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Development of an ab Initio Emulsion Atom Transfer Radical Polymerization: From Microemulsion to Emulsion

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Abstract: Atom transfer radical polymerization (ATRP) has been successfully extended to an ab initio emulsion system using a "two-step" procedure, in which the final emulsion polymerization system was formed by adding monomer to an ongoing microemulsion ATRP. The newly developed AGET (activators generated by electron transfer) initiation technique was employed in the first stage of this ab initio ATRP. It allows using oxidatively stable Cu(II) species that is reduced in situ by ascorbic acid. The surfactant concentration in the final emulsion system was efficiently decreased to ~2 wt % (~10 wt % vs monomer) by decreasing the catalyst concentration and changing the ratio of the monomer added at the microemulsion stage to the monomer added during the second stage. This two-step procedure avoids the necessity of transporting catalysts through the aqueous media during polymerization, resulting in a controlled emulsion polymerization, as evidenced by a linear first-order kinetic plot and formation of a polymer with a relatively narrow molecular weight distribution ($M_w/M_n = 1.2-1.4$). The polymerization typically reached 70−90% monomer conversion in 5−6 h. The resulting polymer had high chain-end functionality and was successfully chain extended to form in situ block copolymers by adding the second monomer to an ongoing emulsion polymerization. The stable latex from the ab initio emulsion ATRP had a particle size ~120 ± 10 nm.

Introduction

Atom transfer radical polymerization (ATRP) has become a versatile polymerization technique since its discovery in 1995.[1,2] In the past decade, ATRP has been extensively studied for preparation of polymers with predetermined molecular weight, narrow molecular weight distribution (low M_w/M_n), high chain-end functionality,[3] and desired molecular architectures.[4−10] Attempts have been made to extend ATRP to more environmentally friendly aqueous dispersed media, due to their economical and environmental importance. However, compared with the well-documented rapid progress of ATRP in both bulk and solution systems, ATRP in aqueous dispersed media has advanced at a slower pace.[11,12] To date, the most successful approach to aqueous dispersed ATRP has been the miniemulsion system, mainly because the polymerization environment is almost identical to that of a bulk system.[13,14] The miniemulsion ATRP process has been successfully applied to the synthesis of numerous well-defined polymers.[15−23]

However, miniemulsion is a less viable approach for large-scale industrial application because it is difficult to operate high shear forces such as sonication or fluidization (which are necessary to form miniemulsion) on large volumes of biphasic liquid mixtures. An ab initio emulsion system (as distinct from miniemulsion) should be easier to manipulate and can provide direct-use latex products. This procedure has been the most desirable aqueous dispersed medium for both academic study and industrial applications. A typical emulsion polymerization starts with a high concentration of monomer-swollen micelles and dispersed monomer droplets (1−20 μm). Particle nucleation

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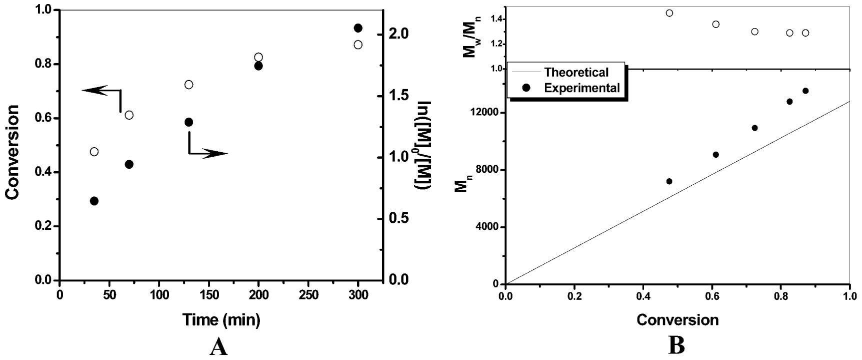

Figure 1. (A) First-order kinetic plot, and (B) molecular weight evolution for AGET ATRP of BA in a microemulsion. [BA]:[EBiB]:[$CuBr_2$]:[BPMODA]:[ascorbic acid] = 100:1:0.5:0.75:0.2, Reaction temp = 80 °C. [Brij 98] = 6.4 wt % (200 wt % vs monomer). Solids content = 9.7% (based on 100% conversion).

