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Cationic Surface-Active Monomers as Reactive Surfactants for AGET Emulsion ATRP of *n*-Butyl Methacrylate

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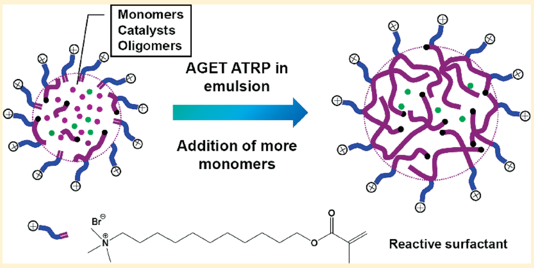
ABSTRACT: A surface-active monomer 11′-(methacryloyloxy)-undecyl-(trimethyl)ammonium bromide (MUTAB) was synthesized and used as a stabilizer and comonomer for activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) of *n*-butyl methacrylate (BMA) in emulsion. This reactive "surfactant" was applied in a continuous two-step microemulsion to emulsion technique. Stable polymer latexes with size ranging from 40 to 200 nm were obtained by adjusting the amount of reactive surfactant introduced to the system. The surfactant concentration could be decreased to as low as 1.3 wt % in the final emulsion (5.9 wt % vs monomer), while still maintaining good colloidal stability. The cationic reactive surfactants were covalently anchored on the surfaces of the formed particles, as indicated by a positive zeta potential. In addition, a well-controlled polymerization process was achieved by ATRP, as evidenced by the smooth growth in molecular weight of the polymer chains as the polymerization progressed and by the formation of polymers with preserved chain-end functionalities.



INTRODUCTION

Since its discovery in 1995, atom transfer radical polymerization (ATRP)[1−5] has emerged as one of the most powerful synthetic techniques for preparation of well-defined polymeric materials, i.e., polymers with predetermined molecular weight and narrow molecular weight distribution as well as a variety of compositions, topologies, and well-maintained functionalities. In the past decade, considerable research efforts have been made to extend ATRP to all aspects of aqueous dispersed media.[6−10] When compared to solution polymerization, carrying out radical polymerization in aqueous dispersed media is an environmentally benign procedure, due to the use of water as the dispersion medium instead of volatile organic solvents. Additionally, the involvement of water also allows more efficient heat dissipation during the polymerization. To date, ATRP has been successfully conducted in various aqueous dispersed media, including microemulsion,[11,12] miniemulsion,[13−23] emulsion,[24−31] etc. Polymer latexes with size ranging from tens of nanometers up to several hundred nanometers have been successfully prepared.[10] However, due to the multicomponent nature of ATRP as well as the complex nature of aqueous dispersed media, the polymerization conditions have to be carefully designed in order to conduct a successful aqueous dispersed ATRP, including selection of suitable surfactant, catalyst, ligand, activator for systems starting with higher oxidation state transition metals, and so on.[8,10]

In ATRP systems, the surfactants should not only trap the initiators and catalyst complexes in the oil phase and provide a stable dispersed system throughout the polymerization but also should not interfere with the equilibrium between the propagating radicals and the dormant species. Both nonionic surfactants with hydrophilic−lipophilic balance (HLB) values ∼15, such as commercially available polyoxyethylene (20) oleyl ether (Brij 98), and cationic surfactants have proven successful for a controlled ATRP as well as preparation of stable latex particles.[17,32] However, conventional surfactants, which are physically adsorbed on the polymer particles, may migrate or desorb from the product during postpolymerization processes.[33−36] Recently, surfactants containing reactive end groups—an initiating moiety (inisurf), a moiety capable of chain transfer (transurf), or a vinyl group capable of copolymerization (surfmer)—were widely studied to overcome the limitations of conventional surfactants.[33−35] The reactive surfactants participate in the polymerization process and become covalently attached to the surfaces of polymer particles.

Reactive surfactants were successfully applied when controlled/living radical polymerization (CRP)[4] was carried out in miniemulsion, such as ATRP or reversible addition−fragmentation chain transfer (RAFT).[37] In case of miniemulsion ATRP, amphiphilic block copolymers were designed and utilized as both stabilizers and macroinitiators (inisurf) for activator generated by electron transfer (AGET) ATRP[15,38] of various monomers.[39−42] Polymer latexes with no free surfactants or low molecular weight species remaining in the products were obtained. Furthermore, a simple cationic surface-active initiator (11′-(*N*,*N*,*N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate) has also proven to work well as a reactive stabilizer for miniemulsion ATRP. Stable polymer latexes containing high molecular weight polymers were generated in this case.[43] Considering RAFT-mediated miniemulsion polymerization, either amphiphilic/hydrophilic RAFT agents (transurfs)[44,45] or comonomers (surfmers)[46] can serve as reactive stabilizers. For instance, Sanderson et al.[46]

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reported the use of cationic and anionic amphiphilic monomers, (11′-(methacryloyloxy)undecyl(trimethyl)ammonium bromide and 11-methacryloyloxyundecan-1-yl sulfate), to stabilize particles. The reaction rates of the surfmer-stabilized miniemulsion polymerization of styrene and final particle size were similar to those of the classical-surfactant-stabilized miniemulsion polymerizations. Reactive surfactants were also carefully designed and studied for RAFT in an emulsion system.[47−53] A series of macro-RAFT agents were applied as both stabilizers and control agents in *ab initio* batch emulsion polymerization, resulting in the formation of core−shell particles with good colloidal stability and well-maintained living characters.

