DOI: 10.1021/ma1012286

Macromolecules
ARTICLE

Nitroxide-Mediated Surfactant-Free Emulsion Polymerization of *n*-Butyl Methacrylate with a Small Amount of Styrene

Mary E. Thomson,[†] Anna-Marie Manley,[†] Jason S. Ness,[‡] Scott C. Schmidt,[‡] and Michael F. Cunningham*,[†]

[†]*Department of Chemical Engineering, Queen's University, Kingston, ON, Canada K7L 3N6, and* [‡]*Arkema Group, King of Prussia, Pennsylvania 19406-1308*

Received June 1, 2010; Revised Manuscript Received August 13, 2010

ABSTRACT: Nitroxide-mediated emulsion polymerization of *n*-butyl methacrylate (BMA) can produce highly living and well-controlled polymer chains when polymerized in the presence of 10 mol % styrene (St) using a one-pot, differential monomer addition technique. When *n*-BMA-*co*-St is polymerized in the presence of a surfactant above the critical micelle concentration, bimodal particle size distributions are obtained, likely as a result of combined micellar and aggregative nucleation mechanisms. This phenomenon is not observed for the more hydrophilic monomer system of methyl methacrylate and styrene. In the absence of surfactant, however, it is possible to prepare stable, monomodal latexes. Using *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1), we report the first nitroxide-mediated polymerization of *n*-butyl methacrylate with a small amount of styrene in a facile surfactant-free emulsion polymerization system. The surfactant-free system requires no separate macroinitiator synthesis step and produces highly living polymers with monomodal particle size distributions. The initiator efficiency can be increased by the addition of methyl acrylate or by the addition of surfactant at concentrations below the critical micelle concentration in the absence of methyl acrylate.

Introduction

Controlled/living polymerization has emerged as a versatile and elegant method of creating polymers with tailored molecular architectures, including block copolymers and polymers with very narrow molecular weight distributions, under mild reaction conditions. Conducting these polymerizations in an emulsion polymerization system is highly desirable if these products are to be produced at an industrial scale.[1,2] Early attempts to conduct nitroxide-mediated *ab initio* emulsion polymerization resulted in severe coagulation formation,[3,4] but a two-step emulsion polymerization procedure[5−7] introduced by Charleux's group using the commercially available alkoxyamine initiator BlocBuilder from Arkema, based on the nitroxide SG1 (*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide), yields a coagulum-free latex. BlocBuilder is water-soluble in its carboxylated form when neutralized with a base. In the first step, a small amount of monomer is added to the aqueous phase along with surfactant and the alkoxyamine initiator in its ionized form to create first stage particles in the absence of monomer droplets. Following this, the remainder of the monomer can be added in a batch or semibatch process.

While nitroxide-mediated polymerization (NMP) has proved successful for styrenics and acrylates, polymerization of methacrylate monomers has, until recently, remained elusive due to their very high activation/deactivation equilibrium constant for reversible termination (K_{eq}). This causes a large quantity of irreversible termination to occur early on in the polymerization, leading to nitroxide accumulation, suppressing further polymerization. In systems with large excess of SG1 (>40 mol %), β-hydrogen transfer from the PMMA radical to the nitroxide can also become a significant chain ending event.[8,9] It has been shown that methyl methacrylate (MMA) can be polymerized in a controlled manner, using SG1, through the addition of 4.4−8.8 mol % styrene (St), which decreases the equilibrium constant[10] and results in the majority of the dormant chains possessing the structure MMA−St−SG1.[11] The monomer *n*-butyl methacrylate (BMA) has also been demonstrated to polymerize in solution in a controlled manner in the presence of < 10 mol % styrene and an additional 10 mol % SG1 with respect to BlocBuilder. It was also noted that the lengthening of the alkyl tail of the monomer, BMA vs MMA, leads to a lower degree of control as the rate constant of propagation increases.[12]

Surfactant-free SG1-mediated emulsion polymerization has been reported for styrene using a bicomponent initiation system (thermal decomposition of a water-soluble initiator, potassium persulfate, in the presence of free SG1) in a two-step emulsion procedure.[13] The polymerization exhibited long induction periods prior to polymerization as a result of the reversible termination of SG1-capped styrene oligomers in the aqueous phase prior to nucleation coupled with broad particle size distributions but did produce living polymer chains capable of being extended.