occurs when radicals (generated by decomposition of free radical initiators under heating) enter the micelles. As the micelles are depleted of monomer (forming polymerizing particles), the monomer droplets function as a monomer reservoir with monomer diffusing through the aqueous phase to these polymerizing particles. Particles continue to grow until the monomer droplets are depleted. The unique feature of kinetics in emulsion polymerization results from the compartmentalization of the propagating radicals within separate particles, which facilitates a high polymerization rate as well as high molecular weight. Since its implementation more than half a century ago, emulsion polymerization has been the dominant aqueous dispersed polymerization process and has found numerous applications in industry.[24,25]

Relative to the success of ATRP in miniemulsion, little progress has been achieved on ATRP in an ab initio emulsion system. The extension of ATRP to an emulsion system was initially attempted in 1998 and led to a controlled aqueous dispersed polymerization.[26] However, the mechanisms of nucleation and particle growth during the polymerization deviated from a classical emulsion approach. Since direct ATRP was adopted and the oil-soluble initiators and catalysts preferentially stayed in the large droplets, a (mini)suspension polymerization was the more probable process, as demonstrated by the relatively large particle size and broad particle size distribution in the final product. Recently similar approaches were reported, in which results indicating controlled polymerizations were obtained. However, colloidal stability was a serious problem, given the relatively large particle size.[27−30] A true emulsion ATRP was later approached when reverse ATRP was employed to ensure that nucleation did not occur in the monomer droplets.[31] However, most of the oil-soluble catalysts were still initially distributed in the large monomer droplets and were reluctant to diffuse across the aqueous phase to the micelles. Consequently the polymerization was not well regulated, due to insufficient catalyst concentration at polymerization loci, as evidenced by the low initiation efficiency.

In short, ATRP has not yet been successfully implemented in an ab initio emulsion. Prior problems have been attributed to the inefficient transport of Cu-based catalysts from monomer droplets to micelles/polymerizing particles. To overcome this problem, a general two-step ab initio emulsion ATRP was designed as reported in this paper. In the first step, all ATRP initiators, catalysts, and a small amount of monomer were encapsulated in microemulsion micelles.[32] This was accomplished in the absence of any high-shear environment. After activating the catalyst and initiating the reaction, the rest of the monomer was fed to the polymerization system. During the polymerization, the diffusion of monomer from monomer droplets to the polymerizing particles containing the catalyst and growing polymer chains mimicked a normal ab initio emulsion system. Therefore, this two-step procedure successfully avoided the need for transportation of catalysts across the aqueous phase and enabled an ab initio emulsion ATRP system.

Experimental Section

Materials. All chemicals were purchased from Aldrich and used as received unless otherwise stated. *n*-Butyl acrylate (BA, 99%) and styrene (St, 99%) were purified by passing the monomers through the column filled with basic aluminum oxide to remove inhibitor. Bis(2-pyridylmethyl)octadecylamine (BPMODA) was synthesized according to the procedures previously published.[33]

AGET ATRP of BA in Microemulsion. Before conducting a microemulsion polymerization, the Cu(II) complex was prepared by dissolving $CuBr_2$ (7.8 mg, 0.035 mmol) and BPMODA (23.7 mg, 0.053 mmol) in BA (1 mL, 7 mmol) at 60 °C. The initiator, ethyl 2-bromoisobutyrate (EBiB, 10.2 μL, 0.07 mmol), was then dissolved in this complex. The resulting solution was slowly added to an aqueous solution of polyoxyethylene(20) oleyl ether (Brij 98) (30 mL, 0.06 mol·L^{-1}) under stirring to form an optically clear microemulsion. After purging the microemulsion with nitrogen for 30 min, the flask was immersed in an oil bath thermostated at 80 °C. A predeoxygenated aqueous solution (0.5 mL) of ascorbic acid (2.4 mg) was injected into the microemulsion to initiate polymerization. Aliquots were withdrawn at regular intervals to measure the monomer conversion gravimetrically.

AGET ATRP of BA in ab Initio Emulsion. In a typical reaction, a microemulsion ATRP was prepared using the same procedure as described above. Ten minutes after initiation, the predeoxygenated second part of monomer BA (2 mL, 14 mmol) was added to the microemulsion. The ab initio emulsion system was formed in situ.