Emulsion polymerization[54−56] is actually a more dominant industrial polymerization process for preparation of a directly usable stable colloidal latex than miniemulsion polymerization,[57] since emulsion systems do not require high shear forces, such as sonication or fluidization, to form uniform monomer droplets. Previously, our group successfully conducted ATRP in an *ab initio* emulsion medium using a continuous two-step procedure. In this procedure the emulsion system was formed by adding pure monomers to an ongoing microemulsion ATRP.[28] A well-controlled polymerization was achieved by avoiding the need to transport the copper catalysts across the aqueous phase, as indicated by the first-order kinetics and high initiation efficiency. Moreover, through the adjustment of the amount of monomer added to the initial microemulsion stage, the surfactant concentration was efficiently decreased to ca. 10 wt % vs monomer in the final emulsion, ∼2 wt % of the total emulsion.[28] Nevertheless, 10 wt % vs monomer, i.e., 10 wt % of surfactant vs formed polymers, is still considerable large amount of low molar mass components in the final product.

Herein, we describe the use of a simple surface-active monomer 11′-(methacryloyloxy)undecyl(trimethyl)ammonium bromide (MUTAB) or initiator (11′-(*N,N,N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate) (TABUB) as the stabilizer and comonomer/initiator for AGET ATRP of *n*-butyl methacrylate (BMA) in an emulsion polymerization using the previously reported two-step *ab initio* procedure: from microemulsion to emulsion, as introduced above.[28] This procedure expands the scope of the concept of using reactive surfactants for ATRP from miniemulsion to an emulsion system, and the covalent attachment of the stabilizer to the formed polymer particles ensures that no free surfactants remain in the formed products. In addition, as compared to the macroinitiator surfactant,[40] the use of monomer-based reactive surfactant (surfmer, MUTAB) allowed the easy tuning of the particle size by surfactant concentration, without affecting the molecular weight of formed polymers.

■ EXPERIMENTAL SECTION

Materials. *n*-Butyl methacrylate (BMA, 99%) and *n*-butyl acrylate (BA, 99%) were purchased from Aldrich and purified by passing through a column filled with basic alumina to remove the inhibitor and/or antioxidant and then stored at −5 °C. Bis(2-pyridylmethyl)octadecylamine (BPMODA),[58] surface-active 11′-(methacryloyloxy)undecyl(trimethyl)ammonium bromide (MUTAB) monomer,[59] and (11′-(*N,N,N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate) (TABUB) initiator[60] were synthesized according to previously published procedures. Sodium chloride (NaCl) was purchased from Fisher. All other reagents—$CuBr_2$ (98%), L-ascorbic acid (AA, >99%), and ethyl 2-bromoisobutyrate (EBiB)—and solvents were purchased from Aldrich and used as received.

Emulsion Polymerization of BMA Using MUTAB as Reactive Stabilizer/Comonomer via AGET ATRP. Cationic surface-active monomers (MUTAB) or initiators (TABUB) were used as reactive surfactants for AGET ATRP of BMA in a two-step emulsion procedure. Typically, $CuBr_2$ (0.006 g, 0.027 mmol) and BPMODA (0.0156 g, 0.034 mmol) were dissolved in BMA (0.4 g, 2.81 mmol) at 50 °C to form a solution of the copper complex, which was then cooled to room temperature prior to dissolving the initiator EBiB (0.026 mL, 0.177 mmol) in the solution. Meanwhile, MUTAB (0.5 g, 1.32 mmol) and NaCl (0.02 g) were dissolved in 10 g of water. The organic BMA solution, containing the precursor to the copper catalyst, was then slowly added to the aqueous solution under stirring to form an optically clear microemulsion. The resulting stable microemulsion was purged with nitrogen for 30 min. A predeoxygenated aqueous solution of AA (0.2 mL, containing 1.2 mg AA) was injected into the microemulsion to activate the catalyst and start the polymerization. Five minutes after the initiation, a second portion of predeoxygenated BMA monomer (2.5 g, 17.6 mmol) was added to the ongoing microemulsion polymerization to form an *ab initio* emulsion system wherein the added monomer could diffuse across the aqueous medium to the active micelles. Samples were taken at timed intervals to measure the conversion gravimetrically and to determine the molecular weight by size exclusion chromatography (SEC) and ^{1}H NMR. Additional reducing agent was also injected to the system, 1 and 3.5 h after the initiation of the reaction, to increase the rate of polymerization.

Characterization. Molecular weight and polydispersity of the formed polymers were measured by size exclusion chromatography (SEC) (Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å), with DMF eluent at 35 °C, flow rate 1.00 mL/min, and differential refractive index (RI) detector (Waters, 2410)). Toluene was used as the internal standard to correct for any fluctuation of the DMF flow rate. The number-average molecular weights (M_n) and polydispersity (M_w/M_n) were determined with a calibration based on linear poly(methyl methacrylate) standards using WinGPC 6.0 software from PSS. The average diameter of the polymer particles (D_n), coefficient of variation (cv), and mean zeta potential were measured by dynamic light scattering (DLS) on a high performance zeta-sizer from Malvern Instruments, Ltd. ^{1}H NMR spectra of the polymer solutions in $CDCl_3$ were collected on a Bruker Avance 500 MHz spectrometer at 27 °C. Transmission electron microscopy (TEM) analysis was conducted using a Hitachi H-7100 TEM (Hitachi High Technologies America) operating at 50 kV.