A surfactant-free emulsion polymerization of MMA with 4 mol % St was successfully conducted by first synthesizing an amphiphilic poly(methacrylic acid-*co*-styrene)−SG1 macroinitiator in a 1,4-dioxane solution.[14] Following purification, the macroinitiator was used as both a surfactant-like species and alkoxyamine initiator for the polymerization of MMA-*co*-St, which was added in a single shot. This procedure resulted in a well-controlled polymerization with high initiation efficiency but produced bimodal particle distributions containing a small fraction of aggregates that were attributed to the presence of styrene at the outer surface of the particles. Monomodal PSDs are desirable if the latex is to be used for film forming applications, especially if specialized morphologies, such as core shell particles, are to be created. Herein we report the first nitroxide-mediated

*Corresponding author. E-mail: michael.cunningham@chee.queensu.ca.

 Published on Web 09/14/2010

polymerizations of *n*-butyl methacrylate with a small amount of styrene in a facile surfactant-free emulsion polymerization system, using the nitroxide SG1. Through the addition of the hydrophilic, fast propagating monomer methyl acrylate in the first stage, termination during the nucleation stage is suppressed. The surfactant-free system requires no separate macroinitiator synthesis step and produces highly living polymers with monomodal particle size distributions.

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-((*tert*-butyl-(1-(diethoxyphosphoryl)-2,2-dimethylpropyl)amino)oxy)-2-methylpropanoic acid (BlocBuilder, supplied by Arkema, 99%), *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, supplied by Arkema, 89%), methyl acrylate (MA, Aldrich, 99%), Dowfax 8390 (Dow Chemicals, 35 wt % solution in water), sodium dodecyl sulfate (SDS, Aldrich, >99%), sodium formaldehyde sulfoxylate (SFS, Aldrich, >98%), and sodium carbonate (Na_2CO_3, Aldrich, >99%) were used as received.

Emulsion Polymerization. BlocBuilder (0.15 g, 0.392 mmol), Na_2CO_3 (0.037 g, 0.350 mmol), and deionized water (DIW, 4.0 g) were mixed and stored in a refrigerator overnight to form the ionized alkoxyamine initiator in solution. The first stage latex was prepared with a 35 wt % Dowfax 8390 solution (2.0 g of solution, 1.1 mmol), butyl methacrylate (1.12 g, 7.89 mmol), styrene (0.35 g, 3.37 mmol, 30 mol % of monomer charge), and DIW (146 g). Following a 30 min N_2 purge, the reaction mixture was immersed in a hot oil bath at 90 °C, and the similarly purged ionized BlocBuilder solution was injected. Following the first stage (20 min), the monomer feed of butyl methacrylate (11.79 g, 83.03 mmol) and styrene (0.96 g, 9.23 mmol, 10 mol % of the second monomer charge) 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. The average targeted molecular weight (M_n) of these experiments is 36 700 g mol^{-1}.

Surfactant-Free Emulsion Polymerization. BlocBuilder (0.15 g, 0.392 mmol), Na_2CO_3 (0.037 g, 0.350 mmol), and DIW (4.0 g) were mixed and stored in a refrigerator overnight to form the ionized alkoxyamine initiator in solution. The first stage latex was prepared with methyl acrylate (0.101 g, 1.18 mmol), butyl methacrylate (1.12 g, 7.89 mmol), styrene (0.35 g, 3.37 mmol, 30 mol % of the monomer charge), and DIW (146 g). Following a 30 min N_2 purge, the reaction mixture was immersed in a hot oil bath at 90 °C and stirred at 600 rpm, and the similarly purged ionized BlocBuilder solution was injected. Following the first stage (20 min) the stirring was slowed to 300 rpm, and the monomer feed of butyl methacrylate (11.79 g, 83.03 mmol) and styrene (0.96 g, 9.23 mmol, 10 mol % of the second monomer charge) was added over 3 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. When SG1 or SFS was also used, the SG1 (0.0083 g, 0.030 mmol) was added in combination with the first stage latex, while SFS (0.0036 g, 0.030 mmol) was dissolved in DIW and added at the end of the first stage prior to the beginning of the monomer feed. The average targeted molecular weight (M_n) of these experiments is 36 700 g mol^{-1}.

Emulsion Polymerization of MMA. MMA-*co*-St emulsion polymerization in both the presence and absence of surfactant was conducted in a similar manner to the procedures listed above for BMA-*co*-St, but MMA was substituted for BMA on a mass basis. This substitution leads to 7 mol % St with respect to MMA, which is within the studied range of control of MMA by St for NMP.[10] The average targeted molecular weight (M_n) of these experiments is 36 700 g mol^{-1}.

