarbon). Aqueous-phase-initiated oligomers then migrate into the miniemulsion droplets in a process referred to as droplet nucleation[9] to begin the polymerization process.

Two SFRP miniemulsion systems have been reported in which a preformed TEMPO-terminated polystyrene was used as both the co-stabilizer and initiator, thus avoiding aqueous phase initiation. Particles were formed with a piston homogenizer in one case[10] and by sonication in the other.[11] In the former example, sodium dodecylbenzene sulfonate (SDBS) was used as the surfactant, while DOWFAX 8390 was used in the latter case. While primary initiation by either aqueous-phase[12] or organic-phase initiators[13] can also be used in living-radical miniemulsion polymerizations, avoiding primary initiation may be desirable so as to simplify an already complicated system.

In contrast to a miniemulsion system, particles in a conventional emulsion polymerization are formed by either micellar or homogeneous nucleation or a combination of both, depending upon the water solubility of the monomer. While some of the monomer for these polymerizations is contained in monomer-swollen micelles, the majority exists in large monomer droplets that are typically 1−10 μm in diameter. These droplets act as monomer reservoirs and provide monomer to the growing particles. While highly unstable, the monomer droplets become depleted and shrink as polymerization proceeds and at about 40% conversion the droplets are completely gone.[14] In an SFRP emulsion polymerization, the monomer droplets may not disappear as readily. SFRP is performed at elevated temperatures (>125 °C), temperatures above which styrene is known to autopolymerize.[15] Autoinitiation and subsequent polymerization in the monomer droplets would cause them to lose their ability to act as effective reservoirs since there is no longer a driving force for the monomer to leave the droplets once polymer is present. Thus, these large unstable droplets can remain indefinitely in the reaction mixture, contributing to phase separation or the formation of large polymer particles depending upon the conditions of the polymerization.

Alternatively or in combination with the aforementioned autoinitiation issue, the difference in the rate of

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chain growth in conventional and living-radical polymerizations may also contribute to the failure of living-radical emulsion polymerizations. In a conventional radical polymerization chain growth is fast and within seconds very high molecular weight chains are formed, which in the case of an emulsion polymerization help to stabilize the polymer particles. Chain growth is much slower in a living-radical polymerization system. The polymer chains continuously increase in molecular weight throughout the polymerization, but at the beginning of the process the chains are not large enough to effectively stabilize the polymer particles. This lack of stabilization causes the particles to stabilize themselves by reducing their total free interfacial surface energy by increasing in size through particle coalescence and Ostwald ripening.[16]

Several groups have demonstrated the ability to achieve stable lattices under living-radical conditions by using high molecular weight preformed polymers to stabilize the emulsion particles. Bon et al.[17] reported a successful seeded emulsion under SFRP conditions wherein a polystyrene seed latex was prepared by conventional free-radical emulsion polymerization. The particles were swollen with styrene, and a living-radical polymerization was conducted inside these swollen particles using an alkoxyamine initiator. While a high conversion stable latex was obtained, the reaction was very slow and the molecular weight distributions were broad and showed tailing in the lower molecular weight region, an indication of dead chains.

In a similar manner, Gilbert et al.[12c] performed a seeded living-radical emulsion polymerization under RAFT conditions. A seed latex was prepared by a conventional free-radical emulsion polymerization, and a RAFT agent was transported into the particles using acetone as a vehicle. The living portion of the polymerization was then conducted using styrene as the monomer and potassium persulfate as the initiator. The latex produced was colloidally stable, and the polymer chains were living, showing an increase in molecular weight with conversion.

Cao et al.[18] also reported nitroxide-mediated emulsion polymerizations. While not explicitly described as such, these were also seeded emulsions; under the reaction conditions high molecular weight conventionally formed polymers, which probably served to stabilize the polymer particles, were always present early in the polymerization. Most of the polymers produced had very broad molecular weight distributions, an indication of a lack of control in the polymerizations.

These results demonstrate that a living-radical emulsion polymerization can be accomplished when higher molecular weight chains are present to stabilize the particles and wherein the formation of monomer droplets is avoided. The disadvantage of the seeded emulsion experiments is that the product always contains a significant number of dead chains with a broad molecular weight distribution from the conventionally polymerized seed, which nullifies the benefits of performing a living-radical polymerization.

