PEO-Based Block Copolymers and Homopolymers as Reactive Surfactants for AGET ATRP of Butyl Acrylate in Miniemulsion

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ABSTRACT: Amphiphilic block copolymers poly(ethylene oxide)-*b*-polystyrene (PEO-PS-Br) with various molecular weights and poly(ethylene oxide) homopolymer (PEO-Br) were synthesized and used as macroinitiators and stabilizers (reactive "surfactants") for activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) of *n*-butyl acrylate (BA), in miniemulsion either with or without ethyl 2-bromoisobutyrate (EBiB) as co-initiator. Under both conditions, the reactions were well controlled and stable latexes were formed. In the absence of EBiB, polymer particles with diameter around 120–230 nm were obtained, and the particles contained polymers with molecular weight M_n = 16 000–25 000 g/mol and relatively low polydispersity (M_w/M_n = 1.2–1.4). In the presence of a low molecular weight initiator, EBiB, the amount of surfactant used can be reduced in the reaction (1.7–4 wt % vs monomer). The percent of initiating sites from EBiB was changed from 30% to 90%, and the majority of the obtained polymers were initiated by EBiB. Nevertheless, because of the covalent linking of the surfactants to polymer chains, no free surfactant was left in the reaction system. The final diameter of latexes stabilized by reactive surfactants was around 200–390 nm, the number-average molecular weight M_n of the polymers obtained was 10 000–25 000 g/mol, and the polydispersity index was around 1.2.

Introduction

Controlled/"living" radical polymerizations (CRP) processes,[1–4] such as atom transfer radical polymerization (ATRP),[1] have been extensively studied during the past decade. Through these polymerization techniques, polymers with predetermined molecular weight and narrow molecular weight distribution as well as a variety of compositions, topologies, and well-maintained chain end functionalities have been successfully prepared, either in bulk or in solution.[5–8] There are also some studies that focus on extending ATRP to environmentally friendly aqueous dispersed media, such as miniemulsion process.[9–15] Miniemulsion polymerization starts with stabilized oil droplets with average diameter between 50 and 500 nm dispersed in water.[16,17] Particle nucleation occurs in the monomer droplets, and each droplet turns into a polymeric particle after polymerization. Therefore, when ATRP is conducted in miniemulsion, all components including the initiator, catalyst, and monomers are initially located in the oil droplets. Ideally, mass transfer between particles is limited. Since miniemulsion mimics a "mini-bulk" system, it has been proven as an appropriate media for various CRP processes.

In miniemulsion process, surfactants are used to stabilize the latexes and control the particle size. They play a very important role during the polymerization process and also during the subsequent storage. However, conventional surfactants are physically adsorbed on the polymer particles and may migrate or desorb from the product. To avoid these negative features of conventional surfactants, reactive surfactants have attracted increasing attention.[17,24–29] Reactive surfactants participate in the polymerization process and become constituents of the product. Thus, reactive surfactants are not physically adsorbed but covalently attached to the surfaces of polymer particles. A reactive surfactant can serve as either a (co)polymerizable macromonomer containing reactive double bonds, a macroinitiator, or a transfer agent.[30] Reactive surfactants have already been successfully used when CRP was carried out in miniemulsion or emulsion. For instance, Gilbert et al.[31] used amphiphilic RAFT agents to synthesize a reactive poly(acrylic acid)-*block*-poly(butyl acrylate) diblock macro-RAFT agent, which can self-assemble into micelles in water with the active RAFT end located inside the micelles to continue the polymerization of hydrophobic monomers to produce latexes particles. Manguian et al.[32] and dos Santos et al.[33] reported the use of a hydrophilic macro-RAFT agent for the emulsion polymerization of styrene. Recently, Stoffelbach et al.[34] used an amphiphilic block copolymer poly(ethylene oxide)-*b*-polystyrene diblock copolymer (PEO-*b*-PS) as the stabilizer and macroinitiator for activator generated by electron transfer (AGET) ATRP[11,35] of *n*-butyl methacrylate (BMA), styrene (St), and *n*-butyl acrylate (BA) in miniemulsion.

Herein, we describe amphiphilic block copolymers poly(ethylene oxide)-*b*-polystyrene (PEO-PS-Br) and PEO-Br homopolymer as the stabilizers and macroinitiators for AGET ATRP of BA. We expand the scope of the concept of reactive surfactants in miniemulsion ATRP systems by introducing two new features. The first one is use of low molar mass co-initiator (ethyl 2-bromoisobutyrate, EBiB) together with PEO-PS-Br and PEO-Br macroinitiator, which results in the reduced amount of the reactive surfactants and majority of polymer chains initiated from EBiB. The second one is use of PEO-Br homopolymer, without a PS block, as a reactive surfactant that forms in-situ amphiphilic block copolymer with BA during miniemulsion AGET ATRP.

