Living Radical ab Initio Emulsion Polymerization of *n*-Butyl Acrylate by Reverse Iodine Transfer Polymerization (RITP): Use of Persulfate as Both Initiator and Oxidant

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ABSTRACT: Reverse iodine transfer polymerization (RITP) represents a new straightforward way to prepare controlled macromolecular architectures and relies on the use of molecular iodine (I_2) as control agent. In this work, a one-step ab initio emulsion polymerization of *n*-butyl acrylate in the presence of molecular iodine has been successfully performed with potassium persulfate playing the dual role of radical initiator and oxidant. The polymerization was initiated by potassium persulfate at $T = 85$ °C with sodium 1-hexadecanesulfonate as surfactant, yielding a stable and uncolored latex. The hydrolytically disproportionated iodine was regenerated by potassium persulfate as oxidant (also serving as radical initiator), leading to the expected targeted molecular weight (e.g., butyl acrylate conversion = 99%, $M_{n,theoretical} = 10\,100$ g mol^{-1}, $M_{n,SEC} = 9800$ g mol^{-1}, $M_w/M_n = 1.8$, particle diameter $d_p = 83$ nm with a monomodal particle size distribution). The use of potassium persulfate as both radical initiator and oxidant offers a convenient way to overcome the upward deviation of the molecular weights due to hydrolytic disproportionation of iodine, which was a limitation for the implementation of the RITP process in dispersed aqueous media. The persulfate is able to regenerate iodine, and hence the molecular weight of the polymer chains can be accurately controlled by the concentration of iodine. Furthermore, a poly(butyl acrylate)-*b*-poly(butyl acrylate-*co*-styrene) block copolymer was synthesized in seeded emulsion polymerization, proving the living character of the polymerization.

Introduction

In recent years controlled radical polymerization (CRP) has emerged besides ionic polymerization because of the unique possibility to synthesize complex architectures like block copolymers and graft or star copolymers[1,2] and therefore to gain a better control of the polymer properties. The most extensively studied methods are nitroxide-mediated polymerization (NMP),[3] atom transfer radical polymerization (ATRP),[4] iodine transfer polymerization (ITP),[5] and reversible addition−fragmentation chain transfer polymerization (RAFT/MADIX).[6] All these methods[7] rely on a reversible activation−deactivation of the polymer chains, i.e., an equilibrium between a reservoir of dormant chains (capped polymer chains) and a tiny population of active chains (propagating radicals), and therefore allow all polymer chains to grow at the same rate.

Excellent results were obtained in bulk or solution polymerization, but until now, fewer studies dealt with CRP in dispersed aqueous medium. The implementation of CRP in aqueous medium, largely used in industry, remains a challenge.[8,9] Some reports dealt with aqueous suspension, miniemulsion, or emulsion polymerization by NMP, ATRP, ITP, and RAFT/MADIX, but only a few systems were effective in ab initio emulsion polymerization.[9,10]

RAFT in emulsion polymerization has met problems like loss of colloidal stability, loss over the molecular weight and polydispersity index control, and/or formation of a red oily layer.[11,12] This was attributed to a poor diffusion of the RAFT agent through the aqueous phase and/or the formation of oligomers in the monomer droplets (droplet nucleation). These problems could be overcome by working in miniemulsion,[13,14] by performing seeded emulsion polymerization, or by using multistep procedures. In seeded emulsion polymerization, a highly hydophobic RAFT agent was transported through the aqueous phase to the polymer particles thanks to the addition of acetone as cosolvent, and acetone was then removed by rotary evaporation prior to polymerization.[15,16] A similar system has been developed where the seed particles were prepared by nanoprecipitation of an acetone solution of a macroRAFT agent into an aqueous solution of poly(vinyl alcohol). Acetone was removed by rotary evaporation; the latex was swollen with monomer and then polymerized.[17] Concerning multistep procedures, emulsion polymerization was achieved by using an amphiphatic RAFT agent which can mediate polymerization in both aqueous and organic phases. This RAFT agent was first involved in the aqueous phase polymerization of the water-soluble acrylic acid to a low degree of polymerization.[18,19] This oligomeric $(AA)_x$-RAFT agent was then used in the polymerization of the hydrophobic butyl acrylate, giving micelles (eventually frozen micelles; e.g., formed by copolymer chains that cannot diffuse any more across the continuous aqueous phase) in which the controlled polymerization of butyl acrylate was continued. No surfactant was necessary because the latex was stabilized by the anchored poly(AA) moieties.[18−20] A similar approach was conducted by Manguian et al.,[21] who used a protonated poly(2-(diethylamino)ethyl methacrylate) homopolymer prepared by RAFT as electrosteric stabilizer in the ab initio batch emulsion polymerization of styrene, although in this case the authors did not intend to control the molecular weight of the latex particles. Besides, good control of the molecular weight and a low polydispersity index was obtained for the ab initio RAFT emulsion polymerization of MMA[22] by using the