Making use of both SFRP and ATRP technologies, Charleux et al.[19] synthesized a variety of block copolymers of acrylic acid and styrene or acrylic acid and *n*-butyl acrylate, which contained both a hydrophobic and hydrophilic segment enabling the chains to assemble themselves into seeds for the creation of particles. The living-radical capping agents of the block copolymers were removed, and these polymers were then used as emulsion stabilizers for conventional radical polymerizations. Gilbert et al.[20] used the same idea with RAFT and made a block copolymer of acrylic acid and *n*-butyl acrylate in which the capping agent was not removed. These block copolymers were then used as both an emulsion stabilizer and macroinitiator for starved-feed *n*-butyl acrylate polymerizations. This process proved successful to give colloidally stable latex and a living polymer, although the molecular weight distribution plots showed a high molecular weight shoulder, signifying imperfect control over molecular weight as suggested by the authors. This work again illustrates that if stabilized particles are present initially and monomer droplets are avoided, a living-radical emulsion polymerization can be achieved.

In this paper we report a new technique capable of producing colloidally stable latexes by an SFRP emulsion process. A microprecipitation process is used to create particles containing a preformed TEMPO-terminated oligomer that serves as a macroinitiator and a particle stabilizer. The particles are then swollen with monomer, and subsequent polymerization produces a living polymer under emulsion (phase III)[21] conditions in which excellent chain growth is demonstrated. Importantly, no high shear device is required to form small particles, and the use of a high molecular weight conventionally formed polymer that would contaminate the living polymer product is avoided. As will be demonstrated, a judicious choice of surfactant is important to the success of this technique.

Experimental Section

(a) Materials and Equipment. The inhibitor was removed from styrene (Aldrich) by passing it through a 4-*tert*-butylcatechol inhibitor removal column (Aldrich). Inhibitor was removed from *n*-butyl acrylate (Aldrich) by passing it through a 4-methoxyphenol inhibitor removal column (Aldrich). Benzoyl peroxide (BPO) (Aldrich) was purified by recrystallization from methanol. 4-HydroxyTEMPO (Chemipan, Russia) was purified by recrystallization from hexanes. Sodium dodecylbenzene sulfonate (SDBS) (Aldrich), potassium persulfate (KPS) (Aldrich), poly(vinyl alcohol) (PVA), 87−89% hydrolyzed, average M_w 31 000−50 000 g/mol (Aldrich), and TEMPO (Chemipan, Russia) were used as received. The acyclic nitroxide, 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide, **1**, was synthesized according to a reported procedure.[22a] The alkoxyamine unimer 1-(benzoyloxy)-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (BST), **2**, was synthesized according to a procedure developed in our laboratory.[23] For starved-feed experiments, monomer was added to the reactor using a Harvard PHD 4400 syringe pump equipped with a 9 mL stainless steel syringe (diameter = 9.525 mm) that was connected to the reactor using stainless steel HPLC tubing as a needle (1/16 o.d., 0.040 i.d., void length of tubing 69.5 cm). Polymer molecular weights and polydispersity indices (PDIs) were estimated by gel-permeation chromatography (GPC) using a Waters 2690 Separations Module with Ultrastyragel columns HR1, HR3, and HR4E and a Waters model 410 differential refractometer (RI). Polystyrene standards were used for calibration.[24] THF was used as the eluent at a flow rate of 0.5 mL min^{-1}. GPC was performed on samples taken directly from the reaction mixture without any prior precipitation that may remove low molecular weight

Table 1: *n*-Butyl Acrylate Emulsion SFRP

sample	M_n (g mol^{-1})	PDI	conversion
1 h	12 000	1.47	30%
2 h	17 500	1.35	44%
4 h	25 900	1.39	69%
6 h	31 400	1.45	77%

Table 2: SFRP Styrene Starved-Feed Emulsion

sample	M_n (g mol^{-1})	PDI
2 h	5 500	1.22
4 h	14 700	1.40
6 h	31 800	1.22

chains. Excess monomer was removed by evaporation with a stream of air before GPC analysis. Percentage conversions were determined gravimetrically. Particle sizes were determined by dynamic light scattering using a Nicomp model 370 submicron particle sizer.