■ RESULTS AND DISCUSSION

Scheme 1 shows the use of a cationic surface-active monomer MUTAB as the reactive surfactant for an AGET emulsion ATRP of BMA. To minimize the necessity of transporting hydrophobic copper-based catalysts (hydrophobic ligands are used for ATRP in aqueous dispersed media to prevent the migration of catalysts from the organic to aqueous phase) across the aqueous phase, a two-step procedure was employed in this study.[28] First, a stable microemulsion system was generated using MUTAB as a cationic surfactant. There were no large monomer droplets existing in the microemulsion system due to the large amount of surfactant initially added. Small microlatexes with the copper catalysts encapsulated inside formed after initiating the microemulsion ATRP. They served as the nuclei for the latex particles in the next step after the second part of monomer was injected to the ongoing microemulsion polymerization to transform the system to an emulsion polymerization medium. As the polymerization continued, monomers diffused from the monomer droplets to

Scheme 1. Cationic Surface-Active Monomer as a Reactive Surfactant for an AGET Emulsion ATRP of BMA

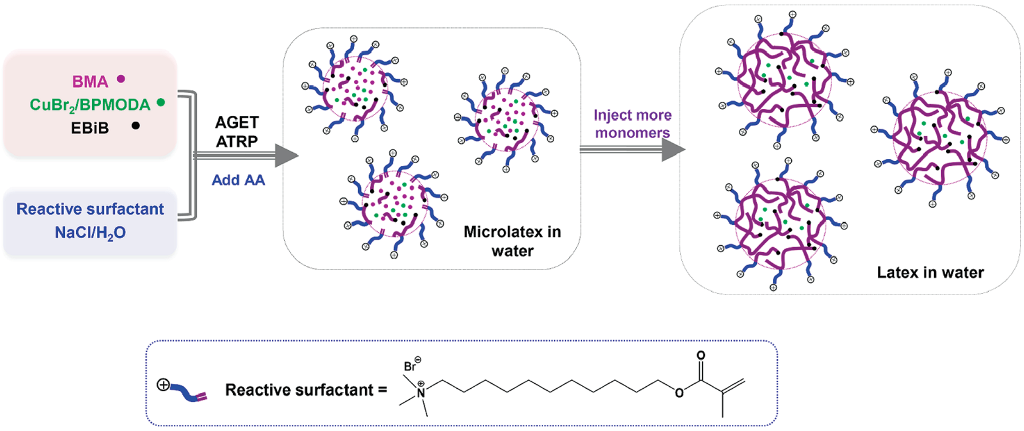

Table 1. AGET ATRP of BMA in an Emulsion Polymerization with Either a Cationic Surface Active Monomer or Initiator as Reactive Surfactant[a]

entry	DP_{RS}	DP_{BMA}	RS/BMA (step I, wt)	RS/BMA (total, wt)	time/conv	M_{theo}	M_n	M_w/M_n	$M_{n,\,NMR}$	D_n (nm)	*cv*	zeta potential (mV)
S-1	47	100 + 200	1.25/1	0.417/1	2 h/99%	6.1×10^4	1.9×10^4	1.28	6.9×10^4	44	0.15	77.4
S-2	23	100 + 200	0.625/1	0.208/1	2 h/98%	5.2×10^4	1.9×10^4	1.35	5.7×10^4	73	0.12	75.9
S-3[b]	1	6 + 36	0.55/1	0.076/1	5 h/94%	5.9×10^3	4.1×10^3	1.25	7.4×10^3	141	0.18	70.9

[a] Polymerization conditions: $[BMA]_0/[MUTAB]_0/[EBiB]_0/[CuBr_2]_0/[BPMODA]_0/[AA]_0 = DP_{BMA}/DP_{RS}/1/0.5/0.67/0.15(\times2)$; a second portion of AA was added to the system 1 h after the initiation of the polymerization; 60 °C, 0.2 wt % of NaCl compared to water; solid content 10.5 wt % based on 100% monomer conversion. DP_{RS} and DP_{BMA} represent the targeted degree of polymerization of reactive surfactant (RS) and BMA, respectively. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by DMF SEC with linear polyMMA standards. $M_{n,NMR}$ is the molecular weight of formed polymers determined by NMR, assuming 85% initiation efficiency.[31] The average diameter of the polymer particles (by volume distribution), coefficient of variation (*cv*), and mean zeta potential were determined by DLS with three to five measurements. [b] Polymerization conditions: $[BMA]_0/[\text{TABUB initiator}]_0/[CuBr_2]_0/[BPMODA]_0/[AA]_0 = DP_{BMA}/1/0.15/0.2/0.04(\times2)$; second portion of AA was added to the system 1 h after the initiation of the polymerization; 60 °C, 0.2 wt % of NaCl compared to water; solid content 22 wt % based on 100% monomer conversion.

the growing microlatexes, resulting in the formation of polymer latexes with larger size. The copper catalysts originally loaded in the microlatexes ensured that the polymerization would be well controlled by ATRP with the smooth growth of all polymer chains. The cationic MUTAB surfactants were covalently anchored on the surfaces of formed polymer particles due to the reactive vinyl groups at the chain end.

