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High Solids Nitroxide-Mediated Microemulsion Polymerization of MMA with a Small Amount of Styrene and Synthesis of (MMA-*co*-St)-*block*-(BMA-*co*-St) Polymers

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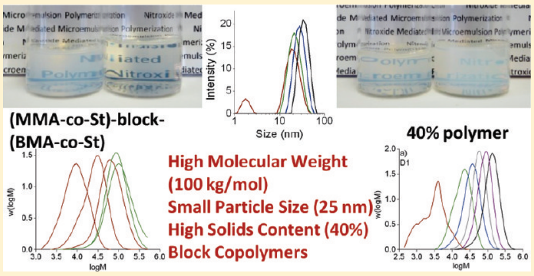
S *Supporting Information*



ABSTRACT: We report the first nitroxide-mediated microemulsion polymerization of methyl methacrylate-*co*-styrene as well as the synthesis of (MMA-*co*-St)-*block*-(*n*-BMA-*co*-St) polymers using a one-pot, two-stage differential monomer addition technique. These microemulsion polymerizations were conducted with commercially available materials and do not require a preliminary synthesis step. The latexes are optically translucent with monomodal particle size distributions, mean particle diameters ranging from 20 to 30 nm, low surfactant-to-monomer ratios (0.13−0.28 w/w), and solids contents up to 40 wt %. The polymerizations exhibited fast reaction rates, resulting in well-controlled reactions yielding high molecular weight polymer (>100 000 g mol^{-1}). The styrene content and duration of the first stage were particularly important for obtaining narrow molecular weight distributions, with 30 mol % styrene in the first stage (∼8−10 mol % styrene overall in the polymer), resulting in the best controlled polymerizations. The overall styrene content in the latexes can be as low as 8 mol % while maintaining excellent control. The MMA-*co*-St microemulsion latexes can readily be chain extended with *n*-BMA-*co*-St while preserving monomodal particle size distributions.

INTRODUCTION

Controlled/living polymerization has emerged as an elegant and simple method of synthesizing polymers with tailored molecular architectures under mild reaction conditions. Nitroxide-mediated polymerization (NMP) was first reported using the nitroxide TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) to reversibly terminate growing polymer chains, thereby minimizing irreversible termination and yielding narrow molecular weight distributions (MWDs), low polydispersities (PDIs), and living chains that are readily extended.[1] Unfortunately, TEMPO is suitable for mediating only styrenic monomers, but the introduction of other nitroxides, such as SG1 (*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, has enabled the mediation of styrenics and acrylates at milder reaction conditions.

Early attempts to perform nitroxide-mediated emulsion polymerization resulted in latex coagulation,[3,4] but the introduction of a two-stage emulsion polymerization procedure using the commercially available water-soluble alkoxyamine BlocBuilder MA (Arkema), based on the nitroxide SG1, has resolved this problem.[5] A first stage latex was synthesized in the absence of monomer droplets; the initial reactor charge contained a small amount of monomer, surfactant, and the alkoxyamine in its ionized form. The remainder of the monomer could then be added to the first stage latex in either batch or semibatch mode.

While NMP can effectively mediate the polymerization of styrenics and acrylates, successful polymerization of methacrylate monomers is limited by a high activation/deactivation equilibrium constant (K_{eq}). This causes significant irreversible termination early on in the polymerization, leading to an accumulation of nitroxide that suppresses further polymerization. However, methyl methacrylate (MMA) can be effectively mediated using SG1 through the addition of 4.4−8.8 mol % styrene (St), which acts to lower the equilibrium constant.[6] K_{eq} depends on both the terminal and penultimate units of the polymer chain; addition of the styrene ensures the majority of the dormant chains possess the structure MMA−St−SG1.[7] Kinetic modeling studies suggest that the addition of too much styrene impedes the polymerization through the formation of St−St−SG1 segments, which are slow to reactivate.[8,9] Another limitation of NMP with methacrylates is that in systems with large excess of SG1 (>40 mol %) β-hydrogen transfer from the methacrylate-derived radical to the nitroxide can be a significant chain stopping event.[10,11]

Surfactant-free emulsion polymerization of MMA (with a small amount of St) has been achieved by first synthesizing an amphiphilic poly(methacrylic acid-*co*-styrene)−SG1 macroinitiator

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Table 1. Forumlations for the First Stage Methyl Methacrylate (MMA) Microemulsion Latexes with 8 or 30 mol % Styrene (St)[a]

experiment	first stage formulation ratios (molar) MMA:St:BB	first stage solids content[b] (wt %)	surfactant/monomer (g/g)
A1	110.9:9.7:1.0	1.8	2.8
A2	82.9:31.2:1.0	1.8	3.0

[a] The alkoxyamine initiator BlocBuilder MA (BB) was added to the aqueous phase in its carboxylated form, neutralized with Na_2CO_3. The surfactant was Dowfax 8390. Polymerizations were conducted at 90 °C, and samples were withdrawn frequently for 300 min. [b] Solids content refers to the loading of monomer (wt %) in the system with respect to all other components.

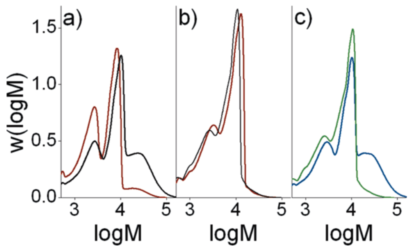

Figure 1. Molecular weight distributions for experiments A1 and A2 (Table 1). The MMA-*co*-St first stage latexes were sampled over 300 min (90 °C, theoretical solids content = 1.5 wt % solids, DP_n^{th} = 120). Distributions are shown for samples collected at 15 min (red line) and 300 min (black line) for (a) 92 mol % MMA, 8 mol % St and (b) 70 mol % MMA, 30 mol % St. The final samples at 300 min are shown together (c) for both 92 mol % MMA, 8 mol % St (blue line) and 70 mol % MMA, 30 mol % St (green line). MWDs are normalized for area.

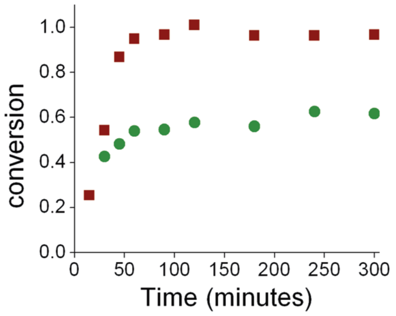

Figure 2. Conversion versus time profiles for experiments A1 and A2 (Table 1). The MMA-*co*-St first stage latexes (90 °C, theoretical solids content = 1.5 wt % solids, DP_n^{th} = 120) contain either 92 mol % MMA, 8 mol % St (■) or 70 mol % MMA, 30 mol % St (●).

in a 1,4-dioxane solution.[12] The macroinitiator acts as both stabilizer and initiator for the polymerization. This procedure resulted in well-controlled polymerizations with high initiation efficiency but sometimes produced bimodal particle distributions, attributed to the formation of aggregates. Particle size distributions of 27−50 nm for the smaller domain and 150−300 nm for the larger domain were reported. Molecular weights between 30 000 and 78 000 g mol^{-1} were produced at conversions of 70−85%, depending upon the characteristics of the macroinitiator.[12] Solids contents were 15−20 wt %.