(b) General Procedure for Emulsion Polymerizations. Once prepared (outlined in detail below), emulsion mixtures were placed in a modified Parr bomb reactor equipped with a pressure gauge, four-bladed propeller mixer, thermocouple, argon inlet, and sampling tube. The reaction mixture was stirred while being purged by pressurizing the reactor to 6.9 bar with argon gas for 1 min and then depressurizing the reactor. This process was repeated 10 times. The reactor was placed under a 6.9 bar atmosphere of argon and heated for typically 6−8 h at 135 °C.

(c) *n*-Butyl Acrylate Emulsion SFRP. An emulsion was prepared by dissolving SDBS (2.0 g) and KPS (206 mg; 0.762 mmol) in distilled water (200 mL) and adding to this a solution of 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide, **1** (340 mg; 1.53 mmol), in *n*-butyl acrylate (50 mL). The resulting mixture was heated for 6 h at 135 °C to produce an emulsion that was colloidally unstable and contained large particles that settled on standing. Over a 12 h period the particles agglomerated into a sticky mass. The M_n and PDI of the polymers produced over the course of the polymerization are shown in Table 1.

(d) SFRP Starved-Feed Styrene Emulsion. An emulsion was prepared by dissolving SDBS (2.0 g), KPS (103 mg; 0.381 mmol), and 4-hydroxyTEMPO (50 mg; 0.291 mmol) in distilled water (100 mL) and adding to this a solution of TEMPO (50 mg; 0.320 mmol) in styrene (2.2 mL). The resulting emulsion was placed in the modified Parr bomb reactor fitted with a stainless steel syringe and heated to 135 °C. Once at reaction temperature, 8.8 mL of styrene was added at a rate of 4 mL/h. The reaction mixture was heated for an additional 4 h after all the styrene had been added. The molecular weight distribution (MWD) curves of the resulting polymers contained a low molecular weight shoulder and a high molecular weight hump, signifying imperfect control over the polymer's livingness. The M_n and PDI of the polymers produced over the course of the polymerization are shown in Table 2. The emulsion obtained was colloidally unstable and contained large particles that settled on standing.

(e) Water-Soluble Styrene Oligomer (3) Synthesis. Styrene (20 mL) and distilled water (100 mL) were shaken vigorously in a separatory funnel. The mixture was allowed to separate, and the styrene saturated aqueous solution was decanted off. KPS (103 mg; 0.381 mmol), TEMPO (80 mg; 0.512 mmol), and an additional 5 drops of styrene were added to the aqueous solution. The resulting mixture was placed in a three-necked round-bottom flask fitted with an argon inlet, condenser, and thermometer. The reaction mixture was purged with argon for 20 min and then heated to 90 °C for 3 h under argon to form a single-phase solution that was subsequently used to initiate the polymerizations described in parts f, g, and h of the Experimental Section.

Table 3: SFRP Batch Styrene Emulsion Using Initiator 3

sample	M_n (g mol^{-1})	PDI
2 h	11 700	1.14
4 h	31 300	1.34
6 h	43 500	1.29
8 h	47 000	1.31

Table 4: SFRP Batch Styrene Emulsion Using Initiator 3 with Excess Free Nitroxide

sample	M_n (g mol^{-1})	PDI
2 h	12 300	1.15
3 h	24 000	1.25
4 h	34 200	1.21
6 h	46 900	1.21

Table 5: SFRP Starved-Feed Styrene Emulsion Using Initiator 3

sample	M_n (g mol^{-1})	PDI
2 h	3300	1.08
4 h	4500	1.13
6 h	5300	1.10

(f) SFRP Batch Styrene Emulsion Using Initiator 3. SDBS (1.0 g) was added to the water-soluble solution (Experimental Section, part e) (100 mL) followed by styrene (10 mL). The reaction mixture was heated in the modified Parr bomb reactor for 8 h at 135 °C. The resulting emulsion was colloidally unstable and contained large particles that settled upon standing. The polymer exhibited an incremental increase in molecular weight with time; however, the molecular weight distribution curves contained a very prominent low molecular weight shoulder. The M_n and PDI of the polymers produced over the course of the polymerization are shown in Table 3.