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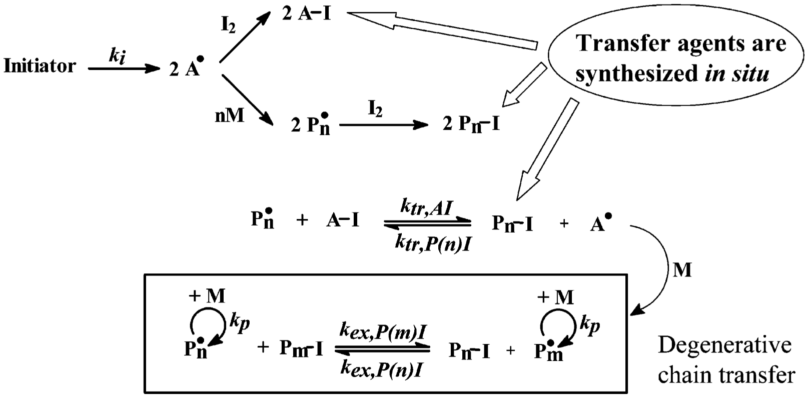
Scheme 1. Simplified Mechanism of Reverse Iodine Transfer Polymerization in Solution[a]



[a] $A^\bullet$ = radical from the initiator, I_2 = molecular iodine, M = monomer unit, and n = number-average degree of polymerization.

traditional emulsion polymerization process but with higher surfactant levels and initiation rates. Last, less reactive MADIX agents were successfully used in ab initio emulsion polymerization of styrene[10] and butyl acrylate.[23]

NMP has given some promising results in ab initio emulsion polymerization. Nitroxide-mediated emulsion polymerizations[24−27] of *n*-butyl acrylate and styrene were performed using monofunctional and difunctional water-soluble alkoxyamine initiators. To favor micellar nucleation instead of droplet nucleation, a multistep process was developed starting with the formation of an ultralow solid content living seed latex from a microemulsion-like system. The rest of the monomer was then added in one shot and polymerized in seeded emulsion polymerization. A good control over the molecular weights was obtained although the particle size distribution was broad. Moreover, a nanoprecipitation technique of an acetone solution of a TEMPO-terminated polystyrene into an aqueous solution of poly(vinyl alcohol) has led to a seed latex. The removal of acetone under vacuum was followed by addition of monomer and polymerization.[28] Like in RAFT, another approach was also possible, based on the prior formation of a hydrosoluble poly(sodium acrylate) macroalkoxyamine, followed by emulsion polymerization of a hydrophobic monomer. The semicontinuous addition of monomer required at the early stages of RAFT emulsion polymerization to avoid droplet nucleation is not necessary with macroalkoxyamine (batch process). The initiator efficiency of the alkoxyamine was however limited to 35% for styrene and 60% for butyl acrylate polymerization.[29,30]

ATRP also encountered many difficulties in emulsion polymerization. A two-step process was recently reported, starting from a microemulsion, which is polymerized and then converted to an emulsion polymerization by continuous addition of monomer.[31] Besides, like in RAFT and NMP, a nanoprecipitation technique has been used to form a seed latex which was swollen with styrene and polymerized by ATRP.[32] However, a slight upward deviation of the molecular weights from the theoretical values has been observed.

Thus, to the best of our knowledge, the most interesting results in RAFT, NMP, and ATRP ab initio emulsion polymerizations were obtained by using multistep procedures, by using preformed water-soluble macromolecular control agents and/or by the continuous addition of monomers.[33] However, until now, none of these methods have fully succeeded in a one-step ab initio batch emulsion polymerization from commercially available compounds.