Experimental Section

Materials. *n*-Butyl acrylate (BA, 99%) and styrene (St, 99%) were purchased from Aldrich, purified by passing through a column filled with basic alumina to remove the inhibitor and/or antioxidant,

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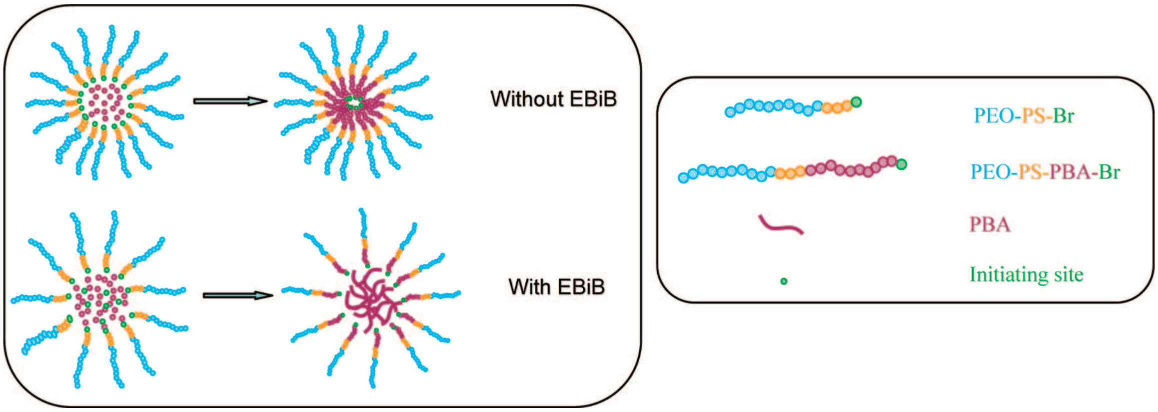
Scheme 1. AGET ATRP of BA in Miniemulsion with PEO-PS-Br as Reactive Surfactants



and then stored at −5 °C. CuBr (98%, Acros) was purified by stirring in acetic acid; it was then filtered, washed with 2-propanol, and then dried in a vacuum. Bis(2-pyridylmethyl)octadecylamine (BPMODA) was synthesized according to the procedure previously published.[36] All other reagents—ethyl 2-bromoisobutyrate (EBiB, 98%), $CuBr_2$ (98%), hexadecane (99%), and L-ascorbic acid (>99%) —and solvents were purchased from Aldrich and used as received.

PEO-Br macroinitiator was prepared by esterification of poly(ethylene glycol) methyl ether (PEO-OH) with 2-bromoisobutyryl bromide (Aldrich, 98%) in the presence of triethylamine in methylene chloride and then chain extended with styrene by ATRP to synthesize PEO-PS-Br block copolymers with various PEO or PS chain lengths (PEO_{44}-PS_{17}-Br: $M_n = 3700$ g/mol, PDI $= M_w/M_n = 1.04$; PEO_{120}-PS_{29}-Br: $M_n = 8200$ g/mol, PDI $= 1.08$; PEO_{120}-PS_{15}-Br: $M_n = 6850$ g/mol, PDI $= 1.05$).

AGET ATRP of BA in Miniemulsion with PEO-PS-Br as Macroinitiator and Stabilizer. PEO-PS-Br block copolymers with various molecular weights (PEO_{44}-PS_{17}-Br, PEO_{120}-PS_{29}-Br, and PEO_{120}-PS_{15}-Br) were used as reactive surfactants for AGET ATRP[11] of BA in miniemulsion. Typically, $CuBr_2$ (0.0012 g, 0.005 mmol) and BPMODA (0.0024 g, 0.005 mmol) are dissolved in BA (0.84 mL, 5.87 mmol) in a round-bottom flask at 60 °C for 1 h. The resulting solution was then cooled to room temperature, and hexadecane (0.027 g) was dissolved in it. PEO_{120}-PS_{15}-Br (0.11 g, 0.013 mmol initiating sites) was dispersed in 8 g of water. The aqueous PEO-PS-Br solution was then added to the organic solution. The resulting mixture was subjected to sonication in an ice bath (Heat Systems Ultrasonics W-385 sonicator; output control set at 8 and duty cycle at 70% for 5 min). The resulting stable miniemulsion was transferred to a Schlenk flask and purged with nitrogen for 30 min before being immersed in an oil bath thermostated at 70 °C. A predeoxygenated aqueous solution of ascorbic acid 0.3 mL (containing 0.002 mmol ascorbic acid) was injected into the miniemulsion to initiate the polymerization.