(g) SFRP Batch Styrene Emulsion Using Initiator 3 with Excess Free Nitroxide. Experiment f was repeated with the addition of excess free nitroxide to the reaction mixture: TEMPO (75 mg; 0.480 mmol) and 4-hydroxyTEMPO (45 mg; 0.261 mmol). The reaction mixture was heated at 135 °C in the modified Parr bomb reactor for 6 h. The emulsion obtained was colloidally unstable and contained large particles that settled upon standing. The M_n and PDI of the polymers produced over the course of the polymerization are shown in Table 4.

(h) SFRP Starved-Feed Styrene Emulsion Using Initiator 3. SDBS (2.0 g) and styrene (10 drops) were added to the water-soluble initiating solution (Experimental Section, e) (100 mL). The resulting emulsion was heated to 135 °C in the modified Parr bomb reactor, and then 8.8 mL of styrene was added a rate of 4 mL/h. After all the styrene had been added, the reaction mixture was heated for an additional 4 h. The resulting emulsion was colloidally unstable and separated into a thick viscous oily layer on top of an opaque aqueous layer. GPC analysis (Table 5) of the reaction mixture indicated that only oligomeric material was present.

(i) BST Initiated SFRP Styrene Emulsion. An emulsion was prepared by dissolving SDBS (1.5 g) and 4-hydroxyTEMPO (15 mg; 0.087 mmol) in distilled water (100 mL) and adding to this a solution of BST, **2**

Table 6: BST Initiated SFRP Styrene Emulsion

sample	M_n (g mol^{-1})	PDI
1 h	4700	1.17
2 h	7 400	1.15
4 h	10 100	1.16
6 h	13 600	1.09
8 h	16 200	1.08

Table 7: SFRP Styrene Emulsion Using a Microprecipitation Process with SDBS as a Surfactant

sample	M_n (g mol^{-1})	PDI
2 h	31 900	1.41
4 h	48 000	1.34
7 h	52 700	1.35

(289 mg; 0.759 mmol), and TEMPO (5 mg; 0.032 mmol) in styrene (25 mL; 0.22 mol). The resulting mixture was heated to 135 °C in the modified Parr bomb reactor for 8 h to yield large beads (0.5 mm) suspended in an aqueous phase. The M_n and PDI of the polymers produced over the course of the polymerization are shown in Table 6.

(j) TEMPO-Terminated Styrene Oligomer Synthesis Under Bulk Conditions. A polystyrene oligomer was prepared by dissolving TEMPO (1.7 g; 10.9 mmol) in styrene (100 mL; 0.87 mol) in a three-necked round-bottom flask equipped with an argon inlet, condenser, and thermometer. The resulting solution was bubbled with argon gas for 20 min. BPO (2.0 g; 8.3 mmol) was added, and the reaction temperature was maintained at 135 °C for 4 h. The solution was cooled to room temperature, diluted with dichloromethane (100 mL), and precipitated into methanol (1000 mL). The resulting polymer was filtered, washed with methanol, and air-dried. By GPC: $M_n = 3300$ g mol^{-1}, PDI = 1.13.

(k) SFRP Styrene Emulsion Using a Microprecipitation Process with SDBS as a Surfactant. The TEMPO-terminated polystyrene oligomer (2.0 g) (prepared according to procedure j) was dissolved in acetone (100 mL) and added dropwise to a stirred solution of SDBS (2.0 g) in distilled water (100 mL). The polymer solution initially precipitated as submicrometer-sized particles that remained dispersed; however, as more of the polymer solution was added, larger particles formed that settled upon standing. The large particles were removed by filtration, resulting in an emulsion of submicrometer-sized particles in water. Acetone was removed from the latex by rotary evaporation. Styrene (5 mL) was added, and the reaction mixture was heated in the modified Parr bomb reactor to 135 °C. Styrene was then added in three 8.8 mL aliquots at a rate of 4 mL/h. After all the styrene had been added, the reaction mixture was heated for an additional 2 h. The resulting emulsion was colloidally unstable and contained small particles that slowly settled out over a 12 h period. The particles were examined under a light microscope fitted with a calibrated micrometer and were found to be on average 2 μm in diameter. The M_n and PDI of the polymers produced over the course of the polymerization are shown in Table 7. All the GPC distributions contained a low molecular weight shoulder.