Use of Cationic Surface-Active Monomer/Initiator as Reactive Surfactant for an *ab Initio* Emulsion AGET ATRP of BMA. In order to achieve the targeted two-stage polymerization, from microemulsion to emulsion, the cationic MUTAB comonomers were first evaluated as surfactants for the generation of a stable microemulsion. The weight ratio of MUTAB and BMA was set at either 1.25/1 or 0.625/1. The mole ratio of $[BMA]_0/[MUTAB]_0/[EBiB]_0/[CuBr_2]_0/[BPMODA]_0 = 100/47$ (or 23)/1/0.5/0.67, providing a solid content 3.6 wt % based on 100% monomer conversion, in the presence of 0.2 wt % of NaCl vs water. The organic BMA solution containing the copper catalyst was mixed with the aqueous solution of MUTAB surfactant, and a stable microemulsion containing micelles with a size ca. 7−8 nm was obtained. Because of the large amount of MUTAB "surfactant" used, there were essentially no large monomer droplets present in the system. Therefore, in a series of separate experiments, the reducing agent ascorbic acid (AA) was added to both systems to activate the copper catalysts and initiate the polymerization. Five minutes after the initiation of the polymerization, the second portion of deoxygenated BMA monomer was injected to the ongoing polymerization, and the reaction medium was transformed to an emulsion system (Table 1, S-1 and S-2). Both systems displayed good colloidal stability, and polymer latexes with an average diameter below 100 nm were formed. The generation of relatively small polymer particles in these two systems could be attributed to the presence of a high concentration of surfactant. For instance, ca. 41.7 wt % MUTAB surfactant/comonomer vs BMA monomer was used in experiment S-1. However, the polymer particle size could be easily tuned by adjusting the weight ratio of MUTAB to BMA; when this ratio was decreased from 0.417/1 to 0.208/1, polymer particle size increased from 44 nm (S-1) to 73 nm (S-2). The particle size distribution was relatively narrow, as shown in Figure 1a. Moreover, the good stability of the resulting latexes indicated that the cationic comonomers were mainly located at the particle surface, which was further confirmed by the measurement of zeta potential. The mean zeta potential of the formed polymer latexes was ca. 76 mV. The positive value proved that the cationic reactive surfactants/comonomers were anchored on the interface and stabilized the particles.

Although stable emulsion polymerization media were achieved using the cationic MUTAB comonomers as reactive surfactants, the molecular weight of formed polymers determined by DMF

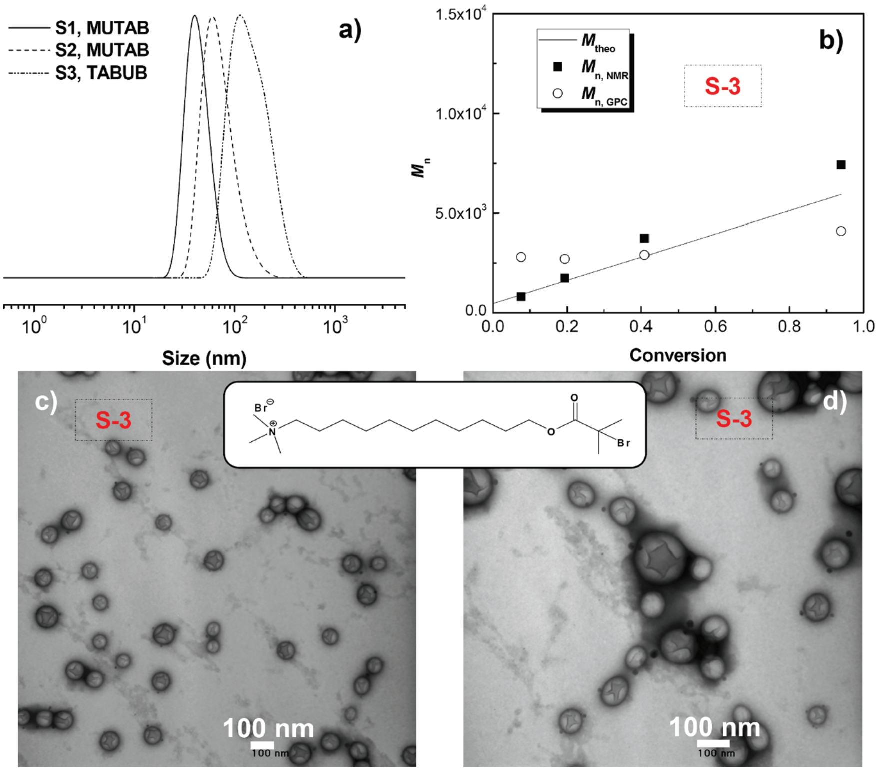

Figure 1. (a) DLS results by volume distribution of the cationic reactive surfactant stabilized polymer particles (S-1, S-2, and S-3). (b) Dependence of number-average molecular weights M_n (determined by either DMF SEC or NMR) on BMA conversions. (c, d) Typical TEM images of cationic reactive surfactant stabilized polymer particles (S3, chemical structure of TABUB shown in the images). Polymerization conditions are summarized in Table 1.

Table 2. AGET ATRP of BMA in an Emulsion Polymerization with Cationic Surface Active Monomer as Reactive Surfactant (Reduce Surfactant Concentration)[a]

entry	DP_{RS}	DP_{BMA}	RS/BMA (step I, wt)	RS/BMA (total, wt)	time/Conv	M_{theo}	M_w/M_n	$M_{n, NMR}$	D_n (nm)	*cv*	zeta potential (mV)
S-4	7.5	16 + 100	1.25/1	0.167/1	5 h/99%	2.0×10^4	1.19	1.8×10^4	98	0.21	85.7
S-5	3.7	16 + 100	0.625/1	0.086/1	5.5 h/83%	1.5×10^4	1.16	1.4×10^4	122	0.14	83.7
S-6	2.8	16 + 100	0.417/1	0.059/1	5.5 h/80%	1.4×10^4	1.11	1.7×10^4	202	0.23	81.8
S-7[b]	3.7	16 + 100	0.625/1	0.086/1	5 h/94%	1.7×10^4	1.13	2.2×10^4	148	0.08	84.4
		50 BA		0.062/1	22 h/65%	2.1×10^4	1.11	2.8×10^4	168	0.06	86.5

[a] Polymerization conditions: $[BMA]_0/[MUTAB]_0/[EBiB]_0/[CuBr_2]_0/[BPMODA]_0/[AA]_0 = DP_{BMA}/DP_{RS}/1/0.15/0.2/0.04(\times 3)$; more AA was added to the system 1 and 3.5 h after the initiation of the polymerization; 60 °C, 0.2 wt % of NaCl compared to water; solid content 22 wt % based on 100% monomer conversion. DP_{RS} and DP_{BMA} represent the targeted degree of polymerization of reactive surfactant (RS) and BMA, respectively. The molecular weight distribution (M_w/M_n) was determined by DMF SEC with linear polyMMA standards. $M_{n,NMR}$ represents the molecular weight of formed polymers determined by NMR, assuming 85% initiation efficiency. The average diameter of the polymer particles (by volume distribution), coefficient of variation (*cv*), and mean zeta potential were determined by DLS with three to five measurements. [b] BA was added to the ongoing emulsion polymerization 5 h after the initiation of reaction.