AGET ATRP of BA in Miniemulsion with PEO-PS-Br as Macroinitiator and Stabilizer and EBiB as Co-initiator. EBiB was used as co-initiator with PEO-PS-Br macroinitiator. The procedure was similar to that described above. Typically, before conducting a miniemulsion polymerization, $CuBr_2$ (0.0095 g, 0.043 mmol) and BPMODA (0.0192 g, 0.043 mmol) were dissolved in BA (2.45 mL, 17.1 mmol) in a round-bottom flask at 60 °C for 1 h. The resulting solution was then cooled to room temperature, and hexadecane costabilizer (0.079 g) and EBiB initiator (14 μL, 0.096 mmol) were added. PEO_{120}-PS_{15}-Br (0.08 g, 0.011 mmol initiating sites) was dispersed in 15 g of water. The aqueous PEO_{120}-PS_{15}-Br solution was then added to the organic solution. The resulting mixture was sonicated for 5 min. The resulting stable miniemulsion was transferred to a Schlenk flask and purged with nitrogen for 30 min before being immersed in an oil bath thermostated at 70 °C. A predeoxygenated aqueous solution of ascorbic acid 0.8 mL (containing 0.017 mmol of ascorbic acid) was injected into the miniemulsion to activate the catalyst and initiate the polymerization. Samples were taken at timed intervals to measure the conversion gravimetrically and to determine the molecular weight by SEC.

PEO_{44}-Br homopolymer was also used as reactive surfactant for AGET ATRP of BA in minemulsion either with or without EBiB as a co-initiator using similar procedures.

Characterization. Molecular weight and polydispersity index were measured by SEC (Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å), with THF 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 THF flow rate. The apparent molecular weights and polydispersity index were determined with a calibration based on linear polystyrene standards using WinGPC 6.0 software from PSS. Latex particle size and size distribution were measured by dynamic light scattering (DLS) on a high-performance particle sizer, model HP5001 from Malvern Instruments, Ltd.

Results and Discussion

Scheme 1 shows AGET ATRP of BA in miniemulsion with amphiphilic block copolymer PEO-PS-Br as stabilizer and macroinitiator in the absence or presence EBiB co-initiator. In the absence of EBiB, with PEO-PS-Br block copolymer as reactive surfactant, pure PEO-PS-PBA triblock copolymer can be obtained. In the presence of EBiB co-initiator, by decreasing the molar ratio of PEO-PS-Br macroinitiator to small initiator EBiB, more polymer chains were initiated by EBiB. However, no free surfactant should be present in the system due to the covalent linking of reactive surfactants to the polymer particles. When PEO-Br was used as initiator for the polymerization, pure PEO-PBA diblock copolymer was obtained in the absence of EBiB. If EBiB was used as co-initiator together with PEO-Br, poly(butyl acrylate) latexes stabilized by amphiphilic block copolymer PEO-PBA would form.

1. PEO-PS-Br with Various Molecular Weights Used as Reactive Surfactants for AGET ATRP of BA in Miniemulsion. As mentioned in the Introduction, an amphiphilic block copolymer PEO-PS-Br has been successfully used as the stabilizer and macroinitiator for miniemulsion AGET ATRP of *n*-butyl methacrylate (BMA), styrene (St), and *n*-butyl acrylate (BA).[34] In that paper, the main focus was the polymerization of BMA. With styrene and BA as monomers, relatively low conversion (less than 25%) was achieved due to the slow polymerization rate.

In this work three block copolymer reactive surfactants, based on either PEO2000 or PEO5000, were synthesized (PEO_{44}-PS_{17}-Br, PEO_{120}-PS_{29}-Br, PEO_{120}-PS_{15}-Br). Each of them was first used as reactive surfactant for ATRP of BA in miniemulsion, without any co-initiator, to examine colloid stability. The target