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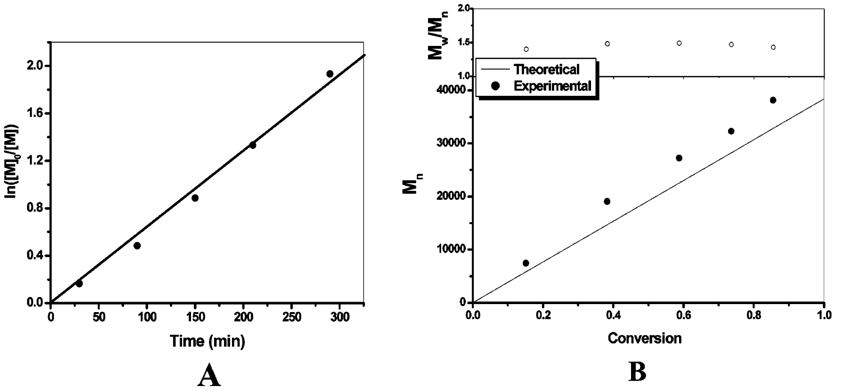

Figure 2. (A) First-order kinetic plot and (B) molecular weight evolution with monomer conversion for AGET ATRP of BA in ab initio emulsion. [BA]:[EBiB]:[$CuBr_2$]:[BPMODA]:[ascorbic acid] = 300:1:0.5:0.75:0.2, 80 °C. [Brij 98]= 6 wt % (75 wt % vs monomer). Solids content = 14% (based on 100% conversion).

Aliquots were withdrawn at regular intervals to measure the monomer conversion gravimetrically.

Block Copolymer Synthesized by AGET ATRP in ab Initio Emulsion. An ab initio emulsion ATRP was initiated using the procedure described above. The second monomer (St) was added to the reaction when the first monomer reached ~50% conversion.

Measurements. Monomer conversion was measured gravimetrically. The molecular weight distribution was measured by Gel Permeation Chromatography (GPC) equipped with an autosampler (Waters, 717 plus), HPLC pump with THF at 1 mL/min (Waters, 515), and four columns (guard, 10^5 Å, 10^3 Å, and 10^2 Å; Polymer Standards Services) in series. Toluene was used as an internal standard. A calibration curve based on linear polySt standards was used in conjunction with a differential refractometer (Waters, 2410). The latex size and size distribution were measured by dynamic light scattering on high performance particle sizer, model HP5001 from Malvern Instruments, Ltd. ^1H NMR was used to determine the chemical composition of copolymers. The ^1H NMR characterizations were performed in $CDCl_3$ on a 300 MHz Bruker spectrometer, using TMS as a standard.

Results and Discussions

To assess the possibility of conducting an ATRP in a standard ab initio emulsion, the prerequisite is to identify whether monomer and catalysts can successfully diffuse from monomer droplets across the aqueous phase to micelles/polymerizing particles. If they cannot be transported, the “emulsion” ATRP either becomes a suspension polymerization, or leads to uncontrolled polymerization, or results in low initiation efficiency. Diffusion of monomer from the monomer droplets to the polymerizing particles has been demonstrated in a conventional ab initio emulsion polymerization. As the monomer is consumed in the polymerizing particles, monomer continuously diffuses from the monomer droplets into the particles to take part in polymerization. Further evidence for the diffusion comes from semi-batch emulsion polymerization, in which only a part of the total monomers is introduced at the beginning of the reaction prior to nucleation. The remainder is added, according to a predetermined schedule, during the course of the polymerization. During this semi-batch emulsion process monomer can constantly transfer across the aqueous phase, as long as polymerization loci remain in the polymerizing particles.

Even if monomer transportation is successful, transportation of catalyst from monomer droplets to polymerizing particles remains the main challenge for standard ab initio emulsion ATRP system. In addition, the catalysts, especially the deactivators (Cu^{II} complexes), may decompose in water by either ligand decomplexation or hydrolysis of Cu−X bonds. To prevent the decomposition of catalysts, strongly hydrophobic ligands are used in ATRP in aqueous dispersed media. Consequently the complexes preferentially stay in the monomer droplets and cannot be transported through aqueous phase to the polymerizing particles. For the above reasons a standard emulsion system is not a viable process for ATRP because only monomer can efficiently diffuse from monomer droplets to polymerizing particles but catalysts cannot.