Considering ITP with iodo-alkyl transfer agents, a bad control over the molecular weights was obtained in ab initio emulsion polymerization of styrene,[34] assigned to the poor diffusion of the transfer agent across the aqueous phase. These problems were overcome in miniemulsion polymerization of styrene,[34−37] seeded emulsion polymerization of *n*-butyl acrylate,[36] and microemulsion copolymerization of vinylidene fluoride with hexafluoropropylene[38] where the diffusion step was bypassed. Besides, suspension polymerization of acrylates[39,40] and vinyl chloride[41] was successfully performed using iodo compounds in competitive single electron transfer/degenerative chain transfer living radical polymerization.

Recently, a new CRP technique, named reverse iodine transfer polymerization (RITP), was developed[42−44] by our group and patented.[45−47] RITP relies on the same degenerative transfer mechanism as ITP but presents the advantage that the transfer agents are synthesized in situ in the reaction medium. For that reason, RITP does not require the synthesis or the storage of transfer agents. Indeed, RITP is based on the use of molecular iodine (I_2) as control agent. In RITP (Scheme 1), the radicals provided by the decomposed initiator react preferably with iodine or propagate with few monomer units before reacting with iodine to form the iodinated transfer agents (A−I and $A-M_n-I$) in situ. Once the whole iodine has been consumed, the core equilibrium of degenerative chain transfer between active and dormant chains takes place. One molecule of iodine will control two polymer chains. So, in this process, the molecular weight of the polymer is controlled by the ratio between the mass of monomer and twice the number of moles of iodine $n_{I_2,\text{initial}}$ (eq 1) (M_{A-I} is the molecular weight of the chain ends):

$$M_{n,\text{targeted}} = (\text{mass of monomer})/(2n_{I_2,\text{initial}}) + M_{A-I} \quad (1)$$

RITP has been successfully applied to a wide range of monomers like acrylates,[43] α-fluoroacrylates,[42,46] styrene,[42,47] MMA,[44] and copolymers of vinylidene chloride and methyl acrylate.[42,45]

Our group polymerized butyl acrylate by RITP in ab initio emulsion polymerization.[48,49] Important side reactions between iodine and water were responsible for an upward deviation of the molecular weight. Nevertheless, molecular weights were efficiently tuned by varying the concentration of iodine. Moreover, the living character of the resulting latex was demonstrated by synthesizing a poly(butyl acrylate)-*b*-poly(butyl acrylate-*co*-styrene) diblock copolymer in seeded emulsion polymerization. It was shown that the side reactions responsible for the upward deviation of the experimental molecular weight consist of hydrolytic disproportionation of iodine to form hydroiodic acid HI and iodate.[50] The experimental molecular weight was in good agreement with the effective amount of iodine.

More recently, the problem of iodine disproportionation was overcome in miniemulsion polymerization of styrene.[51] The disproportionated iodine was regenerated by continuous addition of an aqueous solution of hydrogen peroxide. The molecular weights were efficiently tuned by changing the concentration of iodine. Finally, the living character was demonstrated by a successful chain extension.

Herein, the first results on a one-step ab initio batch emulsion polymerization by controlled radical polymerization from commercially available compounds are reported. The polymerization of butyl acrylate by RITP is initiated by potassium persulfate and stabilized by sodium 1-hexadecanesulfonate. Potassium persulfate, which is a compound largely used at an industrial scale in the latex industry, plays the dual role of the polymerization radical initiator and the oxidant used to regenerate the disproportionated iodine.

Experimental Section

Materials. *n*-Butyl acrylate (BuA, $M = 128.17$ g mol^{-1}, Aldrich, 99%) and styrene ($M = 104.15$ g mol^{-1}, Acros, 99%) were purified by vacuum distillation before use. Iodine (I_2, $M = 253.81$ g mol^{-1}, Aldrich, 99.8%), potassium persulfate (KPS, $K_2S_2O_8$, $M = 270.33$ g mol^{-1}, Aldrich, 99%) Mersolat H40 (Lanxess, 40% aqueous solution), dodecyl sulfate sodium salt (SDS, $M = 288.38$ g mol^{-1}, Aldrich, 98%), and sodium 1-hexadecanesulfonate ($M = 328.49$ g mol^{-1}, Lancaster, 99%) were used as received. α,α′-Azobis-(isobutyronitrile) (AIBN, $M = 164.21$ g mol^{-1}, Fluka, 98%) was purified by recrystallization in methanol. Water was deionized by passing through columns packed with ion exchange resins.