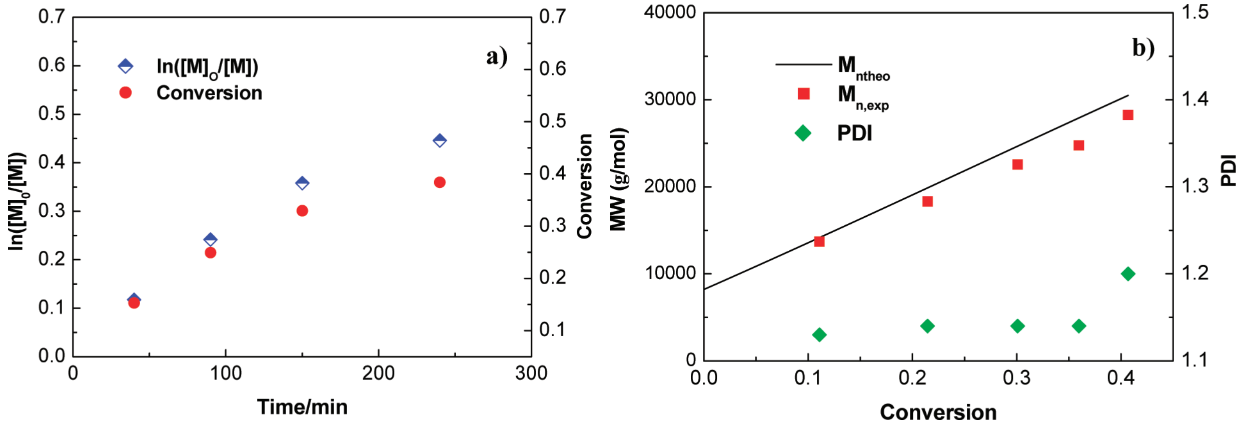


Figure 1. (a) Dependence of BA conversion and ln([M]$_0$/[M]) on reaction time. (b) Dependence of M_n on BA conversions. Polymerization conditions: [BA]:[PEO$_{120}$-PS$_{29}$-Br]:[CuBr$_2$/BPMODA]:[ascorbic acid] = 440:1:0.4:0.16.

Table 1. AGET ATRP of BA in Miniemulsion with EBiB as Co-initiator[a] (Changing Ratio of EBiB to PEO-PS-Br)

sample	reactive surfactant	co-initiator	DP[a]	time/conversion	M_n	PDI	D_n/nm[b]	PSD[b]	solid content[a]
RS1	PEO$_{120}$-PS$_{15}$-Br	EBiB(30%)	440	21.5h/47%	25 000	1.20	230	0.30	0.10
RS2	PEO$_{120}$-PS$_{15}$-Br	EBiB(50%)	440	21 h/54%	24 500	1.20	280	0.30	0.10
RS3	PEO$_{120}$-PS$_{15}$-Br	EBiB(50%)	220	21.5h/74%	21 800	1.20	200	0.28	0.10
RS4	PEO$_{120}$-PS$_{15}$-Br	EBiB(70%)	220	20 h/72%	18 900	1.16	300	0.30	0.10
RS5	PEO$_{120}$-PS$_{15}$-Br	EBiB(90%)	220	22.7h/74%	20 600	1.14	390	0.30	0.12

[a] Polymerization conditions: [BA]:[PEO$_{120}$-PS$_{15}$-Br plus EBiB]:[CuBr$_2$/BPMODA]:[ascorbic acid] = DP:1:0.4:0.16; solid content is based on the 100% monomer conversion, and the amount of hexadecane used is 3.6 wt % based on the amount of monomer used. DP represents degree of polymerization. [b] The average diameter of the polymer particles (D_n) and particle size distribution (PSD) were determined by dynamic light scattering analysis. Linear polystyrene standards were used for THF SEC calibration.

Table 2. AGET ATRP of BA in Miniemulsion with EBiB as Co-initiator[a] (Changing Surfactant)

sample	reactive surfactant	co-initiator	time/conversion	M_n	PDI	D_n[b]/nm	PSD[b]	solid content[a]
RS6	PEO$_{44}$-PS$_{17}$-Br	EBiB	16.8h/89%	14 500	1.12	360	0.11	0.19
RS7	PEO$_{120}$-PS$_{29}$-Br	EBiB	18.4h/73%	13 300	1.14			0.18
RS8	PEO$_{120}$-PS$_{29}$-Br	EBiB	19.5h/53%	9 600	1.15			0.11
RS9	PEO$_{120}$-PS$_{15}$-Br	EBiB	18.6h/74%	13 900	1.20	350	0.25	0.12

[a] Polymerization conditions: [BA]:[reactive surfactant]:[EBiB]:[CuBr$_2$/BPMODA]:[ascorbic acid] = 160:0.1:0.9:0.4:0.16; solid content is based on the 100% monomer conversion, and the amount of hexadecane used is 3.6 wt % based on the amount of monomer used. [b] The average diameter of the polymer particles (D_n) and particle size distribution (PSD) were determined by dynamic light scattering analysis. Linear polystyrene standards were used for THF SEC calibration.

degree of polymerization was set as DP = 440. All these surfactants displayed good colloidal stability with particles diameter around 120−150 nm. For example, with PEO$_{120}$-PS$_{29}$-Br as macroinitiator and stabilizer, monomer conversion reached ca. 40% after 4 h. The first-order kinetic plot was linear, the molecular weight increased smoothly during the polymerization, and the number-average molecular weights M_n were in good agreement with the theoretical values (Figure 1). The average diameter of polymer particles was ca. 120 nm with a particle size distribution of 0.14.