To solve this problem and to create a viable approach to an ab initio emulsion ATRP system, it was necessary to develop a procedure in which all catalyst components are encapsulated in the nuclei before polymerization is initiated. Then, the monomer can be added after the nucleation/initiation period is completed. The newly developed microemulsion ATRP[32] can be considered as a model of the nucleation step for an ab initio emulsion polymerization procedure. A microemulsion ATRP leads to a microlatex with particle size of 30−40 nm (hydrodynamic diameter), which is comparable to the size of polymerizing particle in an ab initio emulsion polymerization. The microemulsion is formed in the absence of a high-shear environment and is therefore scaleable to industrially viable systems. After a microemulsion polymerization is initiated, the rest of the monomers can be fed to the reaction. Monomer can diffuse into the microlatex to participate in the ongoing polymerization because all catalyst has already been encapsulated in the initially formed microlatex. The polymerization should therefore occur inside the microlatex/polymerizing particles.

Microemulsion ATRP of BA*:* The First Step. The recently developed activators generated by electron transfer (AGET) initiation technique[32,34] facilitates successful ATRP in aqueous dispersed media, because polymerization can easily be started with the oxidatively stable catalyst precursors (Cu(II) species). Furthermore, the polymerization kinetics can be delicately adjusted by tuning the amount of reducing agent. AGET ATRP may not require deoxygenation and can be carried out in the presence of an excess of reducing agent which also acts as a scavenger for oxygen.[35]

ATRP has been successfully carried out in a microemulsion system with the Brij 98 surfactant, resulting in stable translucent

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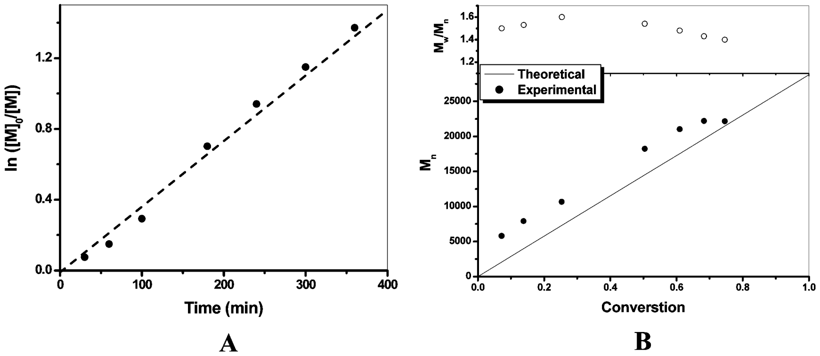
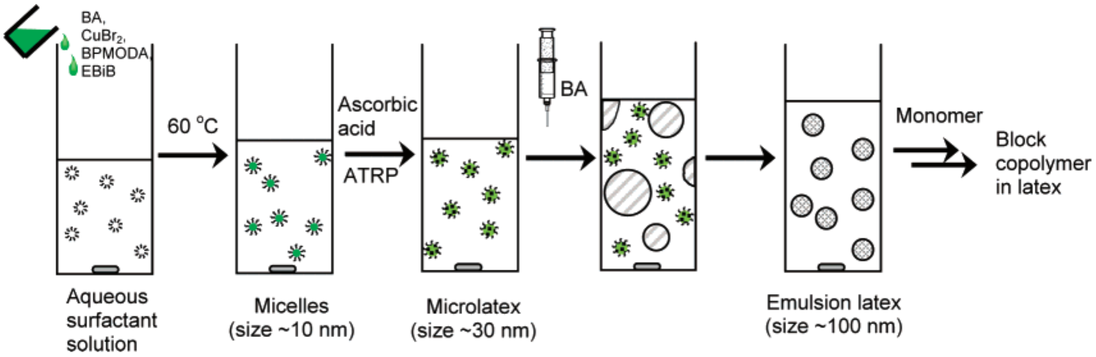


Figure 3. (A) First-order kinetic plot, and (B) molecular weight evolution for AGET ATRP of BA in ab initio emulsion. 80 °C. [BA]:[EBiB]:[$CuBr_2$]:[BPMODA]:[ascorbic acid] = 225:1:0.15:0.22:0.06. [Brij 98] = 2.4 wt % (12 wt % vs monomer). Solids content = 20% (based on 100% conversion).

Scheme 1. Schematic Illustration of ATRP in an ab Initio Emulsion



microlatexes and well-controlled polymerization.[16,32] The ligand BPMODA generates a highly hydrophobic catalyst which suppressed catalyst diffusion to water. An environmentally benign water-soluble reducing agent, ascorbic acid, was selected to efficiently generate activators for AGET ATRP in aqueous dispersed media. Using these strategies, AGET ATRP of BA was successfully carried out in microemulsion. As illustrated by the kinetic plot (Figure 1), a rapid polymerization was obtained, and monomer conversion reached ~30% after 10 min. The experimental molecular weight agreed with theoretical values, indicating high initiation efficiency, and the polymers obtained displayed a narrow molecular weight distribution. Furthermore, the size of the microlatex remained constant at 42 ± 5 nm for the entire microemulsion polymerization. This is an appropriate size for the reaction loci for an ab initio emulsion polymerization.

