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ARTICLE

Ab Initio Batch Emulsion RAFT Polymerization of Styrene Mediated by Poly(acrylic acid-*b*-styrene) Trithiocarbonate

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ABSTRACT: We report an ab initio emulsion reversible addition−fragmentation chain transfer (RAFT) polymerization of styrene using poly(acrylic acid-*b*-styrene) trithiocarbonate as surfactant and RAFT agent. The system is characteristic of high polymerization rate, controlled polymer molecular weight, and free of coagulum. Design of the amphiphilic RAFT agent is found to be critical for the success. Poly(acrylic acid) neutralization increased the colloidal stability but led to uncontrolled molecular weight development and broad molecular weight distribution, attributed to small size and thus large number of micelles resulting in continuous particle nucleation. Polystyrene with molecular weight up to 120 kg/mol and block styrene−butylacrylate copolymer with well-controlled molecular weight were readily synthesized with this method.

Introduction

Controlled radical polymerization (CRP), including nitroxide-mediated polymerization (NMP),[1] atom transfer radical polymerization (ATRP),[2,3] and reversible addition−fragmentation chain transfer (RAFT)[4] received much attention due to their ability to precisely control polymer chain microstructure such as molecular weight, molecular weight distribution, composition, and composition distribution.[5] Conventional emulsion polymerization has been well recognized as a convenient and green industrial process but lack of precise control over the microstructure. Development of emulsion CRP is therefore of great interest to both academia and industrial practitioners.[6] The radical segregation effect in emulsion offers a useful tool to suppress irreversible radical termination and thus to shorten polymerization time in preparation of high molecular weight polymers.

The segregation effect in (mini)emulsion CRP has been well investigated.[7−14] Only RAFT polymerization has a pronounced rate enhancement resulted from the radical segregation effect. However, CRP in emulsion suffered severe colloidal instability.[15,16] The colloidal instability in RAFT emulsion polymerization was puzzling because the corresponding system without RAFT agent was stable. Low polymerization rate, broad molecular weight, and lack of control over molecular weight were often reported in RAFT emulsion polymerization systems.[15,16] Superswelling in an early nucleation stage is believed to be the reason for colloidal instability.[17,18] CRP miniemulsion has had some success by employing high surfactant and costabilizer concentrations, proper RAFT agent type, and oligomer as mediator.[19] However, ab initio (unseeded) RAFT emulsion polymerization remains to be a great challenge. So far, few ab initio RAFT emulsion polymerization can have all the following characteristics at the same time: high colloidal stability with no coagulum, high polymerization rate with short inhibition period, theoretically predicted number-average molecular weight (M_n), and low polydispersity (PDI). Monteiro et al.[20] carried out an ab initio emulsion polymerization of styrene mediated by small RAFT agent with low C_{tr}. The colloidal system was stable, but the PDI was high due to the low C_{tr}. In an ab initio emulsion polymerization mediated by highly active RAFT agent, colloidal instability, slow polymerization rate with long inhibition period, and uncontrolled polymer molecular weight were often observed.[15,16]

The superswelling of particles in nucleation stage, previously proposed to explain colloidal instability in CRP minimeulsion, has been extended to account for the often-observed colloidal instability in RAFT emulsion polymerization.[18] Ab initio emulsion polymerization of methyl methacrylate mediated by 2-cyanoprop-2-yl dithiobenzoate was realized with high initiator and surfactant concentrations, giving low PDI, predicted M_n, little coagulum, and fast rate, as predicted by the superswelling theory.[18] It was argued that it would be difficult for RAFT agent molecules to transport from monomer droplets to polymer particles (polymerization loci) during stages I and II.[21,22] Gilbert et al.[23−25] hypothesized that the often observed colloidal instability resulted from RAFT polymerization in monomer droplets and carried out experiments with monomer-starving feeding during the nucleation to eliminate monomer droplets. An amphiphilic macro-RAFT agent of acrylic acid and butyl acrylate block copolymer was used, and thus RAFT moieties were in the polymerization loci upon particle formation. A very stable latex was achieved in the case of acrylate polymerization. However, the experimental M_n deviated significantly from the theoretical values. Poly(ethylene oxide)-based amphiphilic macro-RAFT agent was employed in surfactant-free ab initio emulsion polymerization of styrene and butyl acrylate.[26]

In the case of butyl acrylate, the polymerization was very successful. However, the emulsion polymerization of styrene mediated by PEO-RAFT was very slow, reaching only 67% after 22.7 h. Very recently, Monteiro developed a sophisticated nanoreactor method for RAFT polymerization of styrene. A diblock copolymer of poly(*N*-isopropylacrylamide-*b*-dimethylacrylamide) ($\mathrm{P(DMA_{49}}$-*b*-$\mathrm{NIPAM_{106})}$) was used to construct nanoreactors.[27] At room temperature, the block copolymer was water-soluble and mixed with styrene, RAFT agent, and initiator. At polymerization temperature (70 °C), the block copolymer formed