(l) SFRP Starved-Feed Styrene Emulsion Using a Microprecipitation Process with PVA as a Surfactant. An emulsion was prepared by dissolving the TEMPO-terminated polystyrene oligomer (1.0 g) (Experimental Section, j) in acetone (50 mL) and adding this solution dropwise to a stirred solution of PVA (1 g) in distilled water (100 mL). The resulting emulsion was stirred uncovered overnight to allow the acetone to evaporate. Styrene (1.6 mL) was added, and the mixture was placed in a modified Parr bomb reactor fitted with a stainless steel syringe and treated according to procedure b. Once at reaction temperature, 8.8 mL of styrene was added at a rate of 4 mL/h. The reaction mixture was heated for an additional 3 h after styrene addition had ceased. The emulsion produced was colloidally stable. The resulting polymers showed an incremental increase in molecular weight with time (Table 8); however, the molecular weight distributions were bimodal (Figure 1). Dynamic light scattering measurements showed two particle populations with mean particle diameters of 400 and 900 nm.

Table 8: SFRP Starved-Feed Styrene Emulsion Using a Microprecipitation Process with PVA as a Surfactant

sample	M_n (g mol^{-1}) (g/mol)	PDI
2 h	6 400	1.40
4 h	9 900	1.30
6 h	17 000	1.26

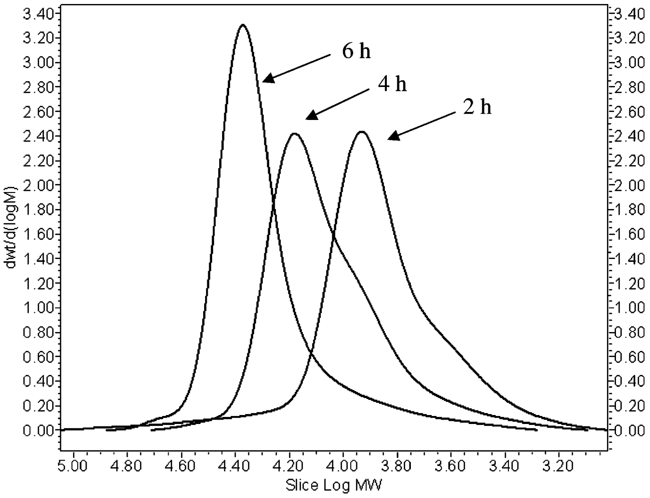


Figure 1. GPC MWD plot for the SFRP starved-feed emulsion polymerization of styrene using a microprecipitation process with PVA as the surfactant. MWs and PDIs are shown in Table 8.

(m) SFRP Styrene Emulsion Using a Microprecipitation Process with PVA and Monomer Particle Swelling. An emulsion was prepared by dissolving the TEMPO-terminated polystyrene oligomer (1 g) (Experimental Section, j) in acetone (50 mL) and adding this solution dropwise to a stirred solution of PVA (1 g) in distilled water (100 mL). This mixture was stirred uncovered overnight to allow the acetone to evaporate. Styrene (10 mL) was added to the emulsion, and the latex was stirred covered for an additional 12 h to allow the particles to swell with monomer. The mixture was then placed in the modified Parr bomb reactor and treated according to procedure b. Monomer conversion was 67% after 6 h, and there was no visible sign of fouling on the reactor surfaces. The latex produced was colloidally stable, with an average particle size of 460 nm. The M_n, PDI, and percent conversions of the polymers produced over the course of the polymerization are shown in Table 9.

(n) SFRP Styrene Emulsion Using a Microprecipitation Process with PVA and Monomer Particle Swelling—Increased Monomer Loading. Experimental procedure m was repeated, but the amount of styrene was increased to 25 mL. The resulting

Table 9: SFRP Styrene Emulsion Using a Microprecipitation Process with PVA and Monomer Particle Swelling

sample	M_n (g mol^{-1})	PDI	conversion
0.5 h	6 200	1.26	19%
1 h	8 200	1.24	27%
2 h	12 900	1.23	41%
4 h	19 200	1.17	60%
6 h	22 900	1.11	67%