Microemulsions are thermodynamically stable oil-in-water dispersions, and polymerization in such systems leads to small (<50 nm) polymer nanoparticles suspended in water. Polymeric microemulsions have high internal interfacial area and are both thermodynamically stable and optically transparent—characteristics which are desirable in specialized applications like adhesives, drug delivery, or microencapsulation.[13] Traditionally microemulsion polymerizations have high amounts of surfactant with respect to monomer (>1:1 w/w), although it has been demonstrated in conventional microemulsion polymerization that high polymer-to-surfactant ratios can be achieved through the use of differential monomer feeding strategies.[13,14]

Nitroxide-mediated microemulsion polymerization was first reported by Wakamatsu et al.[15] for styrene mediated by TEMPO or SG1 in a bicomponent system (using the initiator AIBN) at 120 °C. This system had low solids content (2−5 wt %) and high surfactant-to-monomer ratios (2.5−6.7 w/w). Mean particle diameters were 40−129 nm with TEMPO and 27−35 nm with SG1. In SG1-mediated polymerizations, the molecular weight increased monotonically with conversion, but the PDIs were over 2 upon reaching full conversion. Zetterlund et al.[16] continued studying microemulsion NMP with the nitroxides SG1 and TIPNO to explore compartmentalization effects. Styrene polymerizations with 6% polymer solids content and a 2.50 surfactant-to-monomer ratio (w/w) yielded particles of ~50 nm diameter. They found that polymerization in microemulsion is slower than in bulk but results in lower PDIs at conversions below 20%. However, at high conversions, control over the MWD is superior in the bulk system. Experimentally, these microemulsions exhibited poor initiator efficiency resulting from geminant recombination of AIBN radicals. Controlled radical polymerization in microemulsion has also been demonstrated for RAFT (reverse addition−fragmentation transfer)[17−19] and ATRP (atom transfer radical polymerization).[20]

In this study we report the first nitroxide-mediated microemulsion polymerization of MMA-*co*-St along with the synthesis of (MMA-*co*-St)-*block*-(BMA-*co*-St) polymers. The polymerizations were conducted with commercially available materials and do not require a preliminary macroinitiator synthesis step. The latexes are translucent with monomodal particle size distributions, mean particle diameters ranging from 20 to 30 nm, low surfactant-to-monomer ratios (0.13−0.28 w/w), and solids contents up to 40 wt %. The polymerizations were well controlled with high molecular weights (>100 kg mol^{-1}).

■ EXPERIMENTAL SECTION

Materials. Styrene (St, Aldrich, >99%), *n*-butyl methacrylate (BMA, Aldrich, 99%), and methyl methacrylate (MMA, Aldrich, 99%) were purified by passing through columns packed with inhibitor remover (Aldrich). The compounds 2-[*N*-*tert*-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)-aminoxy]-2-methylpropionic acid (BlocBuilder MA, supplied by Arkema, 99%), Dowfax 8390 (Dow Chemicals, 35 wt % solution in water), and sodium carbonate (Na_2CO_3, Aldrich, >99%) were used as received.

Microemulsion Polymerization. BlocBuilder MA (0.086 g, 0.225 mmol), Na_2CO_3 (0.060 g, 0.566 mmol), and DIW (4.0 g) were mixed and stored in the refrigerator overnight to form the ionized alkoxyamine in solution. The first stage latex was prepared with Dowfax 8390 solution (22.0 g, 11.98 mmol), methyl methacrylate (2.50 g, 25.0 mmol), styrene (0.225 g, 2.16 mmol, 8 mol % of total monomer charge), and DIW (137 g). Following a 30 min N_2 purge, the reaction mixture was immersed in a hot oil bath at 90 °C, and the ionized BlocBuilder MA solution, after also being purged under N_2 for 30 min, was injected. Following the first stage, the monomer feed of methyl methacrylate (22.0 g, 220 mmol) and

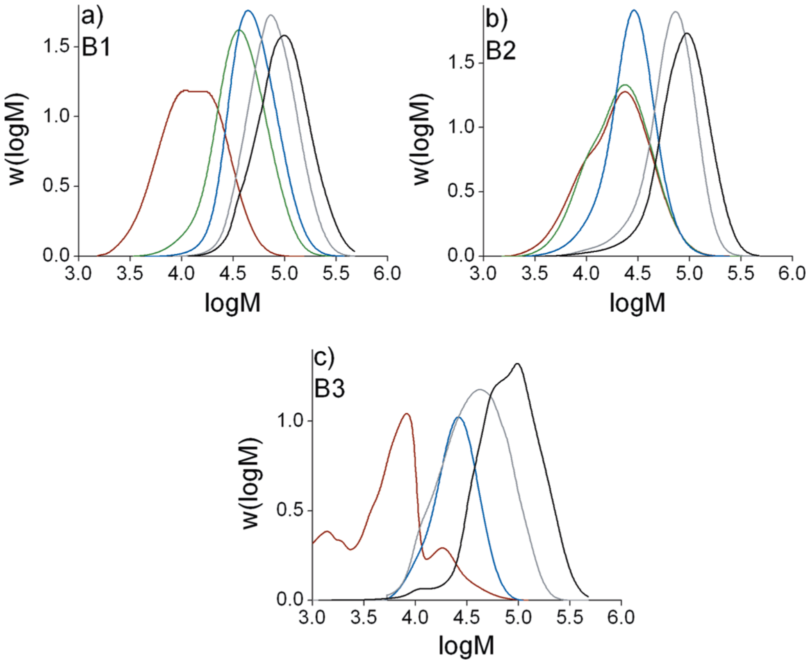

Figure 3. Molecular weight distributions for experiments B1−B3. The first stage latex had a solids content 1.5 wt % (92 mol % MMA, 8 mol % St). The first stage duration was varied: (a) 20 min (B1, MWD shown at 20 min (first stage), 80, 140, 200, 320 min); (b) 90 min (B2, MWD shown at 90 min (first stage), 150, 210, 330, 480 min); (c) 300 min (B3, MWD shown at 300 min (first stage), 420, 645, 1225 min). MWDs are normalized for area.

styrene (2.0 g, 19.23 mmol) was added over 3 h via a syringe pump. The reaction mixture, remaining under N_2, was stirred at a speed of 300 rpm and continued to react for up to 24 h with samples withdrawn periodically.