SEC were much lower than the calculated theoretical values. As summarized in Table 1, the number-average molecular weight determined by SEC was $M_n = 1.9 \times 10^4$ for S-1, while the theoretical molecular weight should be $M_{theo} = 6.1 \times 10^4$, although the determined molecular weight distribution was still relatively narrow ($M_w/M_n = 1.28$). The large discrepancy between M_n and M_{theo} was probably caused by the presence of a high percentage of cationic units in the formed copolymers. The cationic "block" in the polymer chain may result in some special interaction with the column or mobile phase (DMF) or could even introduce the generation of some micelle-like structures during SEC measurement, which may affect the separation of the formed copolymers in the column and the elution time. Therefore, the molecular weight data obtained from DMF SEC analyses in the presence of a large percentage of cationic units were probably not reliable, which was further confirmed when a surface active small initiator was used as reactive surfactant for the emulsion polymerization (Table 1, S-3).

A small surface-active initiator, 11′-(*N,N,N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate, TABUB, was also synthesized and utilized as reactive surfactant for the emulsion polymerization of BMA via ATRP using a "two-step" method. Detailed polymerization conditions and results are summarized in Table 1 and Figure 1, run S-3. In this case,

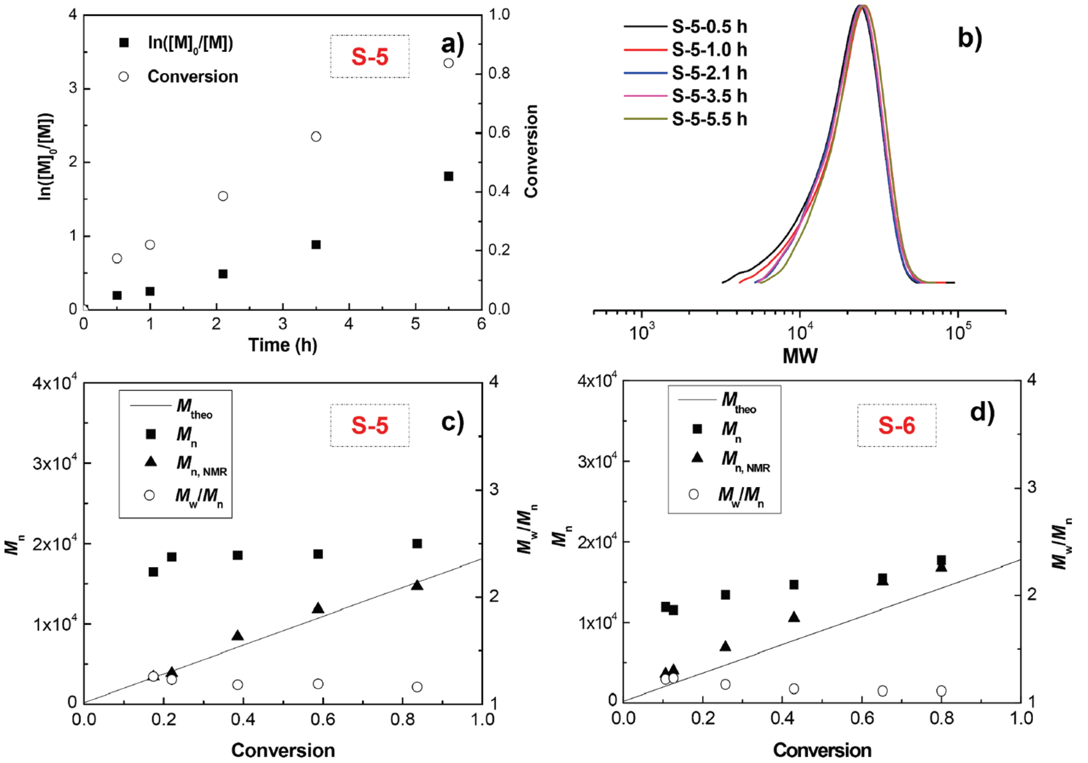

Figure 2. (a) Dependence of BMA conversion and ln([M]$_0$/[M]) on reaction time (S-5). (b) SEC traces during the polymerization of BMA by AGET emulsion ATRP (S-5). (c, d) Dependence of molecular weights (determined by either DMF SEC or NMR) on BMA conversions (S-5 and S-6). Polymerization conditions are summarized in Table 2.