Table 10: Modified SFRP Styrene Emulsion Using a Microprecipitation Process with PVA and Monomer Particle Swelling

sample	M_n (g mol^{-1})	PDI	conversion
1 h	14 100	1.26	40%
2 h	19 900	1.19	55%
4 h	26 000	1.13	63%
6 h	28 100	1.12	69%
8 h	29 500	1.12	79%

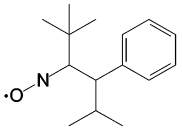
emulsion was colloidally stable, and there was no visible sign of fouling on the reactor surfaces. The polymers produced were living, showing an incremental increase in molecular weight with time. Final results: M_n = 45 309, PDI = 1.12, conversion = 63% after 6 h.

(o) Modified SFRP Styrene Emulsion Using a Microprecipitation Process with PVA and Monomer Particle Swelling. Experiment m was modified to more effectively remove acetone by rotary evaporation at 35 °C. Since water and acetone form an azeotrope, some water also evaporated during this process. The solution was made up to 100 mL by the addition of distilled water. Styrene (10 mL) was added, and the reaction mixture was stirred covered for 1.5 h to allow the particles to swell with monomer. The mixture was then placed in the modified Parr bomb reactor and treated according to procedure b. After 8 h monomer conversion was 79%, and there was no visible sign of fouling on the reactor. The latex produced was colloidally stable, with an average particle size of 420 nm. The M_n and PDI of the polymers produced over the course of the polymerization are shown in Table 10.

Results and Discussion

Two sets of experiments were performed to determine whether autoinitiation in the monomer droplets was contributing to the instability of the SFRP emulsion systems. In one case, polymerizations were performed with *n*-butyl acrylate, which is known to lack an autoinitiation mechanism. The acyclic nitroxide (**1**), reported to work well with acrylates,[22a] was used to moderate the polymerizations. The polymers produced were living as shown by the incremental increases in molecular weight of the polymer with both time and conversion (Table 1); however, the resulting emulsions contained large particles that settled to the bottom of the reaction vessel upon standing for a few minutes. After 12 h the particles had agglomerated to form a large sticky mass.

In a second series of experiments, SFRP starved-feed conditions were employed to polymerize styrene. To avoid monomer droplet formation and thereby eliminate polymerization inside them, the monomer addition rate was adjusted so that the monomer concentration was always below a level that would saturate the aqueous phase.[20] In the initial experiments, the reaction product phase separated into an upper foamy layer and a lower aqueous layer. Assuming that this result was due to low monomer conversion, longer reaction times were employed to achieve higher conversions. These experiments led to the formation of large particles (10−100 μm) that settled upon standing. All the experiments in this series produced polymers that exhibited living character. The M_n and PDI results in Table 2 are typical for these polymerizations. While these results do not completely rule out the monomer droplets as the reason for emulsion failure, they do suggest that there is more to the SFRP emulsion stability problem than just the prolonged presence of the monomer droplets.



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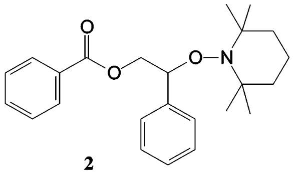

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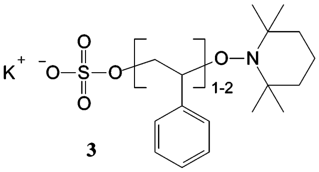

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Our attention turned to determining whether decoupling the initiation step from particle formation and subsequent polymerization would provide any advantages to the polymerization process. A water-soluble TEMPO-terminated styrene initiating species was prepared from a styrene saturated aqueous solution containing potassium persulfate and TEMPO. ^{1}H and ^{13}C NMR data indicate that the major initiating species are 1−2 monomer units in length and terminated with TEMPO (**3**). In one set of experiments, the water-soluble initiating species was mixed with SDBS and monomer and the resulting latex was heated at 135 °C for 6 h. Initially, these experiments resulted in molecular weight distributions that contained low molecular weight shoulders, suggesting that premature chain termination was occurring. Unimodal molecular weight distributions were obtained by adding a fairly significant amount (1.45 equiv) of additional free nitroxide at the beginning of the reaction.[22] In another set of experiments, the aqueous soluble initiating species was mixed with surfactant and styrene was added under starved-feed conditions to avoid the formation of monomer droplets while the reaction mixture was heated at 135 °C. In all three cases, the polymers produced showed an increase in molecular weight with time and narrow molecular weight distributions (MWDs) (Tables 3−5); however, none of the resultant emulsions were stable. The former batch reactions gave latexes with large particles that settled out on standing, while the latter starved-feed reactions provided emulsion mixtures that phase separated into a viscous monomer layer on top of an opaque aqueous layer.