Block Extension in Microemulsion. The preparation and synthesis of the first stage latex remained identical to that described for microemulsion polymerization. Following the first stage, a monomer feed of methyl methacrylate (11.0 g, 110 mmol) and styrene (1.0 g, 9.61 mmol) was added over 1.5 h via a syringe pump. Following 2 h of polymerization, after the end of the first feed, a second monomer feed of butyl methacrylate (11.28 g, 79.4 mmol) and styrene (0.72 g, 6.92 mmol) was added over 1.5 h via a syringe pump. The reaction mixture remained under N_2 and continued to react for up to 24 h with samples withdrawn periodically.

Characterization. Monomer conversion was determined gravimetrically. Gel permeation chromatography (GPC) was used to measure molecular weight and polydispersity. The entire MWD was characterized by a GPC equipped with a Waters 2960 separation module containing four Styragel columns (HR 0.5, HR 1, HR 3, HR 4), coupled with a Waters 410 differential refractive index detector calibrated with PS standards ranging from 347 to 441 000 g mol^{-1}. The final M_n, M_w, and PDI were also determined by a Viscotek GPC (containing two Poly-Analytik SupeRes Series PAS-106 M mixed bed columns) with a differential refractive index detector calibrated with PS standards ranging from 6900 to 860 000 g mol^{-1}. In both GPCs, THF was used as the eluant with a flow rate of 1.0 mL/min. A universal calibration was used to correct the molecular weights obtained for the ratio of PS and *n*-PBMA or PMMA. The Mark−Houwink parameters for PS are $K = 1.14 \times 10^{-3}$ L g^{-1}, $a = 0.716$, for *n*-PBMA are $K = 1.48 \times 10^{-3}$ L g^{-1}, $a = 0.664$,[21] and for PMMA are $K = 7.56 \times 10^{-4}$ L g^{-1}, $a = 0.731$.[22] All of the MWD curves were measured on the Waters GPC. However, in many cases the final sample of each experiment was partially out of the calibration range of the Waters GPC, and as a result, the molecular weight averages reported in the tables are from the Viscotek GPC. The M_n, M_w, and PDI data measured on the Waters GPC are available in the Supporting Information and are in good agreement with those measured on the Viscotek GPC. (The separation efficiency of the Waters GPC is superior to the Viscotek GPC at lower M_w ranges and was used as the primary source for evaluating the evolution of the MWDs.) Particle size measurements were conducted using dynamic light scattering on a Zetasizer Nano ZS (Malvern Instruments) at a temperature of 25 °C and an angle of 173°. Samples, other than the first stage, were diluted with DIW prior to measurement.

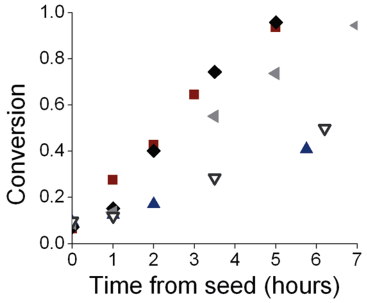

Figure 4. Conversion (at the end of the first stage) versus time profiles for experiments B1−B6 (92 mol % MMA, 8 mol % St for experiments B1−B3 and 70 mol % MMA, 30 mol % St for experiments B4−B6). Duration of first stage was varied: 20 min (■, 92 mol % MMA, 8 mol % St; ◆, 70 mol % MMA, 30 mol % St); 90 min (tilted ▲, 70 mol % MMA, 30 mol % St); or 300 min (▲, 92 mol % MMA, 8 mol % St; ▽, 70 mol % MMA, 30 mol % St).

■ RESULTS AND DISCUSSION

SG1-mediated microemulsion polymerizations were conducted with methyl methacrylate incorporating a low proportion of styrene. We used a two-step, one-pot procedure, where a first stage latex was prepared by the addition of the alkoxyamine BlocBuilder MA in its ionized form to an aqueous solution of surfactant and a small amount of monomer (<2 wt % in water; no monomer droplets were present). Following preparation of the

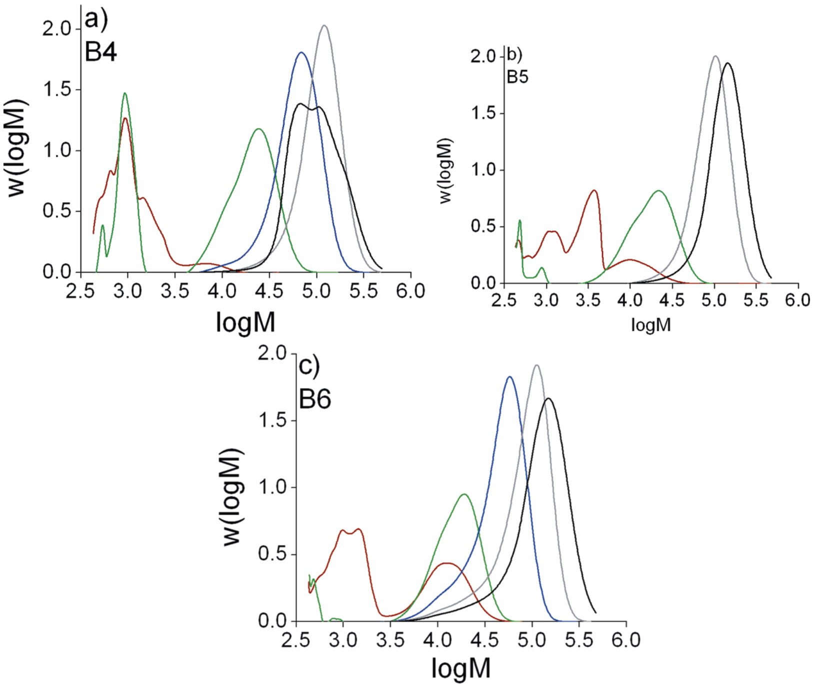

Figure 5. Molecular weight distributions for experiments B4−B6. The first stage latex had a solids content of 1.5 wt % (70 mol % MMA, 30 mol % St). Duration of first stage was varied: (a) 20 min (B4, MWD shown at 20 min (first stage), 80, 140, 230, 320 min); (b) 90 min (B5, MWD shown at 90 min (first stage), 150, 300, 510 min); (c) 300 min (B6, MWD shown at 300 min (first stage), 360, 510, 670, 1290 min). MWDs are normalized for area.