Characterization. Monomer conversion was determined gravimetrically. Gel permeation chromatography (GPC) was used to measure the molecular weight and polydispersity (PDI) of the polymer samples. The GPC was 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 standards ranging from 347 to 441 000 g mol^{-1}. THF was used as the eluent with a flow rate of 1.0 mL min^{-1}. 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 $k = 1.14 \times 10^{-5}$ L g^{-1}, $a = 0.716$, for *n*-PBMA are $k = 1.48 \times 10^{-5}$ L g^{-1}, $a = 0.664$,[15] and for PMMA are $k = 9.44 \times 10^{-6}$ L g^{-1}, $a = 0.719$.[16] Particle size measurements were done by dynamic light scattering on a Zetasizer Nano ZS from 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. Initiator efficiency is calculated from the deviation of the measured M_n from the theoretical M_n by initiator efficiency = M_n^{th}/M_n^{exp}.

Results and Discussion

In this work, nitroxide-mediated emulsion polymerization of *n*-BMA incorporating a small amount of styrene was conducted in both the presence and absence of surfactant. As NMP of methacrylates with SG1 is complicated by the high K_{eq} of the tertiary carbon chain ends, Charleux found that MMA polymerization could be mediated by the addition of a low proportion of styrene (4.4−8.8 mol %).[10,11] This same principle has been successfully applied in this study with another methacrylate, the more hydrophobic *n*-BMA, without the addition of excess SG1. β-Hydrogen transfer from methacrylate-derived propagating radicals to the nitroxide can be a major chain ending event when there is a large excess of SG1 present in the system (>40 mol % excess).[8,9] The polymerizations described here are conducted in the absence of additional SG1 and styrene is used to lower the instances of bimolecular termination between the chains, which also minimizes the accumulation of SG1. As a result, these polymerizations operate in a range where β-hydrogen transfer is minimal. These *n*-BMA polymerizations were conducted in a two-stage manner where a first stage latex was first prepared by the addition of the ionized alkoxyamine initiator, BlocBuilder, to an aqueous solution of surfactant (if used) and a small amount of monomer. Following the formation of the first stage latex, which remained optically transparent in the systems with surfactant and turned opaque white for the surfactant-free systems, an additional feed of BMA with 10 mol % styrene continued the polymerization. The emulsion polymerizations conducted with surfactant present above the cmc (critical micelle concentration) resulted in bimodal particle size distributions (PSD) while those conducted in the absence of surfactant micelles resulted in monomodal particle size distributions. Both systems yield highly living polymers. This surfactant-free nitroxide-mediated emulsion polymerization is the first reported system for a methacrylate monomer that does not require prior synthesis of an amphiphilic alkoxyamine and can be conducted directly from commercially available materials. The formulations and polymerization results of this study are available in Tables 1 and 2, respectively.

Emulsion Polymerization in the Presence of Surfactant above the CMC. Two-stage emulsion polymerization of MMA with 7% styrene (E1) produced well-controlled chains with a PDI below 1.33 and a monomodal particle size distribution (PSD). However, in a similar formulation with BMA and a 10% styrene (E2), while the polymerization was living as demonstrated by the growth of the entire molecular weight distribution (MWD) (please see the Supporting Information for the MWDs) over the course of the polymerization, the PSD was bimodal (Figure 1a).

Table 1. Formulations for the Two-Stage SG1-Mediated Emulsion and Surfactant-Free Emulsion Polymerizations of *n*-Butyl Methacrylate (BMA) and Methy Methacrylate (MMA) with 10 mol % Styrene (St)[a]

expt	surfactant concentration (mmol L^{-1})	first stage formulation ratios (molar) BMA:St:MA:BB: SG1:SFS	second stage (monomer feed) formulation ratios (molar) BMA:St	total solids (%)
E1	7.78[b]	28.5[d]:8.8:0:1:0:0	299[d]:23.8	9.1
E2	7.78[b]	20.6:8.9:0:1:0:0	216:24.2	8.5
E3	0	20.1:8.8:0:1.0:0:0	106:12.0	5.0
E4	0	20.2:8.6:3.2:1:0:0	214:23.8	8.7
E5	0	20.4:8.8:3.2:1.0:0:0	212:23.6	8.6
E6	0	20.2:8.6:3.0:1.0:0.1:0	211:23.7	8.7
E7	0	20.4:2.4:3.0:1:0.2:0.2	229:24.0	8.9
E8	5.14[c]	20.2:8.8:0:1:0:0	211:26.7	9.3

[a] The alkoxyamine initiator Blocbuilder (BB) was added to the aqueous phase in its carboxylated form, neutralized with the weak base Na_2CO_3. Methyl acrylate (MA), excess SG1 nitroxide, and the reducing agent sodium formaldehyde sulfoxylate (SFS) were also used in some of the experiments. [b] Surfactant is Dowfax 8390, present in concentrations above the cmc. [c] Surfactant is SDS, present in concentrations below the cmc. [d] MMA is used rather than BMA.