General Procedure for Emulsion Polymerization of BuA. Typically, 120 g of water was placed in a 250 mL glass reactor and thoroughly purged with argon for 30 min. Then, the reactor was thermostated at 85 °C under stirring at 250 rpm. A solution of sodium 1-hexadecanesulfonate (30 mg, 0.09 mmol) in water (10 g) was added in the reactor under argon flow, followed by a solution of I_2 (190 mg, 0.74 mmol) in BuA (15.00 g, 117 mmol). Last, a solution of KPS (907 mg, 3.35 mmol) in 20 g of water was added, and the polymerization proceeded under an argon atmosphere in the absence of light for 8 h. Samples were withdrawn at regular intervals under positive argon flow using a previously degassed syringe. Monomer conversion was determined by gravimetric analysis. Results: butyl acrylate conversion = 99%, $M_{n,th} = 10\,100$ g mol^{-1}, $M_{n,SEC} = 9800$ g mol^{-1}, PDI = 1.8, particle diameter in intensity $d_p = 83$ nm (monomodal), uncolored latex.

Chain Extension. The seed latex was prepared as above: $[BuA]/[K_2S_2O_8]/[I_2] = 156/4.4/1$ ($M_{n,targeted} = 10\,200$ g mol^{-1}). This seed latex (75% monomer conversion) was used to synthesize a block copolymer PBuA-*b*-poly(BuA-*co*-styrene) by seeded emulsion polymerization of styrene. The seed latex (38.92 g) was introduced in a 100 mL glass reactor and purged by argon bubbling for 20 min. Styrene (3.04 g, 29.2 mmol) and a solution of KPS (0.025 g, 0.093 mmol) in 5.53 g of water were added to the seed latex. The latex was stirred for 1 h to allow styrene diffusion, and then the reaction was performed in the dark under an argon atmosphere with magnetic stirring for 6 h at $T = 85$ °C. During the first 30 min, an aqueous solution of Mersolat H40 (0.078 g in 5 mL of water) was injected to stabilize the growing polymer particles and to avoid particle coagulation. Results: monomer conversion = 52%, $M_{n,th} = 13\,800$ g mol^{-1}, $M_{n,SEC} = 15\,900$ g mol^{-1}, PDI = 1.80.

Butyl Acrylate Polymerization by Reverse Iodine Transfer Polymerization (RITP) in Toluene.[43] Butyl acrylate (4.90 g, 38.3 mmol), toluene (10.1 g, 110 mmol), AIBN (0.0615 g, 0.375 mmol), and iodine (0.061 g, 0.24 mmol) were introduced in a Schlenk flask. After three freeze−thaw−pump cycles, the flask was heated at 70 °C in an oil bath for 24 h. The polymerization was conducted in the dark under an argon atmosphere with magnetic stirring. Conversion was determined by ^{1}H NMR analysis on crude samples in $CDCl_3$ (conversion = 75%). Molecular weights were determined by size exclusion chromatography ($M_{n,targeted} = 10\,400$ g mol^{-1}, $M_{n,th} = 7800$ g mol^{-1}, $M_{n,after\ precipitation} = 7800$ g mol^{-1}, PDI = 1.76) on a sample precipitated in methanol.

Characterizations. Size exclusion chromatography (SEC) was performed on dried samples dissolved in tetrahydrofuran, with a Spectra Physics Instruments SP8810 pump equipped with a Shodex RIse-61 refractometer detector, a Milton Roy Ultra-Violet spectrometer detector, and two 300 mm columns thermostated at 30 °C (columns mixed-C PL-gel 5 μm from Polymer Laboratories: $2 \times 10^2 - 2 \times 10^6$ g mol^{-1} molecular weight range). Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL min^{-1}. Calibration was performed with polystyrene standards from Polymer Laboratories, and Mark−Houwink coefficients for polystyrene ($K = 11.4 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.716$)[52] and poly(*n*-BuA) ($K = 12.2 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.700$)[52] were used for the calculations. ^{1}H NMR analyses were performed in $CDCl_3$ on a Bruker Avance 250 MHz spectrometer apparatus. Particle size of the latex (mean diameter of the intensity distribution) was determined with a Nanotrac 250 particle analyzer (Microtrac Inc.). Standard deviation for the particle size (in microns), also known as the graphic standard deviation, is one measure of the width of the distribution given by (84% − 16%)/2. pH measurements were performed with a Consort P500 apparatus from Bioblock Scientific. Iodide concentrations, $[I^-]$, were measured with a PHM 210 standard pH meter from Radiometer Analytical with an iodide selective electrode ISE25I-9 and a reference electrode REF201 from Radiometer Analytical.