Here PEO-PS-Br reactive surfactant acted as both stabilizer and initiator for the miniemulsion polymerization, which simultaneously affected the size of polymer latexes and degree of polymerization. For instance, if we want to decrease the particle size by using a larger amount of surfactant, the degree of polymerization would also be decreased [a relatively large amount of PEO-PS-Br should be used because all the polymer chains started from PEO-PS-Br macroinitiator (ca. 6−15 wt % vs monomer with targeted DP 440)]. To independently control the number of initiating sites and particle size, and also to reduce the amount of surfactant used, a low molecular weight initiator, EBiB, was used as a co-initiator with PEO-PS-Br macroinitiator in the ATRP miniemulsion polymerization of BA.

The molar ratio of EBiB co-initiator to PEO-PS-Br macroinitiator was changed from 3:7 to 9:1. This way, the amount of reactive surfactant used was gradually decreased and more polymer chains were initiated by EBiB as the ratio of EBiB to PEO-PS-Br increased. Moreover, no free surfactants should remain in the system due to the covalent linking of surfactants to the growing chains. All reactions were well controlled, and stable polymer latexes were obtained. Reaction conditions and results are summarized in Table 1. For instance, with PEO$_{120}$-PS$_{15}$-Br as reactive surfactant and keeping the same targeted degree of polymerization (DP = 220), when the molar ratio of EBiB co-initiator to PEO-PS-Br macroinitiator was increased from 5:5 to 9:1, the average diameter of the latexes increased from 200 to 390 nm, since less surfactant was available to stabilize the polymer particles (samples RS3−5, Table 1). Similar results were observed when we targeted a degree of polymerization of 440 and changed the EBiB to PEO-PS-Br ratio from 3:7 to 5:5 (samples RS1,2, Table 1); the average diameter of the latexes increased from 230 to 280 nm.

In order to examine the effect of reactive surfactants on the polymerization, the miniemulsion experiments using EBiB as a co-initiator were carried out with the other two reactive surfactants (PEO$_{44}$-PS$_{17}$-Br and PEO$_{120}$-PS$_{29}$-Br), with a constant molar ratio of EBiB to PEO-PS-Br set as 9:1. The amount of surfactants used was significantly reduced compared to the reactions in the absence of EBiB. Only 10 mol % of macroinitiator (surfactants) was needed for the same target degree of polymerization, but the latexes remained stable. At the molar ratio of EBiB to PEO-PS-Br 9:1, the majority of the polymer chains should be initiated by EBiB. As previously, reactive surfactants should have been incorporated into the polymer