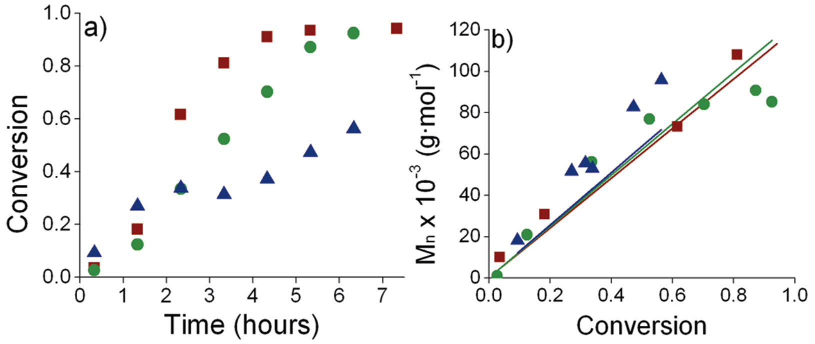

Figure 6. (a) Conversion versus time profiles and (b) the evolution of M_n and PDI with conversion for experiments C1−3. The first stage latexes had 0.75 wt % (■), 1.5 wt % (●), and 3.0 wt % (▲) solids contents (70 mol % MMA, 30 mol % St). Following a 20 min first stage, feed streams of 92.4 mol % MMA with 7.6 mol % St, 93.9 mol % with 6.1 mol % St, and 96.4 mol % MMA with 3.6 mol % St respectively were added.

first stage latex, which remained optically transparent, additional monomer was fed to continue the polymerization, and particles of approximately 20−25 nm were obtained at 17 wt % solids. A low surfactant-to-monomer ratio (0.28 w/w) was used, enabled by semibatch addition of the monomer to the small seed latex made in the first stage. The effects of varying reaction conditions were investigated, including the proportion of styrene in both the first and second (monomer feed) stages, the solids content in the first stage, the duration of the first stage, and the concentration of BlocBuilder MA used to target different molecular weights. High solids MMA-*co*-St microemulsions (up to 40 wt % solids) were made using this approach. We also synthesized (MMA-*co*-St)-*block*-(BMA-*co*-St) and (BMA-*co*-St)-*block*-(MMA-*co*-St) polymers. No excess SG1 was added to the polymerizations to ensure the polymerization conditions were in the range where β-hydrogen transfer from methacrylate-derived propagating radicals to the nitroxide was negligible.[10,11]

Evolution of the First Stage Latex. An investigation of the first stage of the microemulsion polymerization (experiments A1 and A2, Table 1) examined the effects of styrene mole fraction during the first stage (8 and 30 mol %, respectively) on the MWD evolution and conversion. The observations are important for understanding the results presented later for the complete (two-stage) experiments.

Early in the first stage, the conversion increased monotonically (Figure 2), but the entire MWD did not shift with conversion (Figure 1). Two or three distinct molecular weight peaks are evident. Both systems have a DP_n^{th} (theoretical degree of polymerization) of 120 at full conversion, but the DP of the main peak on the MWDs (Figure 1) is ∼52 for both systems over the entire course of the first stage reaction.

On the basis of the difference in concentration of styrene between the two systems, the system with more styrene (30 mol %) would statistically be expected to have a shorter DP_n than the system with less (8 mol %). The rate constant of deactivation

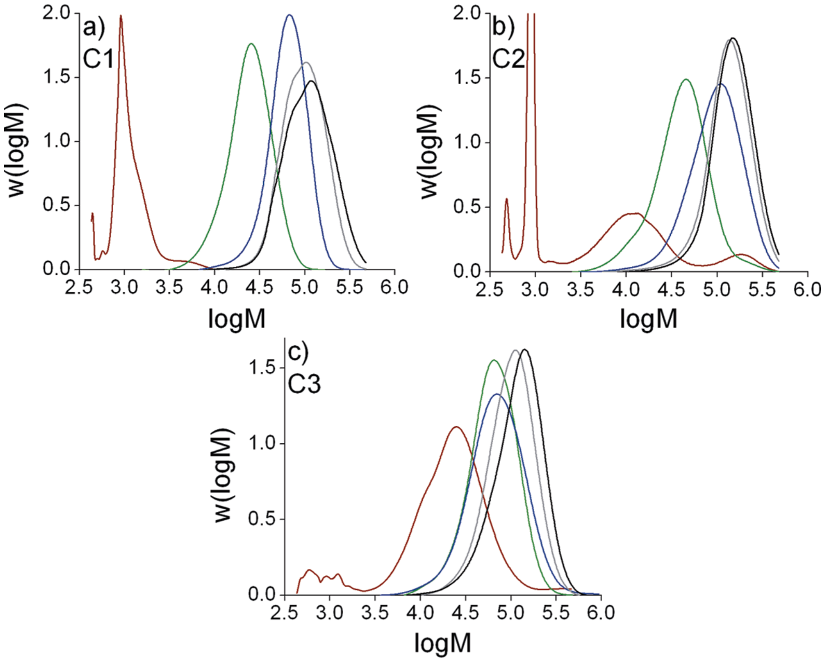

Figure 7. Molecular weight distributions for experiments C1−C3. The first stage latex had (a) 0.8 wt %, (b) 1.5 wt %, and (c) 3.2 wt % solid contents of (70 mol % MMA, 30 mol % St). Following a 20 min first stage, feed streams of (a) 92.4 mol % MMA, 7.6 mol % St (C1, MWD shown at 20 min (first stage), 140, 260, 320 min) (b) 93.9 mol % MMA, 6.1 mol % St (C2, MWD shown at 20 min (first stage), 80, 140, 260, 320 min); and (c) 96.4 mol % MMA, 3.6 mol % (C3, MWD shown at 20 min (first stage), 80, 200, 320, 380 min) were added.

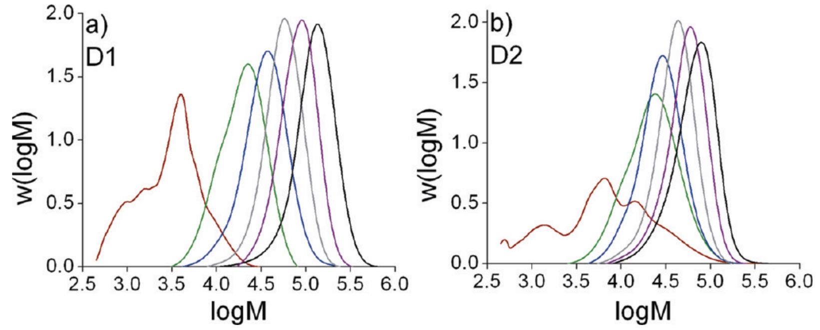

Figure 8. Molecular weight distributions for experiments D1 and D2. The first stage latex had a solids content of (a) 1.8 wt % (D1, MWD shown at 30 min (first stage), 90, 150, 240, 330, 450 min) and (b) 3.4 wt % (D2, MWD shown at 30 min (first stage), 90, 150, 240, 330, 450 min) (92 mol % MMA, 8 mol % St). Following a 20 min first stage, feed streams of 92 mol % MMA, 8 mol % were added; M_n^{th} = 65 500 g mol^{-1}.

depends only upon the terminal unit of the chain, which is higher for St (k_{deact} = 4.6 × 10^{6} L mol^{-1} s^{-1}[8]) than MMA (k_{deact} = 1.1 × 10^{6} L mol^{-1} s^{-1}[8]), and the rate coefficient of propagation is also lower for styrene (see Supporting Information). Therefore, propagating chains in systems with higher styrene content will reversibly deactivate faster, giving rise to shorter chains.