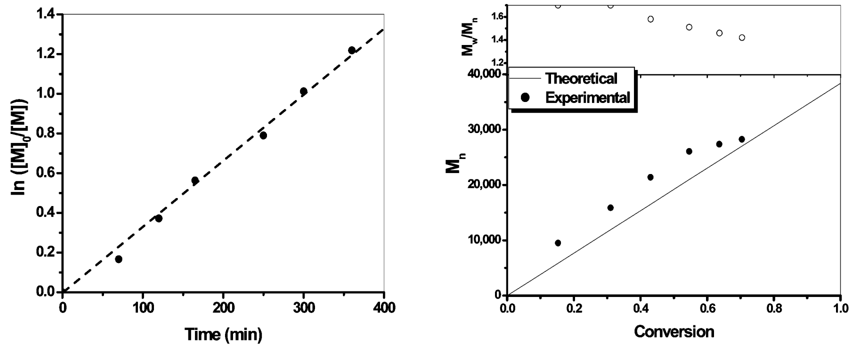
Ab Initio Emulsion ATRP of BA: Two Steps. This microemulsion polymerization was then employed as the first step (nucleation step) in the designed “two-step” procedure to create an ab initio emulsion ATRP. When monomer conversion reached a certain level in the microemulsion polymerization, additional monomer was added to the reaction. The polyBA−Br generated in the initial microemulsion ATRP functioned as a macroinitiator for further emulsion polymerization of additionally added monomer. Because there was no initiator or catalyst in the added monomer, monomer diffused from the droplets to the polymerizing particles. This should be reflected by the continuous monomer conversion and smooth increase of molecular weight. Since Cu-based catalysts were hydrophobic, they remained in the polymerizing particles and mediated ATRP throughout the entire two-step procedure.

An ab initio emulsion ATRP was thereby successfully developed (Scheme 1).

In the initial set of experiments, the degree of polymerization (DP) for the microemulsion polymerization step was set at 100. The monomer conversion reached ~30% after 10 min, when the second batch of monomer (DP = 200) was added to the reaction mixture. In the second stage, the concentration of radicals was constant, as evidenced by a linear first-order kinetics plot (Figure 2A). The degree of control over this ab initio emulsion ATRP was confirmed by the narrow molecular weight distribution of the obtained polymer. The experimental molecular weights were in good agreement with the predicted values (Figure 2B), indicating high initiation efficiency (over 90%). The initiation efficiency was comparable to that from a microemulsion ATRP, which qualitatively proved that no new chains were generated after the addition of the second batch of monomer. High monomer conversion, 87%, was obtained after 5 h. The final latex was stable with particle size ~90 nm.

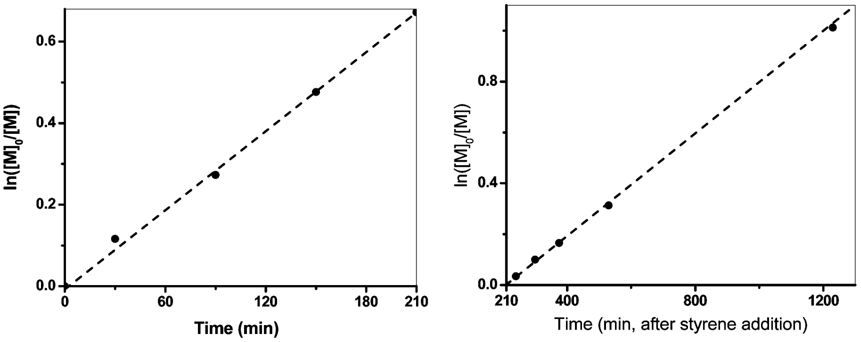
Thus, this two-step ab initio emulsion ATRP proved that a microemulsion ATRP could be successfully transformed into an emulsion polymerization. However, this successful ab initio emulsion ATRP required a relatively high surfactant concentration (~75 wt % vs monomer). The surfactant remained in the latex and could affect the properties of the final product. In commercial latex products prepared by free radical emulsion polymerization, surfactant content is in the range of 1−6 wt % vs monomer. The surfactant concentration is usually higher if a nonionic surfactant is used. Therefore, the additional challenge was to reduce the surfactant concentration to a commercially acceptable level.