Table 2. Polymerization Results for the Two-Stage SG1-Mediated Emulsion and Surfactant-Free Emulsion Polymerizations of BMA and MMA with 10 mol % Styrene

expt	pH (first stage)	conv (%)	time (h)	pH (end)	$M_{n,th}$	$M_{n,exp}$	PDI	initiator eff (%)	PS (diameter) (intensity)	PS (diameter) (volume)	PDI (PSD)
E1	7.91	64.5	11.4	5.35	23 000	30 200	1.33	78.0	469	49	0.116
E2	8.40	38.3	23.1	5.18	14 500	20 800	1.35	69.8	432 (61%), 77 (39%)	451 (39%), 71 (61%)	0.542
E3		30.0	22.0		6 000	11 000	1.55	54.5	233	246	0.094
E4	8.39	67.5	23.1	6.22	25 100	38 400	1.48	65.2	237	246	0.036
E5		49.1	22.0		18 400	26 500	1.52	69.5	236	246	0.066
E6		36.4	22.0		13 683	16 184	1.53	84.5	595 (59%), 217 (41%)	576 (76%), 212 (24%)	0.274
E7	8.28	57.0	23.0	6.29	22 256	34 713	1.92	64.1	487	501	0.081
E8	8.09	50.0	11.2	7.14	18 464	30 179	1.61	61.2	408 (74%), 120 (26%)	439 (73%), 107 (27%)	0.325

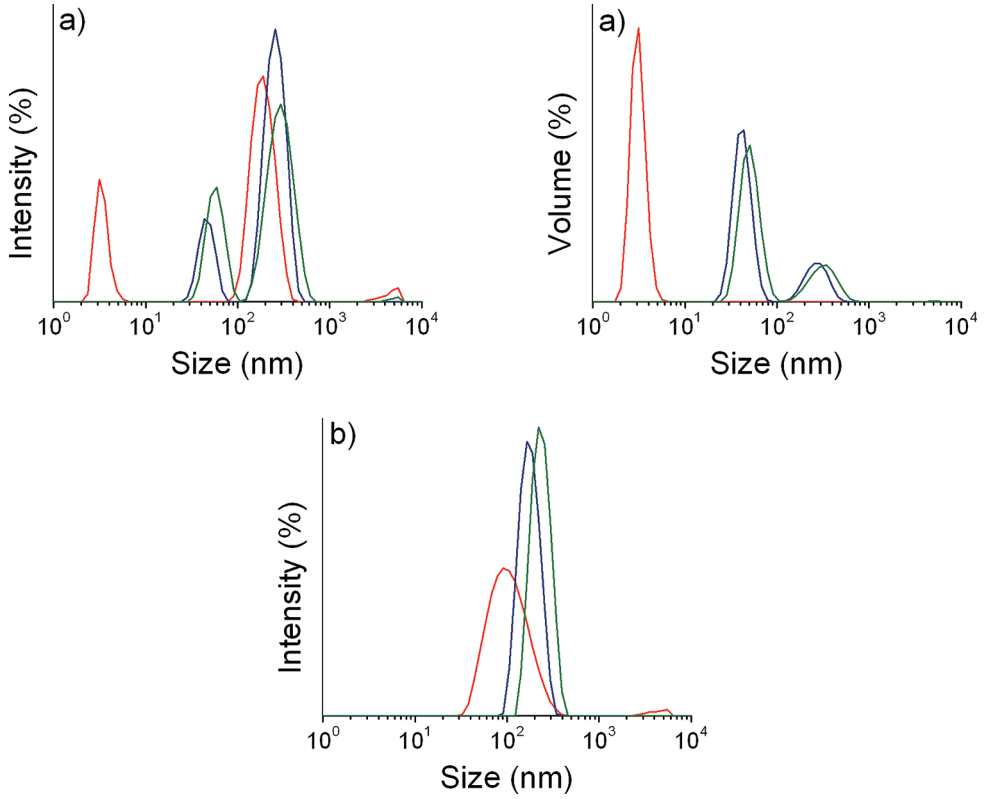

Figure 1. Particle size distributions by dynamic light scattering for: (a) Emulsion polymerization of BMA-*co*-St with 1.09 mmol of surfactant Dowfax 8390 (E2); both the intensity and volume PSDs are shown for samples taken after the first stage (25 min), 5.5 h, and 23.1 h. (b) Surfactant-free emulsion polymerization of BMA-*co*-St with methyl acrylate in the first stage (E4); only the intensity PSD is shown for samples taken after the first stage (20 min) (red), 6.5 h (blue), and 23.1 h (green). The PSD curves are normalized for area.