The *z*-meric length, at which water-soluble MMA-*co*-St radicals become surface active and can enter into a monomer swollen micelle or existing particle, is ∼4[23] (based on a chain with a sulfate end group).[24] When an oligomer enters a micelle/particle containing an SG1 molecule, deactivation will be nearly instantaneous (Supporting Information), which is a consequence of strong compartmentalization effects in small particles.[25] In our experiments, the MMA is added at concentrations below its aqueous saturation concentration,[24] while the St monomer is added at concentrations above saturation. As a result, a higher fraction of the St will reside inside the monomer swollen micelles compared to MMA. While the exact proportions are not known, it can be assumed that the micelles are enriched in styrene with respect to the overall composition (for both 8 and 30 mol % St), and the extent of styrene enrichment is greater for the 30 mol % St system.

Because the first stage latexes rapidly reach a DP (∼52) that significantly exceeds the *z*-meric length of ∼4, it suggests that the limiting step in deactivation is the presence of free SG1 at the locus of deactivation (micelles/particles). The polymerizations have a high target molecular weight for living polymerizations (M_n^{th} = 120 000 g mol^{-1}) and, as such, have a low concentration of BlocBuilder MA (1.60 mmol L^{-1}) and an even lower concentration of free SG1, partitioned between the monomer and aqueous phases. At the beginning of polymerization, there are an estimated 10^{21} micelles L^{-1},[26−28] but only 2 × 10^{18} SG1 molecules L^{-1} (also 2 × 10^{18} propagating chains L^{-1})[8] (Supporting Information). Most oligomers will polymerize in the aqueous phase without undergoing deactivation and continue polymerization upon entry into a micelle until an SG1 molecule also

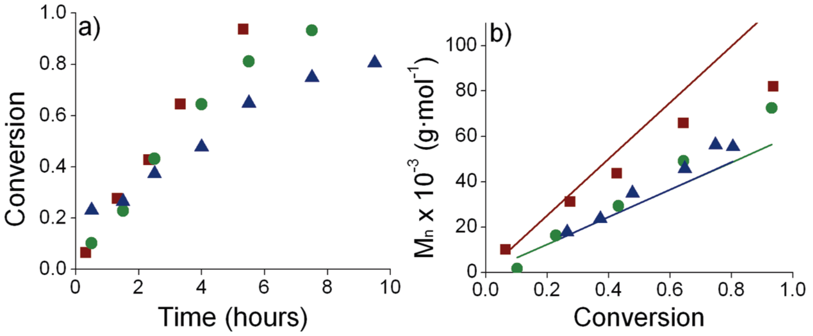

Figure 9. (a) Conversion versus time profiles and (b) the evolution of M_n with conversion for experiments B1, D1, and D2. The first stage latex had solids contents of 1.8 wt % (B1, ■; D1, ●) and 3.4 wt % (D2, ▲) (92 mol % MMA, 8 mol % St). Following a 20 min first stage, feed streams of 92 mol % MMA, 8 mol % St were added. M_n^{th} = 125 000 g mol^{-1} (B1, ■), M_n^{th} = 65 500 g mol^{-1} (D1, ●; D2, ▲).

Table 2. Microemulsion Polymerization Formulations for the MMA-*co*-St Experiments with Varying Styrene Content in the First and Second Stages, Duration of First Stage, Total Monomer Content of the First Stage, and Target Molecular Weight[a]

expt	first stage MMA:St:BB ratio (molar)	first stage reaction time (min)	first stage solids content[b] (wt %)	second stage feed MMA:St:BB ratio (molar)	surfactant/monomer (g/g)	total solids content[b] (wt %)
B1	115:10:1	20	1.8	1026:88:1	0.28	17.6
B2	111:10:1	90	1.7	997:86:1	0.28	17.2
B3	111:10:1	300	1.7	990:85:1	0.28	17.1
B4	80:32:1	20	1.6	976:86:1	0.29	17.0
B5	79:32:1	90	1.6	991:85:1	0.28	17.3
B6	80:32:1	300	1.6	1000:86:1	0.28	17.2
B7	83:31:1	90	1.7	1016:64:1	0.30	17.6
B8	80:32:1	90	1.6	1014:64:1	0.28	17.4
B9	80:32:1	300	1.6	1023:64:1	0.28	17.2
C1	43:16:1	20	0.8	1094:82:1	0.28	17.4
C2	83:31:1	20	1.7	1018:64:1	0.28	17.4
C3	179:66:1	20	3.2	986:35:1	0.28	17.5
C4	77:5:1	20	1.2	1050:90:1	0.28	17.9
C5	110:10:1	20	1.8	969:85:1	0.29	17.6
C6	222:19:1	20	3.5	865:76:1	0.29	17.1
D1	28:3:0.5	30	1.8	248:22:0.5	0.28	17.5
D2	56:5:0.5	30	3.4	221:19:0.5	0.28	17.2

[a] The alkoxyamine initiator BlocBuilder MA (BB) was added to the aqueous phase in its carboxylated form, neutralized with Na_2CO_3. The surfactant was Dowfax 8390. Polymerizations were conducted at 90 °C; the end of the first stage of polymerization occurred when the monomer feed for the second stage began at a rate of 8 mL min^{-1}. [b] Solids content refers to the loading of monomer (wt %) in the system with respect to all other components.

enters that micelle from the aqueous phase. Because deactivation is nearly instantaneous upon the entry of SG1 into a particle containing a propagating radical, the difference in styrene concentration inside the micelles/particles for the two systems plays little role in determining the DP of the first activation/deactivation cycle.

With 30 mol % styrene (A2), the conversion in the first stage latex did not exceed 62% (Figure 2). However, A1, with 8 mol % St, reached full conversion within the first hour of the experiment. With 30 mol % St in the first stage latex, subsequent reactivation of the chains following nucleation appeared minimal (no higher molecular weight peaks are observed in Figure 1c for A2). Because of an enriched styrene concentration in the monomer swollen micelles/particles, chains with terminal St−St−SG1 ends are more prevalent in the 30 mol % St system than the 8 mol % St system.[8,9]

The slow reactivation of St−St−SG1 chains in formulations with high proportions of styrene has been discussed in depth by Nicolas et al.[8] and Wang and Broadbelt.[9] In the 8 mol % St first stage latex, it is probable that the majority of the chain ends have the structure MMA−St−SG1.[7] Further reactivation of these chains is observed in our experiments, with the first stage reaching nearly full conversion within 1 h (Figure 2), accompanied by the appearance of a higher molecular weight peak in the MWD (Figure 1a,c).