Reduced Surfactant Concentration in ab Initio Emulsion ATRP. To reduce the surfactant concentration, the amount of monomer in the microemulsion step should be decreased accordingly, because a stable microemulsion can only be formed when the ratio of surfactant to monomer reaches a high enough



A **B**

Figure 4. (A) First-order kinetic plot, and (B) molecular weight evolution for AGET ATRP of BA in ab initio emulsion. [BA]:[EBiB]:[CuBr$_2$/BPMODA]:[ascorbic acid] = 300:1:0.15:0.22:0.06. [Brij 98]= 2.2 wt % (9.5 wt % vs monomer). Solids content = 26% (based on 100% conversion).



A **B**

Figure 5. First-order kinetic plot for (A) AGET ATRP of BA and (B) for chain extension by adding St in situ at 210 min in an ab initio emulsion. [BA]:[St]: [EBiB]:[CuBr$_2$]:[BPMODA]:[ascorbic acid] = 160:140:1:0.2:0.3:0.008. [Brij 98] = 2.5 wt % (10 wt % vs monomer). Solids content = 26% (based on 100% conversion).

value (e.g., 2:1, as seen in Figure 1). Then, given a decreased amount of monomer in microemulsion ATRP, the amount of catalyst should be decreased as well, since all catalyst (needed to mediate ATRP in both steps) should be added during the microemulsion step, and the catalyst (CuBr$_2$/BPMODA complex) has low solubility in the monomer. Fortunately, some ATRP catalyst is very active; thus, it can effectively mediate ATRP at a low concentration. In the present study the amount of catalyst was reduced to only 15% vs initiator (molar ratio). Hereby, all of the catalyst dissolved completely in the monomer (targeted DP = 15) for microemulsion ATRP, and an optically clear stable microemulsion was formed. Additional monomer (DP = 210) was added to the reaction after the microemulsion polymerization was initiated. Figure 3 shows that a linear first-order kinetic plot was obtained, indicating a controlled polymerization. Monomer conversion reached ~80% after 6 h, and the molecular weights were close to the predicted values. High initiation efficiency, ~90%, was obtained. In this reaction, by reducing the amount of catalysts and the amount of monomer added to the initial microemulsion stage, the surfactant concentration was dramatically decreased to only 12 wt % vs monomer added in the final ab initio emulsion (~2 wt % of the total emulsion). At the same time, the solids content of the emulsion was increased to 20 wt %. This reduction in the concentrations of catalyst and surfactant are significant steps forward toward making the ab initio emulsion ATRP practical for many applications.[36]

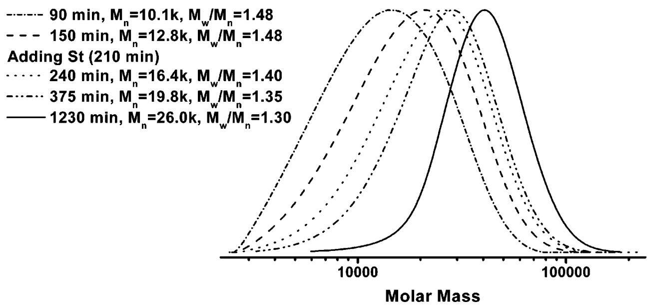


Figure 6. GPC traces of polyBA and polyBA-*co*-polySt (before and after the addition of St) obtained from ab initio emulsion ATRP. Polymerization conditions: see Figure 5.

The surfactant concentration can further be decreased simply by increasing the targeted DP of the second batch of monomer. The polymerization was expected to proceed in a similar way, with a slightly decreased polymerization rate. In the following experiment, the DPs for the two stages of the ab initio emulsion polymerization were set as 15 and 285, respectively (Figure 4). In this way the surfactant concentration was reduced to 9.5% of the weight of monomer and the solids content was increased to 26%. The obtained polymeric latex was stable for more than a month with the latex particle size ~120 ± 10 nm.