It is suspected that the bimodality of the PSD for the BMA-*co*-St system is due to a combination of nucleation mechanisms, namely micellar nucleation and aggregative nucleation, while the greater hydrophilicity of the MMA monomer may predominantly favor micellar nucleation. The large concentration of initiator present in the aqueous phase in the first few minutes of the first stage is extremely high by conventional emulsion polymerization standards, owing both to the low target molecular weights for the polymer (~36 700 g mol^{-1}) and the high rate of decomposition of

BlocBuilder at the reaction temperature ($k_{act,BB}$ = 3.4 × 10^{-2} L mol s^{-1} [17]). As a result, 95% of the initiator decomposes in the first 90 s of the polymerization. Therefore, both micellar and aggregative nucleation mechanisms, which occur in most emulsion polymerizations,[18] are important, although aggregative nucleation in the more hydrophobic BMA-*co*-St system occurs to a greater extent than in most conventional BMA emulsion polymerizations because of the conditions cited above.

Such a phenomenon has been observed in other two-stage NMP emulsion systems. SG1-mediated emulsion polymerization of *n*-butyl acrylate (*n*-BA), a monomer with similar hydrophobicity to BMA (*n*-BA is slightly more hydrophilic), resulted in very broad PSDs[5,7] with PDIs measured by dynamic light scattering which are similar to our own reported PDIs for the bimodal particles formed with BMA-*co*-St in the presence of surfactant. While bimodal PSDs have not been observed by our group for an MMA-*co*-St emulsion system (E1) with the surfactant Dowfax 8390, a bimodal PSD observed by light scattering was reported by Dire et al.[14] for the surfactant-free polymerization of MMA-*co*-St with an amphiphilic alkoxyamine initiator/surfactant combination. The bimodal PSD was attributed to the formation of aggregates due to the presence of styrene in the amphiphilic outer layer of the particles. However, no large particles could be identified by transmission electron microscopy.[14]

In the emulsion polymerization literature,[18] it is common to discuss nucleation mechanisms in terms of the *z*-meric length and the j_{crit} length. The *z*-meric length is the minimum length aqueous phase oligomers reach prior to becoming sufficiently surface active to enter a micelle or particle. These water-soluble oligomers may grow longer than the *z*-meric length if they do not encounter a micelle. The critical length at which an oligomer becomes insoluble in the aqueous phase and forms a precursor particle is known as the j_{crit} value.

One important difference in the MMA and BMA emulsion systems is the difference in hydrophobicity of the two monomers. The *z*-meric lengths for St and BMA have been reported as 2, while the *z*-meric length is closer to 4−5 for the more hydrophilic MMA with a persulfate terminal group.[19] Tsai and Fitch[20] have measured the j_{crit} length of MMA to be ∼65 with a persulfate end group, although Maxwell et al.[19] have observed the minimum chain length of insolubility to be 10−11 under similar experimental conditions but using different analytical techniques. The j_{crit} values of the more hydrophobic monomers, BMA and St, are reported as 4.[19] The j_{crit} and *z* values can be estimated for the copolymer systems of MMA-*co*-St and BMA-*co*-St based on a weighted average of the homopolymer j_{crit} and *z* with respect to the concentration of each of the monomers present in the aqueous phase. When the monomers were added to the aqueous phase in concentrations greater than their saturation, the saturation concentration was used.[19] Following the activation of the alkoxyamine initiator in the aqueous phase and propagation of the MMA-*co*-St aqueous oligomer, this oligomer is able to enter into a micelle or particle (*z*-meric length ∼4−5) prior to reaching its j_{crit} value (∼10), where aggregative nucleation occurs. However, BMA is much more hydrophobic and is a faster propagating monomer (possessing a higher k_p) than MMA, so the BMA-*co*-St water-soluble oligomers add units more quickly and possess a lower j_{crit} value (∼4) than the MMA-*co*-St oligomers Therefore, it is probable that some BMA-*co*-St oligomers will begin aggregating and precipitating prior to entering a micelle or existing particle (*z*-meric length ∼2), especially in a system with very high initiator fluxes. While this discussion is based on chains with a persulfate end group, the behavior is likely similar for oligomers with a BlocBuilder end group (COO^-).