cationic reactive surfactant stabilized particles with average size ca. 141 nm determined by DLS were obtained, when the final weight ratio of TABUB surfactant and BMA monomer was set at 0.076 to 1. These polymer particles showed well-defined spherical shape in the TEM images; they were pretty stable in water, and similar morphology could be observed after 4 months storage. However, considering the degree of control over the polymerization process, the fact that the number-average molecular weight M_n determined by DMF SEC remained almost constant as the polymerization continued (Figure 1b) raised questions as to the validity of the SEC measurement. Since the cationic reactive surfactant also served as initiator for the polymerization, i.e., one surfactant unit per polymer chain, NMR provided an alternative way to determine the degree of polymerization (DP) or molecular weight of the generated polymers. The samples taken at different times during the polymerization were purified and analyzed by NMR to confirm the molecular weights through comparison of the peaks between $-N^+(CH_3)_3$ and $-COOCH_2-$. Results are shown in Figure 1b. According to NMR measurement, molecular weight increased linearly with conversion and was in good agreement with the theoretical molecular weight, indicating a well-controlled polymerization process. These results also confirmed that if a large percentage of cationic units are present in the copolymer chain, SEC with DMF as eluent is not a good method for the analysis of the polymers. NMR was also used to calculate molecular weights of samples S-1 and S-2; details of the characterization method will be discussed in the following section. In addition, it is worth noting that due to the large amount of surfactant necessary for the generation of a stable microemulsion in the first step, only a very low DP can be targeted in case of using an initiator-based reactive surfactant. For example, in run S-3, the final targeted DP was only 42, even after the addition of more monomers in the second step. Thus, it is difficult to prepare polymers with high molecular weight under these conditions.

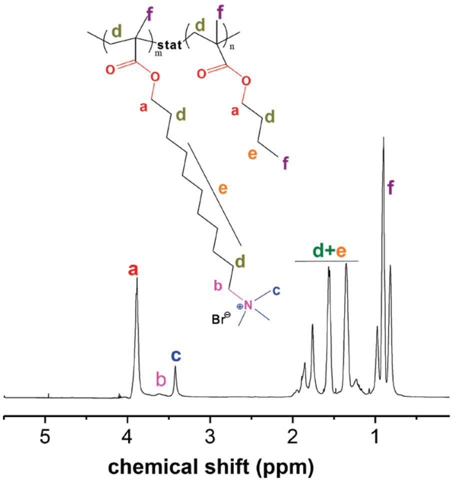

Figure 3. Typical ^{1}H NMR spectra of the formed poly(BMA-MUTAB) copolymers.

Reducing the Concentration of Reactive Surfactant in an AGET Emulsion ATRP of BMA. To further reduce the percentage of MUTAB surfactant/comonomer in the final products, a lower DP = 16 was targeted in the first step. The weight ratio of MUTAB and BMA was maintained at 1.25/1 or 0.625/1, in order to generate a clear and stable microemulsion. The amount of

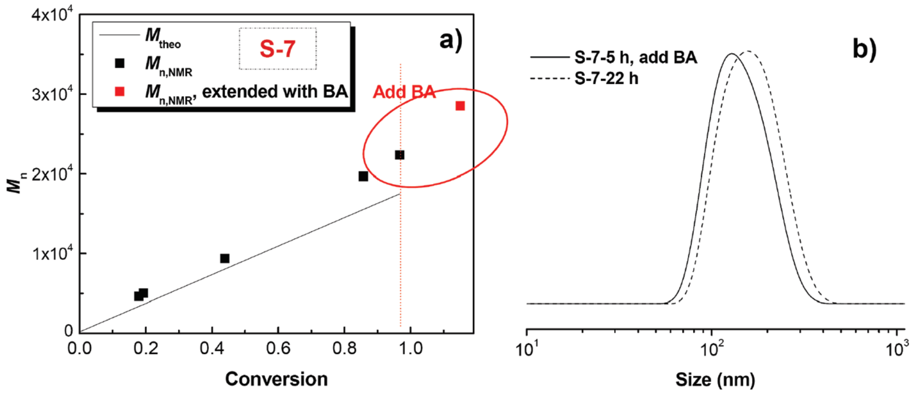

Figure 4. (a) Dependence of molecular weights (determined by NMR) on BMA conversions (S-7); increase of molecular weight after the chain extension with BA as highlighted in the circle. (b) DLS results by volume distribution of formed polymer particles before and after extension of BA. Polymerization conditions are summarized in Table 2.

copper catalysts introduced to the systems was adjusted accordingly to ensure that all the catalyst was dissolved in the BMA monomers, forming $CuBr_2$/BPMODA complex. The mole ratio of reagents was set at $[BMA]_0/[MUTAB]_0/[EBiB]_0/[CuBr_2]_0/[BPMODA]_0$ = 16/7.5 (or 3.7)/1/0.15/0.2 (Table 2, S-4 and S-5). In both reactions, additional monomers were also added to the systems 5 min after the polymerization was activated, and the targeted DP for the second step was 100. The reaction mixture gradually changed to a stable milk-like system as the polymerization progressed. Polymer particles, with the cationic surfactants covalently anchored on the surfaces, were obtained in these systems, and the mean zeta potential of the formed particles was around 85 mV. The much larger amount of BMA monomers introduced to the polymerizations in the second step resulted in a solid content of 22 wt %, assuming 100% monomer conversion and the total surfactant concentration was efficiently reduced to 8.6 wt % vs BMA and 1.9 wt % in total emulsion, S-5. Polymer particles with larger size were generated in these two systems, 98 nm for S-4 and 122 nm for S-5, due to the reduced concentration of reactive surfactants in these reactions. Even larger polymer particles with average diameter around 202 nm could be prepared, when less MUTAB was used in the first step, run S-6 with 41.7 wt % of MUTAB vs BMA in the first step. In this case, the final surfactant concentration was further decreased to 5.9 wt % vs BMA and 1.3 wt % in total emulsion. However, in the current system any further decrease of reactive surfactant concentration in the first step would result in the formation of polymer particles with multiple peaks in DLS analysis.

Typical results for the two-stage emulsion polymerization process are shown in Figure 2. BMA conversion smoothly increased as the polymerization progressed (Figure 2a). In order to maintain the rate of polymerization, or even accelerate it, more reducing agents were injected to the system 1 and 3.5 h after initiation of the reaction. High monomer conversion over 80% was reached 5.5 h after the polymerization was started. The molecular weight M_n determined by DMF SEC did not change significantly as the polymerization progressed, similar as in the previous examples, and the SEC traces of samples taken at different times overlapped with each other (Figure 2b,c). As discussed above, this observation was probably caused by the presence of the cationic units in the formed polymer chains.