An experiment was also performed in which (**3**) was replaced with BST (**2**), a monomer soluble initiator, to see if that change would affect emulsion stability. It did not. The resulting latex contained large particles (0.5 mm diameter) that settled on standing, although as in the previous examples, M_n increased with time and the MWDs were impressively narrow (Table 6).

In parallel with these studies with the preformed initiating species (**3**), we also investigated precipitation techniques to make small particles with TEMPO-terminated styrene oligomers. Early attempts to make polymer particles, for example, by precipitating a 2.5 wt % solution of a TEMPO-terminated polystyrene oligomer (3300 g·mol^{-1}) in acetone into an aqueous solution containing 2 wt % SDBS were unsuccessful. Upon addition of the oligomer solution, large particles, which settled once the stirring was stopped, continually resulted. A polymerization with the filtrate of one of these precipitation experiments proceeded to give polymer, which behaved in a living manner (Table 7). More importantly, the resulting latex was composed of particles with average particle sizes of 2 μm. While still too large to give a stable latex, these were the smallest particle sizes that we had obtained up to that point. Adding the oligomer as a more dilute solution in acetone (0.5−1.25%) provided more stable emulsions; however, after the acetone was removed by evaporation, large particles of polymer, which settled from the reaction mixtures over time, were evident. Presumably, these particles formed by agglomeration of the initially formed smaller particles.

In the process of trying to improve this precipitation approach to make particles, SDBS was replaced by the nonionic surfactant poly(vinyl alcohol) (PVA). When a 2.5 wt % solution of the TEMPO-terminated polystyrene oligomer in acetone was added dropwise to a 1 wt % solution of PVA in water, a white stable emulsion resulted. In contrast to the SDBS experiments, no large particles were evident. Removal of the acetone by air evaporation over a 12 h period and subsequent polymerization under starved-feed conditions gave an emulsion that was colloidally stable. Unfortunately, the molecular weight distributions of the polymer products formed in the early stages of the polymerization were distinctly bimodal (Figure 1). Also, the particle size distribution of the emulsions was similarly bimodal with one population of particles having a mean diameter of 400 nm and the second 900 nm.

Allowing the precipitated particles to swell with monomer over a 12 h period before polymerization instead of adding the monomer under starved-feed conditions led to a colloidally stable latex with a narrow, unimodal Gaussian particle size distribution. The average particle size was 460 nm. Particles larger than 1 μm, so prominent in all previous attempts to prepare stable latexes, were completely absent. In an effort to eliminate the lengthy process involved in making these particles, acetone evaporation was performed using a rotary evaporator instead of air evaporation and the particle swell time was decreased to 1.5 h. These changes appeared to have no adverse effects on the outcome of the polymerization. The polymers produced were living, showing an incremental increase in molecular weight with both time and conversion (Table 10 and Figures 2 and 3). The emulsion was colloidally stable with a unimodal mean particle size of 420 nm. Two factors that may be contributing to the colloidal stability of the latex obtained are the choice of surfactant and the rapid nucleation of all particles, which is known to increase particle stability. PVA is a better stabilizer for larger particles than SDBS, and because of the way the particles are created in our process, nucleation of all particles is effectively completed before polymerization begins.[25]