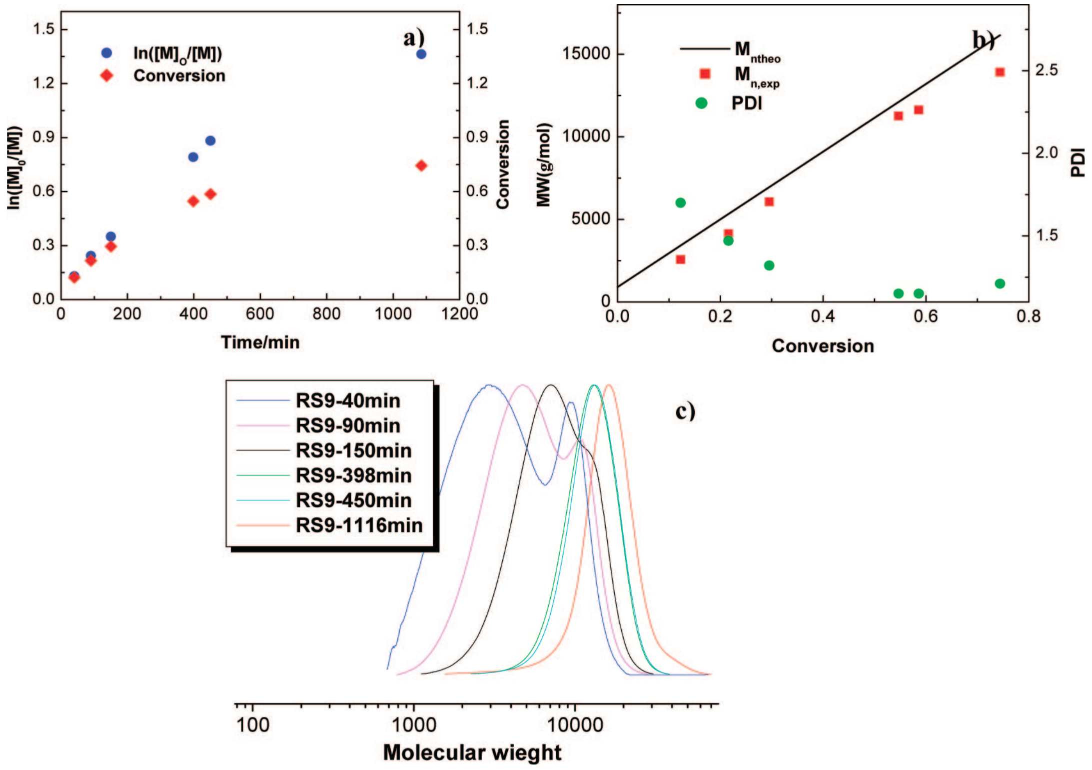


Figure 2. (a) Dependence of BA conversion and ln([M]$_0$/[M]) on reaction time. (b) Dependence of M_n on BA conversions and (c) SEC traces during the polymerization of BA by ATRP. Polymerization conditions: [BA]:[PEO$_{120}$-PS$_{15}$-Br]:[EBiB]:[CuBr$_2$/BPMODA]:[ascorbic acid] = 160:0.1:0.9:0.4:0.16.

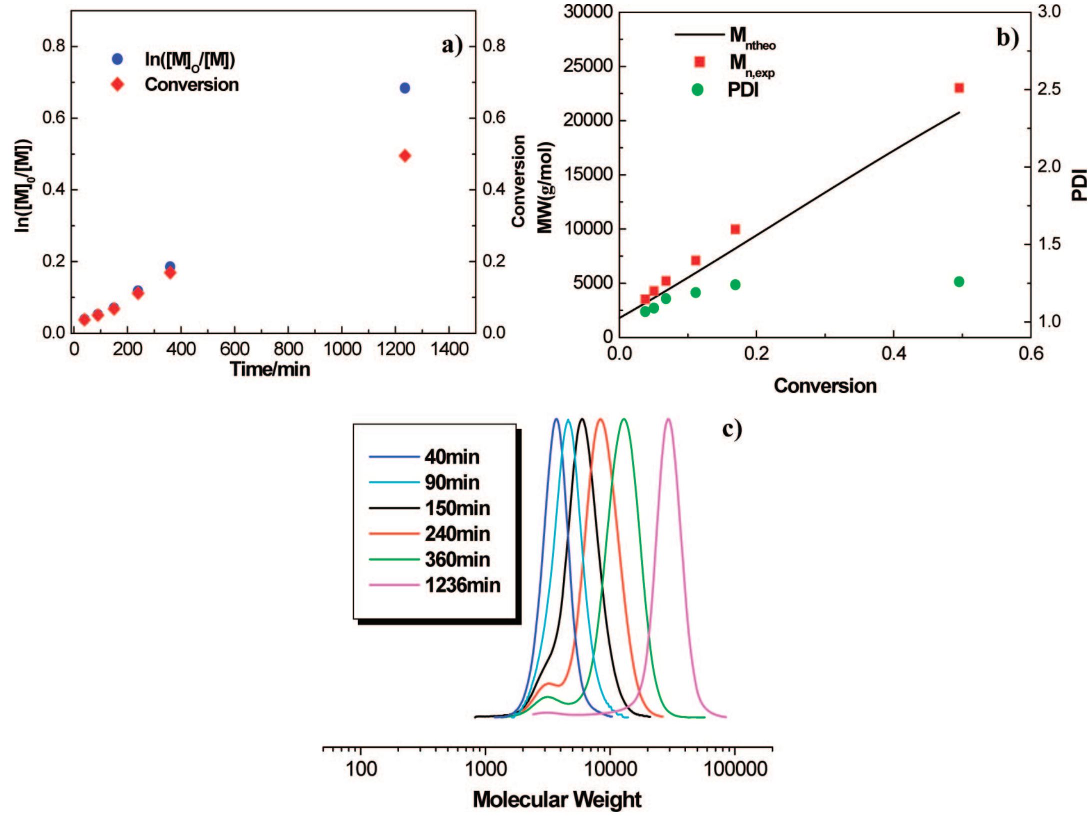


Figure 3. (a) Dependence of BA conversion and ln([M]$_0$/[M]) on reaction time. (b) Dependence of M_n on conversion and (c) SEC traces during the polymerization of BA by ATRP. Polymerization conditions: [BA]:[PEO$_{44}$-Br]:[CuBr$_2$/BPMODA]:[ascorbic acid] = 300:1:0.4:0.16, [hexadecane] = 3.6 wt % based on monomer, 14% solid content and solid content is based on the 100% monomer conversion.

particles during the polymerization. The results are summarized in Table 2.