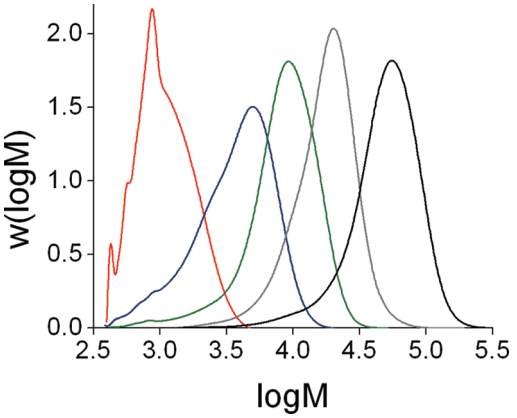

Figure 2. Molecular weight distributions for the surfactant-free emulsion polymerization of BMA with 10 mol % styrene (E4). Samples shown for first stage (20 min) (red), 2.3 h (blue), 4.4 h (green), 6.5 h (gray), and 23.1 h (black). The MWD curves are normalized for area.

Surfactant-Free Emulsion Polymerization. In surfactant-free emulsion polymerization of BMA-*co*-St, oligomers can only undergo aggregative nucleation due to the absence of surfactant micelles. Early experiments (E3) suffered from poor initiator efficiency and slow polymerization rates because of termination during nucleation, which occurs in the first stage of the polymerization. In aggregative nucleation, several water-soluble oligomers precipitate to form a precursor particle. However, when using BlocBuilder, which has a very high rate of decomposition at the reaction temperature, about 95% of the water-soluble oligomers are present in their active, propagating form in the first 90 s of the polymerization. The aggregation of these radicals in small particles results in irreversible termination. This leads to an accumulation of SG1 in the system which suppresses further polymerization due to the persistent radical effect. While the initiator efficiencies of these initial experiments were low, they did produce monomodal PSDs, the goal of this series of experiments.

Increasing the Initiator Efficiency by the Addition of Methyl Acrylate. Low BlocBuilder initiator efficiencies in styrene miniemulsions were found to be caused by extensive termination of the oligomers in the aqueous phase, and the accumulation of excess SG1, leading to extremely slow growth of the oligomeric radicals in the aqueous phase prior to entry into the monomer droplets.[21] The initiator efficiency was shown to be greatly increased by the addition of a small amount of the hydrophilic, fast propagating monomer methyl acrylate (MA), leading to much more efficient oligomer entry into the miniemulsion droplets.[21] We believe that in our system methyl acrylate adds preferentially to the oligomeric chain over BMA and St as it is propagating in the aqueous phase and lowers the overall interfacial tension during aggregative nucleation. Lower interfacial tension then minimizes the number of oligomers (and their charged end groups) required to stabilize the precipitating particles, thus lowering the instances of termination between these species. The addition of MA monomer during the first stage (at an equivalent of 3 MA units per chain) greatly improved the initiator efficiencies of the resulting latexes (E4 and E5), while creating highly living polymers as demonstrated by the growth of the full MWD over the course of the reaction (Figure 2 and the Supporting Information) and narrow, monomodal PSDs (Figure 1b). A similar phenomenon of

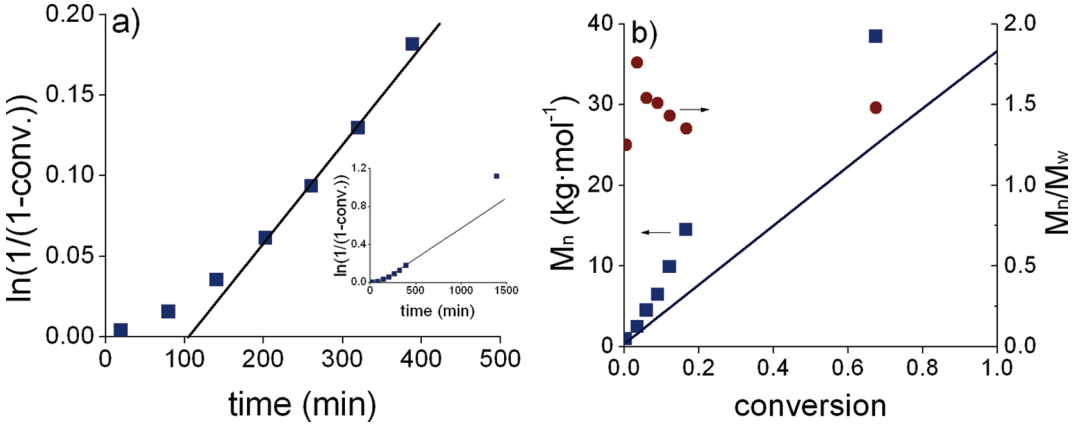

Figure 3. Kinetic plots for the surfactant-free, two-stage emulsion polymerization of BMA with 10 mol % styrene (E4). (a) The ln(1/(1 − conversion)) vs time plot for samples taken during the first 7.5 h with an inlay of the same plot including all the samples up to 22 h. (b) The number-average molar mass (M_n) and polydispersity (M_n/M_w) vs conversion plot (the full line represents the theoretical M_n).

increased initiator efficiency is demonstrated when surfactant is present but in concentrations below the cmc and in the absence of MA (E8). The surfactant lowers the interfacial tension of the particles formed by aggregative nucleation and with fewer oligomers present per particle and an increased initiator efficiency is observed.