Results and Discussion

This work has focused on ab initio emulsion polymerization[53−55] because this is an often used process in industry. The monomer is butyl acrylate, the control agent is iodine, the initiator is potassium persulfate, the temperature of the polymerization was kept constant at $T = 85$ °C, and sodium 1-hexadecanesulfonate was used as the surfactant (critical micelle concentration, cmc = 0.25 g L^{-1}; Krafft point = 47−57 °C). Sodium 1-hexadecanesulfonate was used instead of dodecyl sulfate sodium salt (SDS) because SDS presents a sulfate group which can be hydrolyzed at acidic pH, decreasing the stability of the polymer latex. Sodium 1-hexadecanesulfonate presents a sulfonate group which is resistant at acidic pH.

Previous studies[49,50] have shown that for RITP polymerization in aqueous medium there is an upward deviation of the molecular weight due to the hydrolytic disproportionation of iodine[56,57] in the aqueous phase. Iodine solubility in water represents 1.1×10^{-2} mol L^{-1} at 85 °C.[58] But in the presence of an organic phase (monomer droplets), the iodine concentration in the aqueous phase is much lower since the iodine is preferably located in the monomer droplets ($K = [I_2]_{aq}/[I_2]_{BuA} = 2.03 \times 10^{-3}$ at 25 °C).

Herein, the aqueous iodide I^-_{aq} formed by side reactions (e.g., hydrolytic disproportionation of iodine I_2 in the aqueous phase or hydrolysis of A−I adduct in which A stands for the moiety from the initiator) is oxidized by potassium persulfate (eq 2),[59,60] which also acts as the hydrosoluble polymerization initiator, in the continuous water phase to regenerate iodine I_2. Since one part of the initiator is consumed to regenerate iodine I_2, the excess of initiator over iodine has to be larger than in solution polymerization.

$$S_2O_8^{\ 2-} + 2I^- \rightleftharpoons I_2 + 2SO_4^{\ 2-} \tag{2}$$

The use of other oxidants to regenerate the disproportionated iodine is conceivable. However, in order to ensure that the second oxidant is used to regenerate the hydrolyzed iodine (and therefore that persulfate is available to initiate the polymerization), the standard reduction potential $E°$ of the second oxidant

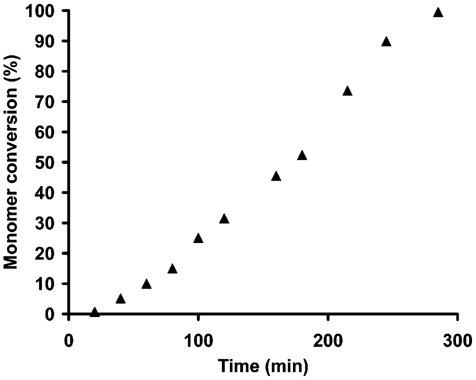


Figure 1. Evolution of monomer conversion (▲) vs time for reverse iodine transfer polymerization of butyl acrylate in ab initio emulsion at $T = 85$ °C using potassium persulfate as both radical initiator and oxidant to regenerate the hydrolyzed iodine ($[K_2S_2O_8]/[I_2] = 4.5$, [sodium 1-hexadecanesulfonate] $=$ 0.8 $\times$ critical micelle concentration, $M_{n,targeted} = 10\,200$ g mol^{-1}).