Each polymerization exhibited a good control. The first-order kinetic plots were nearly linear during the polymerization, and

Table 3. AGET ATRP of BA in Miniemulsion with PEO_{44}-Br as Reactive Surfactant and EBiB as Co-initiator[a]

sample	reactive surfactant	co-initiator	DP[a]	time/conversion	M_n	PDI	D_n/nm[b]	PSD[b]
RS1a	PEO_{44}-Br	EBiB(30%)	220	28h/73%	18 400	1.25	210	0.15
RS2a	PEO_{44}-Br	EBiB(50%)	220	27h/71%	24 500	1.22	230	0.15
RS3a	PEO_{44}-Br	EBiB(80%)	160	28h/77%	15 800	1.15	360	0.30

[a] Polymerization conditions: [BA]:[PEO_{44}-Br plus EBiB]:[$CuBr_2$/BPMODA]:[ascorbic acid] = DP:1:0.4:0.16; solid content is 14% based on the 100% monomer conversion, and the amount of hexadecane used is 3.6 wt % based on the amount of monomer used. DP represents degree of polymerization. [b] The average diameter of the polymer particles (D_n) and particle size distribution (PSD) were determined by dynamic light scattering analysis. Linear polystyrene standards were used for THF SEC calibration.

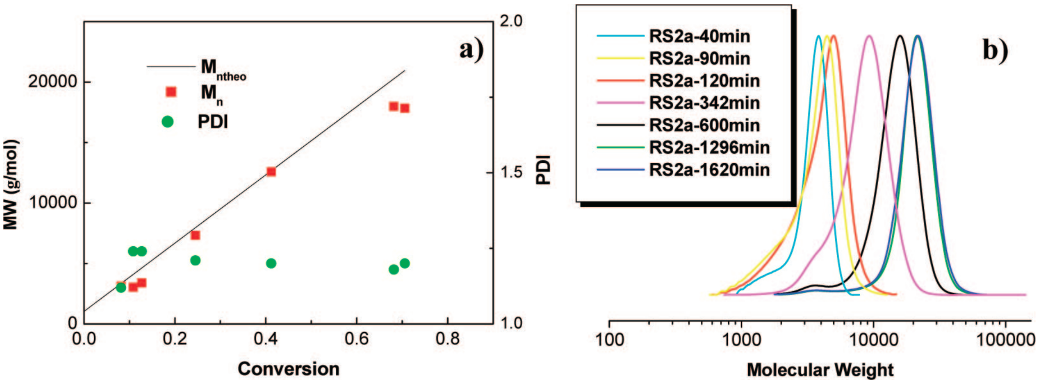


Figure 4. (a) Dependence of M_n on BA conversions and (b) SEC traces during the polymerization of BA by AGET ATRP. Polymerization conditions: [BA]:[PEO_{44}-Br]:[EBiB]:[$CuBr_2$/BPMODA]:[ascorbic acid] = 220:0.5:0.5:0.4:0.16.

the conversion of BA reached 70−90% when the reactions were stopped at ~20 h. Molecular weights increased linearly with conversion and were in good agreement with the theoretical molecular weights, indicating high initiation efficiency. During each of these reactions two peaks were observed in the SEC traces at the beginning of the reaction. The peak appearing at lower molecular weight should represent the polymer chains initiated by EBiB, and the peak appearing at higher molecular weight should result from initiation by the polymeric surfactants PEO-PS-Br. As higher conversions were reached, only one peak was observed in SEC measurement because the polymer chains initiated by PEO-PS-Br had a smaller weight fraction. At the end of the reaction the obtained polymer mainly composed of the polymer chains initiated by EBiB. The PDI of the obtained polymer was low (M_w/M_n ~ 1.1−1.2). Typical results using PEO_{120}-PS_{15}-Br as reactive surfactant and EBiB as co-initiator are shown in Figure 2.

When PEO_{120}-PS_{29}-Br was used as a reactive surfactant in the presence of large amount of EBiB, the formed latexes were less stable. Two peaks were observed by DLS. The colloid stability was slightly improved, when the solid content was decreased from 18% to 11% (samples RS7,8, Table 2). The molecular weight of PS block affected the colloid stability. With the surfactants containing shorter PS chains (PEO_{120}-PS_{15}-Br), the stability was improved and the diameter of the stable latexes particles was ca. 350 nm.

2. PEO-Br Used as Reactive Surfactant for ATRP of BA in Miniemulsion. PEO-PS-Br block copolymers were prepared separately and then used as reactive surfactant. It will be even more convenient to prepare such reactive surfactant in situ from PEO-Br homopolymer. The resulting PEO-PBA-Br amphiphilic block copolymer would continue polymerization and stabilize the polymer latexes even better.