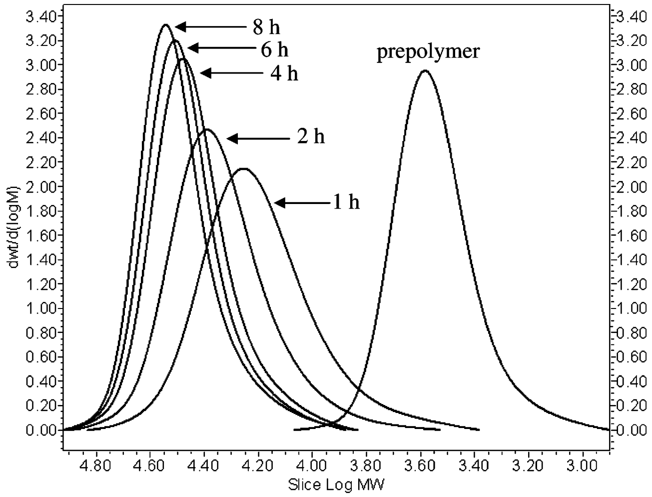

Figure 2. GPC MWD plot for the SFRP styrene emulsion polymerization using a microprecipitation process with PVA and monomer particle swelling. MWs and PDIs are shown in Table 10.

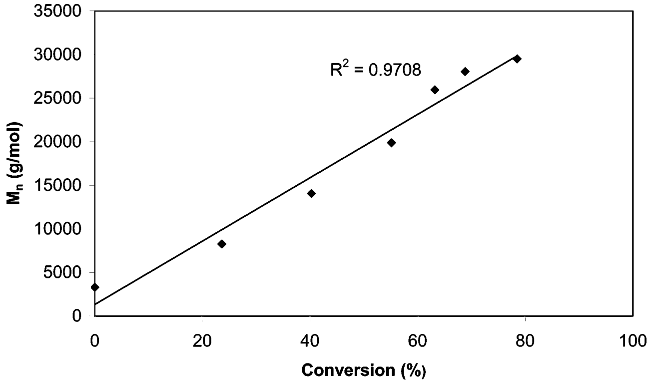

Figure 3. Number-average molecular weight vs conversion plot for the styrene emulsion polymerization using a microprecipitation process with PVA and monomer particle swelling.

Dynamic light scattering was performed on various samples of the emulsion throughout both the particle formation and polymerization processes. The initial particles formed by precipitation of the prepolymer solution into the aqueous PVA solution had a mean particle diameter of 300 nm, and the distribution was Gaussian. However, upon evaporation of the acetone from the emulsion, the particle size shifted to a bimodal distribution where one peak had a mean diameter of 135 nm and the second a mean diameter of 470 nm. This could be caused by some of the smaller particles collapsing upon acetone removal while the larger particles, having a larger interfacial surface area, remain as they are. The particle distribution returned to a Gaussian distribution with a mean particle diameter of 340 nm after the particles were swollen with styrene. Also, when heated to reaction temperature, the particles showed further swelling due to expansion to give a mean particle diameter of 400 nm. Over the course of the reaction the particles typically grew an additional 50 nm in size and the particle size distributions would remain Gaussian.

Initial experiments conducted with the microprecipitation procedure were performed using 10% monomer loading; however, no adverse effects on the polymer's livingness, the colloidal stability of the latex, or the resulting particle size were observed when the monomer loading was increase to 20%.[26]

Conclusions

We investigated the role of autoinitiation in monomer droplets as a contributor to the instability of the emulsion SFRP process and concluded that while it may be advantageous to avoid this process, avoiding it does not provide stable latexes. We also investigated whether bypassing primary water phase initiation would contribute to more stable emulsion systems and concluded it does not. On the other hand, successful emulsion polymerizations using the SFRP process can be performed by using monomer-swollen preformed particles stabilized with a TEMPO-terminated polystyrene oligomer. In essence, by creating these particles and subsequently polymerizing them to provide colloidally stable emulsions, what we are doing is avoiding phases I and II of a conventional polymerization and going directly to phase III. One of the advantages of this system is the ease with which the particles can be prepared. There is no need for a high shear device as in the case of a miniemulsion polymerization, and the product does not contain conventionally formed polymer, as was the case for the earlier seeded emulsion polymerizations. Also, by choosing the right surfactant for particle stabilization, the system is robust enough to withstand the rigors of the emulsion polymerization process at 135 °C. These results constitute the first successful example of a completely controlled SFRP emulsion process to provide collodially stable latexes containing polymers with narrow MWDs uncontaminated with conventionally formed broad MWD polymer.

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(25) We acknowledge and appreciate one reviewer's comments on this subject.

(26) We are currently investigating the maximum monomer loading possible with this system while still maintaining colloidal stability.

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