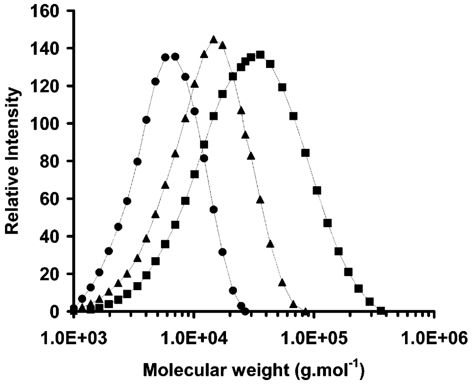


Figure 3. Molecular weight distributions of poly(butyl acrylate) samples prepared by reverse iodine transfer polymerization in ab initio emulsion at $T = 85$ °C using potassium persulfate as both radical initiator and oxidant to regenerate the hydrolyzed iodine ($[K_2S_2O_8]/[I_2] \approx 4.5$, [sodium 1-hexadecanesulfonate] $=$ 0.8 $\times$ critical micelle concentration). Targeted molecular weight: (●) 5200 g mol^{-1}, (▲) 10 200 g mol^{-1}, (■) 20 100 g mol^{-1}.

has to be higher than the reduction potential of persulfate. One has to note that persulfate is one of the strongest oxidants available and therefore that the use of other common oxidants (like hydrogen peroxide) in combination with persulfate is not favorable ($E°_{persulfate} = 2.01$ V $> E°_{H_2O_2} = 1.776$ V).[61] Since persulfate presents a higher reactivity than hydrogen peroxide, persulfate will preferentially react with iodide to regenerate iodine while hydrogen peroxide will not be consumed (or only in a minor extent). The use of a nonoxidant water-soluble radical initiator (like azo-initiators) in combination with an oxidant (like hydrogen peroxide) is conceivable and should allow the control of the polymerization. However, in that case, the advantage of persulfate playing the dual role of initiator and oxidant would be lost.

Kinetics of BuA Polymerization by RITP in ab Initio Emulsion Polymerization. Iodine is known to be a strong radical scavenger. The polymerization can be divided into two separate periods: first, an inhibition period when the formed radicals react preferably with iodine to form the iodinated transfer agents (A$-$I and A$-$M$_n$$-$I) in situ and, then, a polymerization period where propagation takes place (once the whole iodine has been consumed). Figure 1 shows the monomer conversion vs time. Since there is a large excess of initiator over iodine, the inhibition period is very short.

Figure 2a shows that the molecular weight increases smoothly with conversion. During the whole polymerization, polydispersity indexes are around 1.8. At low conversion, the experimental molecular weights are above the theoretical molecular weights (if considering a linear evolution, i.e., a high chain transfer constant which is not the case for butyl acrylate polymerization by degenerative transfer, e.g., $C_{ex} = 2.2$ for RITP of methyl acrylate at $T = 70$ °C).[43] But as the conversion proceeds, the experimental molecular weights tend toward the theoretical line. Moreover, in Figure 2b one can see that even if a slight tailing at low molecular weights is observed, the whole molecular weight distribution is shifted toward higher molecular weights as the conversion proceeds.

Influence of the Iodine Concentration. To check the controlled character of the polymerization, the iodine concentration was varied in order to target different molecular weights. As can be seen in Table 1, the experimental and theoretical molecular weights are rather close. The polydispersity index PDI is in an acceptable range for ab initio emulsion polymerization of butyl acrylate by a degenerative transfer mechanism. Moreover, the RITP experiment (Table 1, run 2a) leads to a much narrower molecular weight distribution than the corresponding reference experiment without iodine but with the same amount of initiator (Table 1, run 2b).

Figure 3 shows the overlay of the molecular weight distributions when changing the iodine concentration. Even if a slight tailing at low molecular weight is observed, the whole molecular weight distribution is shifted toward higher molecular weights when the iodine concentration is decreased.