Indeed, the miniemulsion system in the presence of PEO-Br homopolymer was stable at 70 °C for 2 days before polymerization was initiated by adding ascorbic acid (conditions: [BA]:[PEO_{44}-Br]:[$CuBr_2$/BPMODA] = 220:1:0.4, [hexadecane] = 3.6 wt % based on monomer, 14% solid content). The initial diameter of the monomer droplets after sonication was 150 nm with particle size distribution 0.2; this value increased to 175 nm after stirred at 70 °C for 23 h. The system remained stable after stirred at 70 °C for 2 days, with the average diameter of the monomer droplets 195 nm and particle size distribution relatively low, ca. 0.1.

Thus, in a separate experiment, PEO_{44}-Br macroinitiator, i.e., without a PS block, was used directly as reactive surfactant for the miniemulsion AGET ATRP of BA. The polymerization started after Cu(II) species were reduced with ascorbic acid. The initial diameter of monomer droplets increased from 140 to 200 nm, as targeted degree of polymerization (DP) increased from 150 to 300, and the average diameter of final polymer particles increased from 150 to 230 nm, correspondingly. Stable colloids were achieved. Typical results for these polymerizations are presented in Figure 3, with targeted DP set as 300. Despite a slow polymerization, the first-order kinetic plot was linear throughout the reaction and the conversion of BA reached ~50% after 20.6 h. During SEC analysis, some dead PEO chains were observed at the beginning of the reaction. At the end of the reaction, these dead chains were not visible in the SEC traces because of their small weight fraction. Molecular weights increased linearly with conversions during the polymerization and closely matched the calculated theoretical values; PDI was low (~1.2) for the final product (Figure 3).

3. PEO-Br Used as Reactive Surfactant for AGET ATRP of BA in Miniemulsion with EBiB as Co-initiator. Although PEO_{44}-Br worked well as stabilizers for AGET ATRP of BA in miniemulsion, a relatively larger amount of reactive surfactant was needed even with a high targeted DP because PEO_{44}-Br reactive surfactant has to play the roles of both initiator and stabilizer. For instance, for targeted DP = 300, the amount of reactive surfactant used was ca. 4.4 wt % vs monomer, and this value would increase to 8.8 wt % vs monomer for targeted DP = 150. To reduce the amount of reactive surfactant used, EBiB was used as co-initiator with PEO_{44}-Br macroinitiator. The molar ratio of EBiB co-initiator to PEO_{44}-Br macroinitiator was gradually increased from 3:7 to 8:2. When the amount of reactive surfactant used was gradually decreased, colloidal stability still remained. Similarly to previous cases, as the ratio of EBiB to PEO_{44}-Br increased, the relatively larger fraction of polymer chains were initiated by EBiB. Reaction conditions and results are summarized in Table 3. For instance, with targeted DP 220, when the molar ratio of EBiB co-initiator to PEO_{44}-Br macroinitiator was increased from 3:7 to 5:5, the average diameter of the latexes increased from 210 to 230 nm, and the diameter of polymer particles further increased to 360 nm when the EBiB to PEO_{44}-Br ratio increased to 8:2, even with a lower DP (160), due to the lower amount of PEO_{44}-Br used (1.7−4 wt % vs monomer, samples RS1a−3a, Table 3).

Typical results for these polymerization processes are shown in Figure 4, with the molar ratio of EBiB co-initiator to PEO_{44}-Br macroinitiator set as 5:5. The polymerization was stopped after 27 h, at monomer conversion 71%. Molecular weight increased smoothly with conversion during the polymerization process. Compared to the SEC traces in Figure 3 (in the absence of EBiB), polymer chains with relatively low molecular weight could be observed in the SEC traces at the beginning of the polymerization, indicating that some of the polymer chains were initiated by EBiB. But only one peak appeared in the SEC traces when higher conversion was reached. When molecular weight increased to higher values, the influence of initiator on the molecular weight of final product was smaller. PDI of final products was low, ca. 1.2.

Conclusions

AGET ATRP of BA was successfully conducted in miniemulsion with amphiphilic PEO-PS-Br block copolymers or PEO-Br homopolymer as reactive surfactants. Stable polymer latexes with diameter around 120−230 nm containing polymers with number-average molecular weight 16 000−25 000 g/mol and low polydispersity index ($M_w/M_n = 1.2-1.4$) were obtained. EBiB was successfully used as a co-initiator to decrease the amount of surfactant used. In the case of using EBiB, the final diameter of latexes stabilized by reactive surfactants was around 200−390 nm and number-average molecular weight of the polymers obtained was 10 000−25 000 g/mol and polydispersity index was less than 1.3. No free surfactants remained in the final products due to the covalent linking of reactive surfactants to the polymer particles, which also improved the latex stability.

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