According to the NMR analysis, over 90% of the reactive surfactant (MUTAB) was consumed during the first 0.5 h, meaning that the polymers formed at the early stage of the polymerization process already contained a large percentage of cationic units; the short "cationic block", comprised of MUTAB and BMA units, was then further chain extended with BMA as the reaction continued. The fast consumption of reactive surfactant comonomer, MUTAB, was probably caused by the reduction of the oil-soluble Cu^{II} catalyst precursor by ascorbic acid at the interface of the droplets, which promoted an interfacially preferred copolymerization at the initial stage.

Because of the fast generation of a short "cationic block", NMR could be used as an alternative method for the characterization of the molecular weight of the final product, with the "cationic block" acting as an internal standard. However, it is worth noting that the calculation of the molecular weight using the short "cationic block" as an internal standard is valid only when a fast initiation was achieved. According to the previous work in our group, in which a two-stage emulsion polymerization was used for the preparation of hairy nanoparticles, the initiation efficiency in the microemulsion step when using the same initiator, catalysts, and similar target DP = 18 for methacrylate-based monomers was 84%.[31] Therefore, a fast initiation was also expected for the current system. This can be further supported by the SEC traces shown in Figure 2b. Because of the faster incorporation of the MUTAB comonomers to the polymer chain, if a slow initiation had occurred in the current system, two peaks should be expected in the SEC traces as the BMA conversion increased. One from the pure polyBMA, which was generated after the full consumption of the MUTAB comonomers due to the slow initiation process, and this peak should gradually shift to higher molecular weight as the reaction continued. The other peak should result from the poly(MUTAB-BMA) copolymer, which would show the similar elution volume for all the samples due to the presence of the cationic block, or at least a long tailing should be observed in the SEC traces due to the slow initiation. However, only narrow monomodal peaks were observed in the SEC traces, meaning that a slow initiation process was very unlikely to have occurred. Thus, we can use the short cationic block as internal standard to evaluate the molecular weight of the growing polymer chains by NMR.

Typical NMR spectra of the formed poly(MUTAB-BMA) block copolymer is shown in Figure 3. The degree of polymerization of BMA block was calculated by comparing the ratio between the peaks $-N^+(CH_3)_3$ and $-COOCH_2-$. The initiation efficiency was assumed to be 85%. Typical results are summarized in Table 2 and Figure 2c,d. The molecular weight determined by NMR increased linearly with conversion and closely matched the calculated theoretical values, indicating that a well-controlled polymerization process was achieved in these systems.

Synthesis of Block Copolymers Using an AGET Emulsion ATRP. Poly(MUTAB-BMA-*b*-BA) block copolymers were synthesized via emulsion ATRP. Detailed polymerization conditions and typical results are summarized in Table 2, run S-7. First, a poly(MUTAB-BMA) copolymer was synthesized using the two-step emulsion polymerization method. Deoxygenated BA monomer was injected into the emulsion system after high conversion of BMA was reached, >90%. The targeted DP for BA was set at 50. The BA conversion reached 65%, after allowing the reaction to continue overnight. Both an increase of molecular weight and an increase in polymer particle size were observed during the consumption of BA monomers (Figure 4). Stable polymer particles containing block copolymers with molecular weight ca. 2.8×10^4, determined by NMR, and an average diameter ca. 168 nm were obtained. The successful chain extension of BA confirmed the presence of well-preserved chain-end functionality during the first emulsion polymerization process.

CONCLUSIONS

AGET ATRP of BMA was successfully conducted in an emulsion system using cationic surface-active small molecules as comonomers/stabilizers. A series of polyBMA latexes with the cationic reactive surfactants covalently attached to the particle surfaces were obtained. The polymer latexes displayed good colloidal stability with no apparent aggregates generated after 4 months storage. The final particle size could be easily tuned, from 40 nm up to 200 nm in the exemplified system, by adjusting the amount of reactive surfactant initially added to the reaction. ATRP allowed the preparation of polymers with well-preserved chain-end functionality in the two-step emulsion polymerization process, which was proved by the successful *in situ* chain extension of the formed BMA copolymers with BA to form block copolymers in latex particles. The use of reactive surfactants resulted in the formation of pure polymer particles with no free surfactants left in the final products but with still well-maintained stability.

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REFERENCES

(1) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615.

(2) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921–2990.

(3) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270–2299.

(4) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93–146.

(5) di Lena, F.; Matyjaszewski, K. *Prog. Polym. Sci.* **2010**, *35*, 959–1021.

(6) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 2083–2134.

(7) Cunningham, M. F. *Prog. Polym. Sci.* **2002**, *27*, 1039–1067.

(8) Cunningham, M. F. *Prog. Polym. Sci.* **2008**, *33*, 365–398.

(9) Oh, J. K. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6983–7001.

(10) Min, K.; Matyjaszewski, K. *Cent. Eur. J. Chem.* **2009**, *7*, 657–674.

(11) Min, K.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8131–8134.

(12) Kagawa, Y.; Kawasaki, M.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromol. Rapid Commun.* **2007**, *28*, 2354–2360.

(13) Matyjaszewski, K.; Qiu, J.; Tsarevsky, N. V.; Charleux, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4724–4734.

(14) Li, M.; Jahed, N. M.; Min, K.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 2434–2441.

(15) Min, K.; Gao, H. F.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2005**, *127*, 3825–3830.

(16) Kagawa, Y.; Minami, H.; Okubo, M.; Zhou, H. *Polymer* **2005**, *46*, 1045–1049.