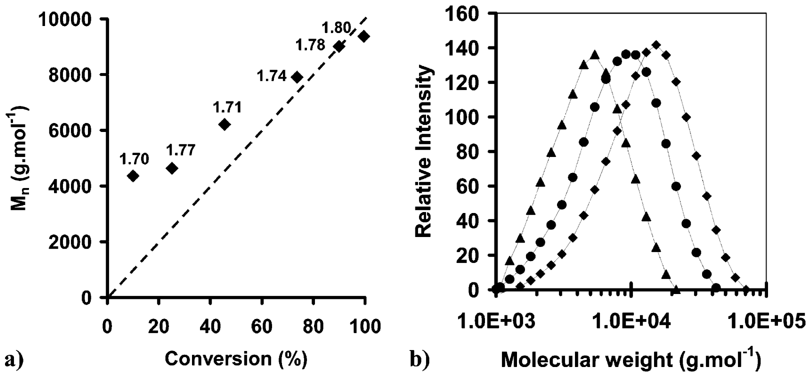


Figure 2. Reverse iodine transfer polymerization of butyl acrylate in ab initio emulsion at $T = 85$ °C using potassium persulfate as both radical initiator and oxidant to regenerate the hydrolyzed iodine ($[K_2S_2O_8]/[I_2] = 4.5$, [sodium 1-hexadecanesulfonate] $=$ 0.8 $\times$ critical micelle concentration, $M_{n,targeted} = 10\,200$ g mol^{-1}). (a) Evolution of molecular weight M_n (◆) and polydispersity index PDI (labels) vs monomer conversion (the dotted line shows the ideal theoretical molecular weight evolution). (b) Evolution of the molecular weight distribution with monomer conversion: (▲) conversion $=$ 10%, (●) conversion $=$ 46%, (◆) conversion $=$ 99%.

Table 1. Effect of Iodine Concentration[a]

run	$[K_2S_2O_8]/[I_2]$	$M_{n,targeted}$ (g mol^{-1})	time (h)	conv (%)[b]	$M_{n,th}$[c] (g mol^{-1})	$M_{n,exp}$ (g mol^{-1})	PDI	d_p (nm)[d]	S_D[e]
1	4.4	5200	17	80	4200	5200	1.52	292	0.072
2a	4.5	10200	8	99	10100	9800	1.80	83	0.019
2b	no iodine	n.a.	4	70	n.a.	4300[f]	7.70	149	0.066
3	4.4	20100	22	86	17300	20500	2.28	111	0.030

[a] Polymerization of butyl acrylate in ab initio emulsion polymerization at $T = 85$ °C in the presence of potassium persulfate as initiator and oxidant to regenerate the hydrolyzed iodine. [b] Conversion determined by gravimetry. [c] $M_{n,theoretical}$ = (mass of monomer) × (monomer conversion)/($2n_{I2}$) + M_{AI} in which $M_{AI} = 223$ g mol^{-1}. [d] d_p = particle diameter. [e] Standard deviation for the particle size. [f] Soluble fraction (microgel formation). n.a. = nonapplicable.

Table 2. Poly(BuA)-*b*-poly(BuA-*co*-styrene) Block Copolymer Synthesis[a]

run	type	time (h)	conv (%)[b]	$M_{n,targeted}$ (g mol^{-1})	$M_{n,th}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	PDI	d_p (nm)[e]	S_D[f]
1	seed PBuA latex	7	75	10 200	7700[c]	7800	1.80	93	0.024
2	block copolymer PBuA-*b*-poly(BuA-*co*-Sty)	6	52	19 300	13 800[d]	15 900	1.80	109	0.027

[a] Block copolymerization in seeded emulsion polymerization of styrene at 85 °C; seed latex (ab initio emulsion): water (150 g), I_2 (0.1923 g, 0.76 mmol), butyl acrylate (15.1 g, 118 mmol), potassium persulfate (0.9 g, 3.33 mmol), sodium 1-hexadecanesulfonate (0.031 g, 0.094 mmol); block copolymerization: seed PBuA-I latex (38.92 g, $M = 7800$ g mol^{-1}, 0.34 mmol), KPS (0.025 g, 0.093 mmol) in 5.53 g of water, styrene (3.04 g, 29.2 mmol) and addition of 0.078 g of Mersolat H40 in 5 mL of water during the first 30 min to avoid particle coagulation. [b] Conversion determined by gravimetry. [c] $M_{n,theoretical}$ = (mass of monomer) × (monomer conversion)/($2n_{I2}$) + M_{AI} in which $M_{AI} = 223$ g mol^{-1}. [d] $M_{n,theoretical}$ = (mass of monomer) × (monomer conversion)/($n_{first\ block}$) + $M_{n,first\ block}$. [e] d_p = particle diameter. [f] Standard deviation for the particle size.