Although a low concentration of styrene in an MMA polymerization is generally recommended for most NMP systems to maintain a reasonable polymerization rate,[8] in the first stage a higher concentration of styrene is advantageous. When subsequent activation and propagation cycles are suppressed in the first stage (with 30 mol % rather than 8 mol % St), a narrower distribution results in the first stage. This leads to lower PDIs throughout the rest of the polymerization (discussed below), although there appears to be little difference in the polymer livingness of the two systems.

Duration of the First Stage Polymerization. The role of the duration of the first stage was investigated for systems with 8 and 30 mol % St in the first stage (8 mol % St in the second (feed) stage), for durations of 20, 90, and 300 min (experiments B1−B6

Table 3. Microemulsion Polymerization Results for MMA-*co*-St Experiments

expt	reaction time (h)	conversion (%)	M_n^{th} (g mol^{-1})	M_n[a] (g mol^{-1})	M_w[a] (g mol^{-1})	PDI[a] (MWD)	z_{avg} particle size (nm)	particle size distribution PDI
B1	5.3	93.7	116 800	89 040	136 200	1.53	23.6	0.031
B2	8.0	59.8	72 620	54 950	85 870	1.56	23.8	0.057
B3	20.4	77.1	92 820	65 280	99 100	1.52	26.3	0.062
B4	5.3	95.8	113 200	141 300	197 200	1.40	21.9	0.078
B5	8.5	94.4	113 000	146 700	216 500	1.48	21.9	0.061
B6	21.5	71.0	85 840	96 100	160 300	1.67	21.2	0.082
B7	5.0	93.9	112 800	69 290	106 800	1.54	20.6	0.069
B8	8.5	91.0	108 900	131 300	205 600	1.57	22.5	0.098
B9	21.5	81.0	97 880	128 200	184 800	1.44	23.2	0.055
C1	6.3	92.5	115 000	122 700	174 800	1.43	19.8	0.066
C2	4.3	89.4	109 600	99 300	152 200	1.53	20.2	0.071
C3	6.3	56.3	71 890	111 300	167 000	1.50	19.3 + droplets	0.150
C4	7.3	91.6	112 700	101 400	161 900	1.60	34.0	0.029
C5	7.3	89.8	106 200	138 400	206 300	1.49	26.7	0.044
C6	12.9	86.6	103 000	144 300	230 900	1.60	23.4	0.069
D1	7.5	93.2	56 400	84 520	115 600	1.37	36.8	0.025
D2	9.5	80.5	48 860	72 760	116 300	1.60	24.2	0.068

[a] Measured on the Viscotek GPC.

respectively, Table 1). In experiments with 8 mol % St in the first stage, broader MWDs were observed for longer first stage durations (Figure 3). As discussed earlier, the conversion of the first stage leveled out within 1 h, and continuing the first stage past this time resulted in increased termination, a decrease in fraction of living chains, and an accumulation of free SG1. This slowed the rate of polymerization (Figure 4) and caused a broadening of the MWD (Figure 3). Particularly worth noting is the extensive tailing in the last MWD for B3 with a first stage (92 mol % MMA, 8 mol % St) duration of 300 min (Figure 3c); the low-molecular-weight tail resulted from significant termination during the first stage and early in the second stage and remains evident in the GPC trace even up to 77% conversion.

When the first stage duration is 20 min, the final MWD is narrower for the system with 30 mol % St in the first stage (B4) (Figure 5) compared to the system with only 8 mol % St (B1) (Figure 3). However, this difference does not appear to be the result of more termination in the system with 8 mol % St since both systems had similar rates of polymerization (Figure 4). (Irreversible termination leads to the accumulation of free SG1 in the system, which inhibits the polymerization.) Instead, the broadness of the MWD with 8 mol % St in the first stage (B1) is likely due to the broader distribution made during the first stage. This leads to larger PDIs throughout the remainder of the polymerization, but not a loss of livingness in the system.

Solids Content in the First Stage. We also conducted a series of experiments targeting 8 mol % St overall in the system while varying the solids content (i.e., total monomer concentration) in the first stage. Experiments were done with 30 mol % St in the first stage. Experiments C1−C3 had first stage solids contents of 0.75, 1.5, or 3.0 wt %, respectively. During the feed stage, the proportions of styrene were varied to achieve an overall proportion of 8 mol % styrene in the final product. The corresponding styrene proportions in the feed were 7.2, 6.1, and 3.6 mol % for C1−C3, respectively.

The MWD of the first stage latexes became broader and of higher molecular weight as the solids content in the first stage was increased (Figure 7) as the chains underwent multiple activation, propagation, and deactivation cycles. There were also monomer droplets present in the experiment with a first stage solids content of 3.0 wt % (C3) as the first stage latex was not transparent prior to the addition of the BlocBuilder MA solution. The rates of polymerization (Figure 6) early in the second (feed) stage were faster when there was a lower mole fraction of styrene in the system, with C3 being the fastest and C1 the slowest. However, as the polymerization continued, C3 slowed considerably due to irreversible termination as there was not enough styrene to effectively mediate the polymerization. An increased rate of termination from the outset in C3 was also evidenced by a higher than theoretical M_n observed throughout most of the polymerization (Figure 6b).

Effect of Initiator Concentration and Target Molecular Weight. Most experiments discussed here have a target theoretical M_n of 120 000 g mol^{-1}, but two experiments (D1 and D2) were done targeting a lower M_n (65 000 g mol^{-1}). The experiments had the same polymer content (17 wt %) and 8 mol % St in the first and second stages as experiment B1, but containing higher concentrations of BlocBuilder MA. The first stage of D1 had a solids content of 1.8 wt % (similar to previous experiments), with $DP_n^{th} = 60$ at the end of the first stage. The solids content of the first stage of D2 was 3.4 wt %, to match the $DP_n^{th} = 120$ of previous experiments. D2 showed significant tailing in the MWD (Figure 8b), indicating significant irreversible termination occurred during the polymerization. Also, this experiment had a slower rate of polymerization (final conversion of D2 = 80.5% in 9.5 h) and did not reach the same high conversion as D1 (final conversion = 93.2% in 7.5 h) (Figure 9a), suggesting there was significant SG1 accumulation. Both experiments produced a higher than theoretical M_n (indicating fewer chains than expected were initiated), a result of termination early in the polymerization (Figure 9b). In fact, the rate of polymerization for D1 was slower than that of B1 (final conversion = 93.7% in 5.3 h), even though D1 possessed double the number of chains, and would be expected to polymerize more quickly. This suggests that in both