E4 shows a linear trend of ln(1/(1 − conversion)) vs time (Figure 3a) for the latter part of the polymerization, indicating that there is little loss of chains in the system. However, the first two samples, after the first stage and 1 h after the monomer feed commences, indicate that there are fewer radicals present in the system at the start of the polymerization; this is the opposite of the tends previously observed by Nicolas et al.[11] for an MMA-*co*-St system. They observed that there is a higher concentration of propagating radicals very early on in the reaction and the system only reached a linear trend of ln(1/(1 − conversion)) vs time later when the MMA−St−SG1 termination sequance was established. Those polymerizations were conducted in batch with 4.4−8.8 mol % St concentrations. The system presented here is quite different, as there is 30 mol % St in the first stage but only 10 mol % St in the feed. The additional styrene in the system inhibits the polymerization through the formation of St−St−SG1 chains ends which are slower to reactivate; therefore, this system is expected to have a lower concentration of propagating chains present in the system during the feed stage and for the first hour or so of the polymerization until the excess St added is consumed and the regular formation of MMA−St−SG1 end groups commences. Further evidence of the living nature of this system is exemplified through the full shifting of the MWD (Figure 2), a linear relationship between ln(1/(1 − conversion)) vs time (Figure 3a), and a continually increasing M_n over the course of the polymerization (Figure 3b).

Addition of SG1 and Reducing Agents. The initiation efficiency was increased with the addition of 10% excess SG1 (with respect to BlocBuilder) in the nucleation stage, which should shift the equilibrium to favor dormant chains. When SG1 was added alone (E6), the polymerization was much slower and exhibited an induction period at the start of the polymerization; however, the initiation efficiencies showed a dramatic improvement, up to 85% from 54% without SG1 (E6 and E3, respectively). It appears that many of the oligomers were reversibly terminated either prior to or during nucleation, protecting them from being irreversible terminated upon aggregative nucleation with other oligomers. However, the extra SG1 appears to have had a detrimental effect on the PSD, resulting in a very broad and possibly bimodal PSD throughout the polymerization. One possible explanation for this is that the presence of the excess SG1, along with 30% St in the first stage, produced water-soluble oligomers that were capped with SG1 prior to reaching the j_{crit} value and precipitating. In environments high in free SG1, the dormant state is favored; therefore, these water-soluble oligomers may have remained dormant for an extended period of time, continuing past the time when the monomer feed was started. These water-soluble oligomers, with an ionized COO^- group, could act as amphiphilic chains and stabilize monomer droplets or form micelles which are nucleated later, leading to a bimodal PSD. However, further characterization is required to fully understand this phenomenon.

Experiments with 20% excess SG1 in the first stage and subsequent addition of the reducing agent SFS (also 20% with respect to the initial concentration of BlocBuilder) prior to the monomer feed were conducted (E7). SFS is a reducing agent which scavenges free SG1 and can restore the activation/deactivation equilibrium toward the active form. While these systems were living, as demonstrated by the growth of the entire MWD (please see the Supporting Information for the full MWDs of all the experiments discussed here), they did not show any improvement in the initiator efficiency compared to the case with no SG1 (E4), and the MWD was more polydisperse. While the PSD was monomodal, the size of the particles was very large (∼500 nm). Interestingly, the experiment with excess SG1 but no SFS addition (E6) had two particle size domains: a large diameter domain (500−600 nm) which matches the particle size obtained in the experiment with addition of SG1 and SFS (E7) and a smaller domain (∼200 nm) which matches closely the particle sizes obtained in the experiments without excess SG1 (E4). The very large particle size domain created in the experiments where SG1 is present may be due to the superswelling effect, where the oligomers (which are shorter and present for a longer time when excess SG1 is present) may be shifting the chemical potential so that the earliest nucleated particles become superswollen with monomer with respect to the later formed particles. A discussion of this has been presented for an *ab initio* RAFT system.[22] The colloidal stability and particle size are known to be very sensitive to ionic strength in NMP emulsion; however, the concentration of SFS added to the system is extremely small, and these effects can likely be discounted. The first stage of the E6 latex was monomodal, which suggests that the bimodality of the PSD occurred during the monomer feed. It is possible that water-soluble

oligomers may have still been present which could have formed micelle-like species to encourage a secondary micellar nucleation. These micelle-like species would have disappeared following the addition of SFS in experiment E7.