(17) Min, K.; Jakubowski, W.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2006**, *27*, 594–598.

(18) Simms, R. W.; Cunningham, M. F. *Macromolecules* **2007**, *40*, 860–866.

(19) Bombalski, L.; Min, K.; Dong, H. C.; Tang, C. B.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 7429–7432.

(20) Esteves, A. C. C.; Bombalski, L.; Trindade, T.; Matyjaszewski, K.; Barros-Timmons, A. *Small* **2007**, *3*, 1230–1236.

(21) Min, K.; Yu, S.; Lee, H. I.; Mueller, L.; Sheiko, S. S.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 6557–6563.

(22) Dong, H. C.; Mantha, V.; Matyjaszewski, K. *Chem. Mater.* **2009**, *21*, 3965–3972.

(23) Dong, H. C.; Matyjaszewski, K. *Macromolecules* **2010**, *43*, 4623–4628.

(24) Qiu, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2872–2875.

(25) Jousset, S.; Qiu, J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 6641–6648.

(26) Okubo, M.; Minami, H.; Zhou, J. *Colloid Polym. Sci.* **2004**, *282*, 747–752.

(27) Eslami, H.; Zhu, S. P. *Polymer* **2005**, *46*, 5484–5493.

(28) Min, K.; Gao, H. F.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 10521–10526.

(29) Eslami, H.; Zhu, S. P. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1914–1925.

(30) Ahmad, H.; Saito, N.; Kagawa, Y.; Okubo, M. *Langmuir* **2008**, *24*, 688–691.

(31) Min, K.; Gao, H.; Yoon, J. A.; Wu, W.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2009**, *42*, 1597–1603.

(32) Simms, R. W.; Cunningham, M. F. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1628–1634.

(33) Guyot, A.; Tauer, K. *Polym. Synth.* **1994**, *111*, 43–65.

(34) Guyot, A. *Macromol. Symp.* **2002**, *179*, 105–132.

(35) Guyot, A. *Adv. Colloid Interface Sci.* **2004**, *108–09*, 3–22.

(36) Thompson, K. L.; Armes, S. P.; York, D. W.; Burdis, J. A. *Macromolecules* **2010**, *43*, 2169–2177.

(37) Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46*, 8458–8468.

(38) Jakubowski, W.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 4139–4146.

(39) Stoffelbach, F.; Belardi, B.; Santos, J. M. R. C. A.; Tessier, L.; Matyjaszewski, K.; Charleux, B. *Macromolecules* **2007**, *40*, 8813–8816.

(40) Li, W.; Min, K.; Matyjaszewski, K.; Stoffelbach, F.; Charleux, B. *Macromolecules* **2008**, *41*, 6387–6392.

(41) Li, W. W.; Matyjaszewski, K.; Albrecht, K.; Moller, M. *Macromolecules* **2009**, *42*, 8228–8233.

(42) Li, W. W.; Yoon, J. A.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2010**, *132*, 7823–7825.

(43) Stoffelbach, F.; Griffete, N.; Bui, C.; Charleux, B. *Chem. Commun.* **2008**, 4807–4809.

(44) Pham, B. T. T.; Nguyen, D.; Ferguson, C. J.; Hawkett, B. S.; Serelis, A. K.; Such, C. H. *Macromolecules* **2003**, *36*, 8907–8909.

(45) dos Santos, A. M.; Le Bris, T.; Graillat, C.; D'Agosto, F.; Lansalot, M. *Macromolecules* **2009**, *42*, 946–956.

(46) Matahwa, H.; McLeary, J. B.; Sanderson, R. D. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 427–442.

(47) Ferguson, C. J.; Hughes, R. J.; Nguyen, D.; Pham, B. T. T.; Gilbert, R. G.; Serelis, A. K.; Such, C. H.; Hawkett, B. S. *Macromolecules* **2005**, *38*, 2191–2204.

(48) dos Santos, A. M.; Pohn, J.; Lansalot, M.; D'Agosto, F. *Macromol. Rapid Commun.* **2007**, *28*, 1325–1332.

(49) Stoffelbach, F.; Tibiletti, L.; Rieger, J.; Charleux, B. *Macromolecules* **2008**, *41*, 7850–7856.

(50) Rieger, J.; Stoffelbach, F.; Bui, C.; Alaimo, D.; Jerome, C.; Charleux, B. *Macromolecules* **2008**, *41*, 4065–4068.

(51) Rieger, J.; Osterwinter, G.; Bui, C. O.; Stoffelbach, F.; Charleux, B. *Macromolecules* **2009**, *42*, 5518–5525.

(52) Wang, X. G.; Luo, Y. W.; Li, B. G.; Zhu, S. P. *Macromolecules* **2009**, *42*, 6414–6421.

(53) Rieger, J.; Zhang, W. J.; Stoffelbach, F.; Charleux, B. *Macromolecules* **2010**, *43*, 6302–6310.

(54) Wang, Q.; Fu, S. K.; Yu, T. Y. *Prog. Polym. Sci.* **1994**, *19*, 703–753.

(55) Gilbert, R. G. *Emulsion Polymerization: a Mechanistic Approach*; Academic Press: New York, 1995.

(56) Chern, C. S. *Prog. Polym. Sci.* **2006**, *31*, 443–486.

(57) Landfester, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 4488–4507.

(58) Xia, J. H.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2434–2437.

(59) Joynes, D.; Sherrington, D. C. *Polymer* **1996**, *37*, 1453–1462.

(60) Wu, D. X.; Yang, Y. F.; Cheng, X. H.; Liu, L.; Tian, J.; Zhao, H. Y. *Macromolecules* **2006**, *39*, 7513–7519.