Table 4. Formulations and Results for High Solids Microemulsion Latexes of MMA with a Small Proportion of Styrene

expt	first stage MMA:St:BB ratio (molar)	first stage duration (min)	first stage solids content[a] (wt %)	second stage feed MMA:St:BB ratio (molar)	surfactant/ monomer (g/g)	complete reaction time (h)	conversion (%)	final solids content[a] (wt %)	theoretical M_n (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	PDI[b]	Z_{avg} particle size (nm)	particle size distribution PDI	no. of chains/ particle[c]
E1	81:31:1	30	1.7	2158:179:1	0.14	22.2	95.6	36.7	235 300	166 600	303 000	1.82	27.40	0.081	14.9
E2	110:10:1	30	1.7	2202:187:1	0.13	10.7	83.5	36.6	210 600	221 600	369 600	1.67	29.05	0.064	19.1
E3	41:18:1	22	1.8	117:102:1	0.13	13.3	93.9	39.3	126 200	152 400	241 900	1.59	33.01	0.041	54.4
E4	82:36:1	22	3.2	1132:99:1	0.19	13.3	89.0	37.2	121 000	152 500	217 000	1.42	40.44	0.050	97.7

[a] Solids content refers to the loading of monomer in the system with respect to the other components. [b] Measured on the Viscotek GPC. [c] Calculated based on the volume average particle size, details are available in the Supporting Information.

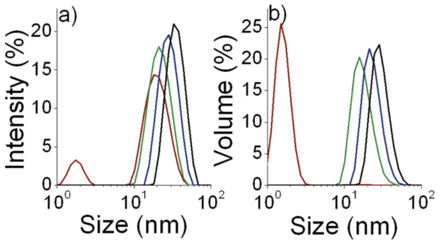

Figure 10. Particle size distribution for high solids (40 wt %) MMA-*co*-St microemulsion polymerization (E3). PSD (Malvern Nanosizer) is shown for both the (a) intensity PSD and (b) volume PSD. Samples shown are obtained at 20 min (end of the first stage), 100, 170, and 735 min. PSDs are normalized for area.

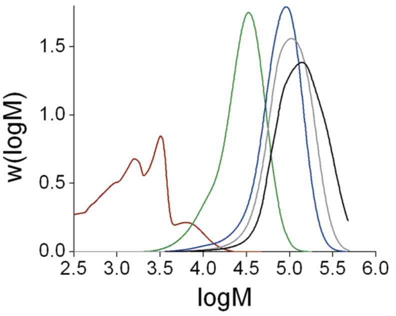

Figure 11. Molecular weight distributions for experiments E3. The first stage latex had a solids content of 1.8 wt % (70 mol % MMA; 30 mol % St). Following a 20 min first stage, a feed stream of 92 mol % MMA with 8 mol % St was added; M_n^{th} = 134 000 g mol^{-1}, theoretical solids content = 40 wt %. The MWD is shown at 20 min (first stage), 100, 170, 285, and 735 min.

experiments with a target M_n of 60 500 g mol^{-1} there was more irreversible termination than in those experiments with a 120 000 g mol^{-1} target M_n.

The final particle sizes for the systems with a target M_n of 65 500 g mol^{-1} were larger (37 nm for D1, Table 2) than those with a 120 000 g mol^{-1} target M_n (22 nm for B1, Table 2), although the experiments had identical monomer and surfactant concentrations. This is contrary to the expected behavior for a traditional emulsion polymerization where increases in surfactant concentration and ionic end groups aid in the stabilization of particles, leading to a higher number of particles in the system.[24] However, this trend is often observed experimentally in our laboratory with NMP and in other reports for different living chemistries in emulsion-based systems[29,30] and is possibly due to superswelling.[31] The thermodynamic basis of the superswelling theory was first presented by Luo et al.[32] for NMP miniemulsion polymerization. The large concentration of oligomers present in the particles early in the polymerization lowers the chemical potential of the nucleated particles compared to droplets or monomer-swollen micelles. This promotes monomer diffusion to the newly nucleated particles and can lead to very broad particle size distributions or colloidal instability.

At higher conversions, the M_n measured by GPC was often lower than that predicted theoretically for experiments conducted with a target M_n of 120 000 g mol^{-1} (Figure 9b). This phenomenon has been studied in styrene TEMPO-mediated systems, where the high temperatures required lead to a significant population of thermally generated radicals, but chain transfer to monomer has also been identified as a possible

Table 5. Microemulsion Formulation and Polymerization Results for the Synthesis of MMA-*co*-St-*block*-BMA-*co*-St and BMA-*co*-St-*block*-MMA-*co*-St Block Copolymers

	experiment	MMA-*co*-St-*block*-BMA-*co*-St (F1)	BMA-*co*-St-*block*-MMA-*co*-St (F2)
first block	first stage *x*MA:St:BB	79:31:1	45:19:1
	second stage (feed 1) *x*MA:St:BB	485:31:1	300:29:1
	time (h)	2.5	2.5
	conversion (%)	86.8	81.3
	M_n (g mol^{-1})[b]	50 340	40 950
	PDI[b]	1.55	1.45
second block	final solids content[a] (%)	18.2	17.6
	third stage (feed 2) *x*MA:St:BB ratio	356:41:1	390:35:1
	time (h)	11.5	7.5
	conversion (%)	90.4	84.8
	M_n (g mol^{-1})[b]	80 150	65 660
	PDI[b]	1.63	1.57
	particle size intensity (nm)	26.3 (98%) + droplets	4.9 (52%), 64.5 (45%) + droplets
	particle size volume (nm)	16.4	4.1 (99.9%), 48.3 (0.1%)
	particle size distribution PDI	0.26	0.39

[a] Solids content refers to the loading of monomer (wt %) in the system with respect to the other components. [b] Measured on the Waters GPC.

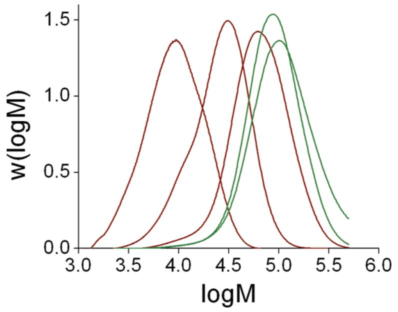

Figure 12. Molecular weight distributions for experiment F1, (MMA-*co*-St)-*block*-(BMA-*co*-St) copolymerization. Following a 20 min first stage, the first monomer feed was added (92 mol % MMA; 8 mol % St); M_n^{th} = 63 000 g mol^{-1}. 2.5 h later, a second feed stream (92 mol % BMA; 8 mol % St) was added. The MWD for the MMA-*co*-St block (red line, shown at 30 min (first stage), 90, 240 min) and the BMA-*co*-St block (green line, shown at 330, 690 min) are included in the plot.

cause.[33−35] This behavior has also been observed in butyl acrylate polymerizations where backbiting can lead to similar observations.[36] However, in these MMA-*co*-St systems, backbiting and thermal initiation are not considered to be significant factors. We believe that lower than theoretical M_n obtained when targeting high molecular weights may be due to chain transfer to monomer, which does not lead to an accumulation of SG1 but does create shorter, but still growing, chains. The chain transfer coefficient of MMA ($C_M = 2.3 \times 10^{-5}$ [37]) is sufficiently large to suggest this mechanism is likely to influence the molecular weight when such a low concentration of BlocBuilder MA is added to the system.