Preparation of Block Copolymers in ab Initio Emulsion ATRP. We have demonstrated that a controlled polymerization can be successfully obtained in an ab initio emulsion system. To prove the livingness of the polymerization, i.e. the retention of active chain-end functionality in the polymers generated from the polymerization, a block copolymer was generated in this in

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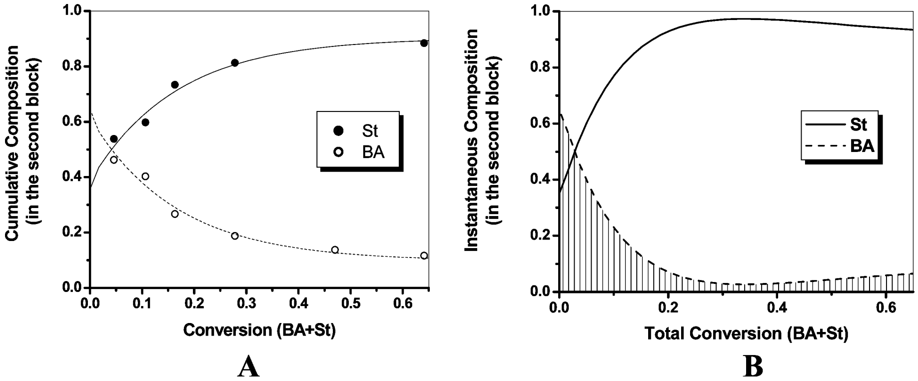

Figure 7. Cumulative (A) and instantaneous (B) compositions of BA and St in the second block of copolymers (after addition of St) obtained from ab initio emulsion ATRP. Polymerization conditions: see Figure 5.

situ system, by adding a second monomer, St, to the active emulsion polymerization. The polyBA formed in the first emulsion polymerization served as the macroinitiator for the polymerization of remaining BA and the added St. Therefore, the final polymer was a block copolymer containing polyBA as the first block and a BA-grad-St gradient copolymer as the second block.

The polymerization was controlled before and after St addition, as evidenced by the two linear first-order kinetic plots (Figure 5). However, the slopes of the two kinetic plots are different, which is attributed to different values of ATRP equilibria and different rate constants of propagation at each stage. After St addition, the GPC traces (see Figure 6) of polymers obtained from the continuous emulsion block copolymerization smoothly moved toward higher molecular weight. No tailing on the GPC curves was observed, indicating no new polymer chains were formed after the addition of St monomer. In other words, all polyBA macroinitiators were successfully chain extended. The chemical composition of the obtained copolymer was analyzed by ^{1}H NMR, suggesting a smooth gradient copolymer formed in the second block. The chemical composition of the second block is shown in Figure 7. The instantaneous composition plot (Figure 7B) shows that during the copolymerization, BA initially reacted with the chain end faster than St, despite the higher reactivity ratio of St in St/BA monomer pair ($r_{\mathrm{St}} = 0.698$, $r_{\mathrm{BA}} = 0.164$).[37] This suggested that St diffused slowly from monomer droplets to the polymeric particles to participate in polymerization. The polymerization of St dominated in the copolymerization because of a higher concentration of St in the polymerizing particles as well as its higher reactivity, as evidenced by the quickly increased composition of St in the second block.

Conclusions

ATRP has been successfully applied to an ab initio emulsion polymerization using a continuous "two-step" procedure, in which the ab initio emulsion was formed by adding monomer to an ongoing microemulsion ATRP. This procedure avoided the need to transport catalysts through the aqueous media during the polymerization and therefore facilitated a controlled ATRP polymerization in the active micelles. In the first step the stable microemulsion was formed without any high-shear forces using oxidatively stable Cu(II) species. The microemulsion started after addition of ascorbic acid as reducing agent to generate Cu(I) via AGET. The surfactant concentration was efficiently decreased to ~2 wt % (~10 wt % vs monomer) by decreasing catalyst concentration and changing the ratio of the monomer added to the microemulsion stage and the monomer added afterward to form the ab initio emulsion. A controlled ab initio emulsion ATRP was obtained, leading to the synthesis of polymers with narrow molecular weight distribution ($M_w/M_n = 1.2-1.4$). The high chain-end functionality of the polymer obtained in this ab initio emulsion was proved by conducting an in situ chain extension to form a block copolymer. The latex formed from the ab initio emulsion ATRP was stable with the particle size 120 ± 10 nm.

The two-step emulsion ATRP procedure, similar to the reported nitroxide-mediated polymerization [38,39] and reversible addition−fragmentation chain transfer polymerization [40,41] in emulsion, provides many options for conducting living/controlled radical polymerization (CRP) in ab initio emulsion and should stimulate the synthesis of new materials by CRP in aqueous dispersed media.

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