Chain End Stability. In order to check the stability of the iodo chain end in aqueous conditions, an iodine end-capped poly(butyl acrylate) was synthesized by RITP in toluene. The final reaction medium (monomer conversion = 75%) containing the PBuA-I chain transfer agent ($M_{n,SEC} = 7800$ g mol^{-1}, PDI = 1.76) was miniemulsified by ultrasonication (PBuA-I transfer agent (0.978 g, 0.125 mmol), toluene (2.7 g, 29.3 mmol), water (40 g), SDS (0.1 g, 0.35 mmol)). After heating for 16 h at 85 °C, the pH had dropped from 8.53 to 7.80. The decrease of pH corresponds to the formation of 5.16×10^{-10} mol of H^+. This would mean that only 4.13×10^{-4}% of the chain ends have been degraded. This shows that the iodine end-capped poly(butyl acrylate) is very stable in the conditions of the emulsion polymerization (aqueous medium, 85 °C).

Block Copolymerization. A block copolymerization reaction was attempted to check the living character of the poly(BuA) latex. A PBuA latex (conversion = 75%, $M_{n,SEC} = 7800$ g mol^{-1}, PDI = 1.80) was further used as a seed in seeded emulsion polymerization of styrene. The theoretical molecular weight of the block copolymer can be calculated by using eq 3

$$M_{n,theoretical} = M_{n,first\ block} + \frac{m_{monomer}}{n_{PABu-I}} \times \alpha \qquad (3)$$

where $m_{monomer}$ is the mass of styrene and remaining butyl acrylate, $n_{(PBuA-I)}$ is the number of moles of PBuA−I, and α is the conversion of monomer.

A good correlation between the experimental and the theoretical molecular weight was obtained (Table 2). Moreover, the polydispersity index remains the same at 1.80 during the seeded emulsion polymerization of styrene.

In Figure 4, one can see that during the seeded emulsion polymerization of styrene the whole molecular weight distribution is shifted toward higher molecular weights. Moreover, the refractive index and UV signal superpose nicely, showing that almost all polymer chains have integrated styrene units and thus that they present a living character. Furthermore, the number of particles N_p remained almost constant (8.5×10^{15}−9.7×10^{15} particles), indicating that neither significant renucleation nor particle coagulation occurred.

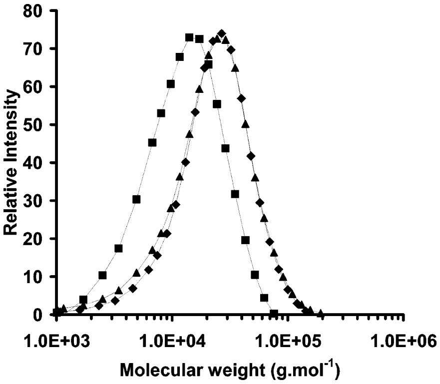


Figure 4. Overlay of the SEC chromatograms of the seed PBuA latex ($[BuA]/[K_2S_2O_8]/[I_2]$ = 156/4.4/1 ($M_{n,targeted}$ = 10 200 g mol^{-1})) (■) and the final copolymer PBuA-*b*-poly(BuA-*co*-styrene) latex with refractive index detector (▲) and UV detector (◆) prepared by seeded emulsion polymerization.

Conclusions

Controlled radical polymerization in a one-step ab initio batch emulsion polymerization is of major interest for the development of CRP methods at an industrial scale. Herein, stable and uncolored poly(butyl acrylate) latexes were obtained by reverse iodine transfer polymerization at 85 °C in a one-step ab initio emulsion polymerization. The careful analysis of the chemistry of iodo compounds in water media allowed us to elaborate an improved RITP procedure to ensure a facile and robust controlled polymerization. Thus, the drawback of iodine I_2 disproportionation and other side reactions forming iodide I^- during RITP in aqueous medium was overcome by using potassium persulfate as both initiator and oxidant to regenerate iodine I_2. This is the first time that an accurate control of the molecular weight has been achieved in ab initio emulsion RITP. Furthermore, a study of the chain-end stability showed that the PBuA−I chain ends were not prone to hydrolysis or degradation in aqueous medium at 85 °C, and the living character of the polymer chains has been confirmed by a successful block copolymerization experiment. Until now, most CRP techniques in ab initio emulsion polymerization required multiple step procedures and/or continuous monomer addition to obtain stable latexes with a good control over the molecular weights. This is the first time that RITP is successfully performed in a one-step ab initio emulsion polymerization using KPS which is largely used in industry, leading to unprecedented high level of control over molecular weights and good livingness to prepare block copolymers.

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Supporting Information Available: Calculation of the number of particles and determination of the ratio $K = [I_2]_{aq}/[I_2]_{BuA}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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