High Solids Microemulsion Polymerization. It is usually very difficult to achieve high solids contents with microemulsion polymerization because of the large quantity of surfactant required to stabilize the particles and the high viscosity associated with latexes of small particle sizes. The early success of our microemulsions at 17 wt % solids lead us to investigate the preparation of high solids, high molecular weight latexes using a similar approach.

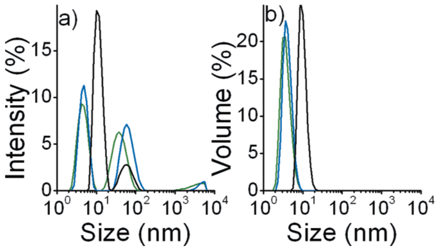

Figure 13. Particle size distribution for (BMA-*co*-St)-*block*-(MMA-*co*-St) block copolymer microemulsion polymerization (F2). Both the (a) intensity PSD and (b) volume PSD are shown. Particle sizes are shown at 30 min after the first stage (green line), 120 min, following the BMA/St feed (blue line), and 660 min, following the MMA/St feed (black line). PSDs are normalized for area.

All of the microemulsion latexes with 40% polymer content (Table 4) were optically translucent with a bluish tinge and were free-flowing. A monomodal particle size distribution evolution over the course of the polymerization was observed (Figure 10). The MWD shifted with conversion, indicative of a well-controlled and living system (Figure 11). Only very small amounts of coagulum were observed for these polymerizations.

When the M_n^{th} was reduced from 252 000 g mol^{-1} (E2) to 134 000 g mol^{-1} (E3), by the addition of more BlocBuilder MA in the first stage (all other factors remaining constant), it was again observed that the particle size increased from 29 to 33 nm (Table 4), despite the addition of more stabilizing groups to the system. However, a greater increase in particle size was observed when the monomer content in the first stage was doubled, coupled with a 1.5× increase in the surfactant concentration (E4), to target the same DP_n^{th} of 120 in the first stage as E2. The increased particle size with increased monomer concentration and initiator concentration in the nucleation stage firmly suggest that superswelling is playing a role in enhancing the diffusion of monomer to the swollen nucleated particles.

Synthesis of Block Copolymers in Microemulsion. The synthesis of (MMA-*co*-St)-*block*-(BMA-*co*-St) polymers was demonstrated in microemulsion with a first stage duration of

Figure 14. Selected microemulsion latexes: 17% solids with either 8 and 30 mol % St in the first stage (B1 and B4, respectively) (MMA-*co*-St)-*block*-(BMA-*co*-St) latex (F1), (BMA-*co*-St)-*block*-(MMA-*co*-St) latex (F2), and 40 wt % solids latexes (E1, E3, and E4).

20 min and 30% St present in the first stage (Table 5). Chain extension upon the addition of the BMA/St feed showed clear shifting of the entire MWD (Figure 12), indicating excellent livingness was obtained in the first block. The particle sizes were ∼26 nm at 90% conversion, and the particle size distribution remained monomodal through the polymerization.

Block copolymers were also made beginning with a BMA-*co*-St first stage, and BMA-*co*-St second stage feed (both with 8 mol % St), and then chain extended by MMA (with 8 mol % St) (Table 5). Although this system was easily chain extended, as demonstrated by the shifting of the full MWD to higher molecular weights, the particle size distribution in the first BMA/St stage was bimodal and remained so following the addition of the MMA/St feed (Figure 13). The fraction of larger particles was quite small and evident only in the intensity distribution. Despite repeated attempts, we were unable to avoid this bimodality when BMA was used in the first stage. BMA's much lower water solubility (compared to MMA) ensures monomer droplets were unavoidably present in the first stage. Multiple nucleation mechanisms (both aggregative and micellar) are believed to be the cause of the bimodal PSDs in the BMA-*co*-St first stage latex.[23]

CONCLUSIONS

Well-controlled SG1-mediated microemulsion polymerizations yielded MMA-*co*-St latexes with small particle sizes (<30 nm), monomodal PSDs, solids content up to 40%, and high molecular weights (>100 kg mol^{-1}). Narrower MWDs were obtained when 30 mol % St was used in the first stage compared to 8 mol %. A shorter first stage is preferable because nucleation is complete within 1 h. Leaving the first stage longer than 1 h results in irreversible termination and the accumulation of SG1, which further slows polymerization. The MWD of the final latex was broader when a lower St fraction was used in the first stage. This is not the result of increased irreversible termination, but rather the result of a broader MWD created during the first stage. While the MWD is broader with lower St fractions in the first stage, the livingness of the polymer chains is not noticeably affected.

Regardless of the concentration of styrene present in the first stage, 8 mol % St in the second (monomer feed) stage provided excellent control over the MWD. Lower styrene concentration in the feed resulted in faster polymerization rates initially, but the accumulation of SG1 due to irreversible termination ultimately suppressed the polymerization rate.

Increasing initiator concentration (decreasing target M_n) yields larger particles, which is contrary to the expected behavior of conventional emulsion polymerization when the concentration of stabilizing groups is increased. Increasing the monomer content during the first stage also leads to increased particle sizes, even in the presence of higher concentrations of surfactant. Both of these phenomena are believed to be the result of superswelling during the nucleation stage, where high concentrations of oligomers result in enhanced monomer swelling of the particles.

Microemulsion polymerizations with solids content ∼40% can be achieved with small particle sizes (30−40 nm), low surfactant-to-monomer ratios (0.13:1−0.19:1 w/w), fast reaction rates, and high molecular weights (100−200 kg mol^{-1}). The MMA-*co*-St microemulsion latexes can be readily chain extended with BMA-*co*-St to make block copolymers. However, beginning with BMA-*co*-St in the first stage (rather than MMA-*co*-St) results in bimodal particle size distributions.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Estimation of the theoretical degree of polymerization of the first activation/deactivation step, the estimation of the concentration of micelles present at the start of the polymerization, the estimation of the average number of chains per particle, and the molecular weight information determined on the Waters GPC. This material is available free of charge via the Internet at http://pubs.acs.org.

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