Conclusion

SG1-mediated emulsion polymerization of *n*-BMA with 10 mol % styrene, in both the presence and absence of surfactant, yielded well-controlled polymerizations with highly living polymer chains. In the presence of surfactant above the cmc, bimodal particle size distributions are observed, which can be attributed to the presence of two different nucleation mechanisms: micellar and aggregative nucleation. SG1-mediated polymerization of MMA-*co*-St in the presence of surfactant above the cmc, however, results in monomodal PSDs. Surfactant-free emulsion polymerization of BMA-*co*-St gives monomodal particle size distributions but suffers from poor initiator efficiencies and slow rates of polymerization as irreversible termination occurs during nucleation. The initiator efficiency can be greatly improved by the addition of a very small amount of the hydrophilic monomer methyl acrylate in the first stage or alternatively when surfactant is added in concentrations below the cmc in the absence of MA. We propose that the increase in initiator efficiency is the result of lower interfacial tension in the presence of both MA and surfactant below the cmc. The addition of excess SG1 greatly increases the initiation efficiency, but at the cost of slower polymerization and very broad PSDs. The addition of the reducing agent SDS to consume the excess SG1 does not impart greater control than simply through the addition of the MA during the first stage. This study represents the first instance of well-controlled nitroxide-mediated polymerization of *n*-butyl methacrylate with a small proportion of styrene in a simple, one-pot surfactant-free emulsion polymerization system. The elimination of surfactant from the system not only allows for better control over the particle size distribution, but it is also an important advance for further applications, where the presence of a large quantity of surfactant can be deleterious to both product properties and performance.

Acknowledgment. We thank Arkema for providing financial support, materials, and fruitful discussions and the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support.

Supporting Information Available: Full molecular weight distributions of all experiments described in Table 2. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Cunningham, M. F. *Prog. Polym. Sci.* **2008**, *33*, 365–398.
(2) Zetterlund, P. B.; Kagawa, Y.; Okubo, M. *Chem. Rev.* **2008**, *108*, 3747–3794.
(3) Bon, S. A. F.; Bosveld, M.; Klumperman, B.; German, A. L. *Macromolecules* **1997**, *30*, 324–326.
(4) Marestin, C.; Noel, C.; Guyot, A.; Claverie, J. *Macromolecules* **1998**, *31*, 4041–4044.
(5) Nicolas, J.; Charleux, B.; Magnet, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4142–4153.
(6) Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 6186–6189.
(7) Charleux, B.; Nicolas, J. *Polymer* **2007**, *48*, 5813–5833.
(8) Mchale, R.; Aldabbagh, F.; Zetterlund, P. B. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 2194–2203.
(9) Dire, C.; Belleney, J.; Nicolas, J.; Bertin, D.; Magnet, S.; Charleux, B. *J. Polym. Sci., Part B: Polym. Phys.* **2008**, *46*, 6333–6345.
(10) Charleux, B.; Nicolas, J.; Guerret, O. *Macromolecules* **2005**, *38*, 5485–5492.
(11) Nicolas, J.; Dire, C.; Mueller, L.; Belleney, J.; Charleux, B.; Marque, S. R. A.; Bertin, D.; Magnet, S.; Couvreur, L. *Macromolecules* **2006**, *39*, 8274–8282.
(12) Lessard, B.; Marić, M. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 2574–2588.
(13) Simms, R. W.; Hoidas, M. D.; Cunningham, M. F. *Macromolecules* **2008**, *41*, 1076–1079.
(14) Dire, C.; Magnet, S.; Couvreur, L.; Charleux, B. *Macromolecules* **2009**, *42*, 95–103.
(15) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Kajiwara, A.; Klumperman, B.; Russell, G. T. *Macromol. Chem. Phys.* **2000**, *201*, 1355–1364.
(16) Hutchinson, R. A.; McMinn, J. H.; Paquet, D. A.; Beuermann, S.; Jackson, C. *Ind. Eng. Chem. Res.* **1997**, *36*, 1103–1113.
(17) Nicolas, J.; Mueller, L.; Dire, C.; Matyjaszewski, K.; Charleux, B. *Macromolecules* **2009**, *42*, 4470–4478.
(18) Gilbert, R. G. *Emulsion Polymerization - a Mechanistic Approach*; Academic Press: San Diego, CA, 1995; p 362.
(19) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629–1640.
(20) Fitch, R. M.; Tsai, C. H. *Polym. Colloids, Proc. Symp.* **1971**, 103–116.
(21) Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* **2004**, *37*, 4453–4463.
(22) Luo, Y.; Cui, W. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2837–2847.