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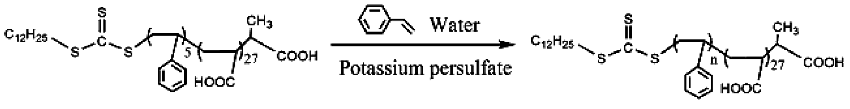
Scheme 1. Scheme of ab Initio Emulsion Polymerization of Styrene Mediated by Poly(acrylic acid)−Polystyrene Macro-RAFT Agent



nanoreactors containing styrene and the RAFT agent because the NIPAM block of the copolymer became water-insoluble. The RAFT agent was carefully designed to match the block copolymer (i.e., low molecular weight PNIPAM$_{18}$-SC(=S)SC$_4$H$_9$), and the PDI of the product (polystyrene with a short end of PNIPAM$_{18}$) was very low. The polymerization rate was fast, and the molecular weight agreed with the predicted one. However, the copolymer/styrene ratio must be higher than 0.1. Otherwise, the system would not give high monomer conversion. The reason was the nanoreactor's inability to hold excess styrene, which might be a challenge for the synthesis of block copolymer. The system is not a typical emulsion polymerization and only effective for those monomers, where polyNIPAM could dissolve at the polymerization temperature. Other ab initio styrene emulsion polymerization systems, including polystyrene-*b*-polyVBTEAC (vinylbenzyltriethylammonium chloride) amphiphilic macro-RAFT agent,[28] polyDEAEMA (diethylaminoethyl methacrylate) hydrophilic macro-RAFT agent,[29] and poly(ethylene oxide)-*b*-polyDEAEMA hydrophilic macro-RAFT agent[30] were also attempted but did not show living characteristics.

So far, a well-controlled ab initio RAFT emulsion polymerization in terms of fast polymerization, predicted molecular weight, low PDI, free coagulum, ease in block copolymer synthesis, and good potential for commercial process development still remains a great challenge. Inspired by the above works, we believe that the ab initio emulsion polymerization of styrene mediated by amphiphilic RAFT agent hold successful promise and hypothesize that the lack of control over molecular weight and slow polymerization rate in the PEO-based amphiphilic macro-RAFT agent system was caused by a continuous and prolonged particle nucleation process. In this work, we investigate the ab initio RAFT emulsion polymerization of styrene using poly(acrylic acid-*b*-styrene) trithiocarbonate, which is carefully designed as both surfactant and RAFT agent.

Experimental Section

Materials. Acrylic acid and styrene were distilled under reduced pressure prior to emulsion polymerization. Butyl acrylate was washed with sodium hydroxide aqueous solution to remove inhibitor. Potassium persulfate (KPS, $>99\%$), 4,4′-azobis(4-cyanopentanoic acid) (V501, $>99\%$), sodium hydroxide (NaOH, $>96\%$), and 1,4-dioxane ($>99\%$) were used without further purification. The small RAFT agent, 2-{[(dodecylsulfanyl)carbonothioyl]sulfanyl}propanoic acid, was synthesized and purified as descried in ref 20.

Synthesis of the Poly(acrylic acid-*b*-styrene) Trithiocarbonate Macro-RAFT Agent. The poly(acrylic acid-*b*-styrene) macro-RAFT agent was synthesized by a two-step solution polymerization. First, a solution containing 1.497 g (4.28×10^{-3} mol) of the small RAFT agent, 0.117 g (4.18×10^{-4} mol) of V501, 9.254 g (0.128 mol) of acrylic acid, and 25 g of dioxane were introduced to a flask, and the reaction proceeded with stirring at 80 °C for 6 h. The flask was then cooled to room temperature, and another solution containing 4.465 g (4.29×10^{-2} mol) of styrene, 0.117 g (4.19×10^{-4} mol) of V501, and 5 g of dioxane was added. The mixture was deoxygenated and reacted for further 12 h at 80 °C. The product (macro-RAFT agent) was collected by precipitation of the mixture in cyclohexane. The macro-RAFT agent was dried under vacuum at 50 °C.

Ab Initio Emulsion Polymerization of Styrene Mediated by Poly(acrylic acid-*b*-styrene) Trithiocarbonate Macro-RAFT Agent. Taking Exp 1 as an example (Scheme 1), 1.072 g (3.81×10^{-4} mol) of the macro-RAFT agent was dissolved in 37.528 g of deionized water without neutralization, and the aqueous pH value was about 2.80. Then, 10.011 g (9.63×10^{-2} mol, 20% solid content based on total latex) of styrene was mixed with the aqueous solution in a 100 mL flask. During 30 min deoxygenation by nitrogen purge, temperature was increased to 70 °C. The initiator potassium persulfate (KPS, 0.021 g, 7.59×10^{-5} mol, in 2.520 g of deionized water) was injected to start the emulsion polymerization. Samples were withdrawn during the process for gravimetric, GPC, and Malvern ZETASIZER analysis.

NMR Analysis. The structure of the macro-RAFT agent was determined by ^{1}H NMR 500 MHz using DMSO as solvent on a BRUKER Avance DMX 500 spectrometer. As shown in Figure 1, ^{1}H NMR signals were assigned as follows (in ppm): 0.86 (3H, $-CH_3$ of $-C_{12}H_{25}$ chain moiety), 1.04 (3H, $-CH_3$ of $-CHCH_3(COOH)$ chain moiety), 1.23 (18H, $-CH_2(CH_2)_9CH_3$ of $-C_{12}H_{25}$ chain), 1.50 ($-C-CH_2-C-$ of PAA−PS chain), 2.20 ($-CH(COOH)-$ of PAA chain), 6.9 ($-Ph-H$ of PS chain), 12.2 ($-COOH$ of PAA chain), 1.76, 3.57 (H of impurities dioxane). The signals at 0.86 ppm (3H, $-CH_3$ of $-C_{12}H_{25}$ chain moiety) was used to estimate the composition. The macro-RAFT agent had 27 acrylic acid units (12.2 ppm, 28 H, which contain one H from the small RAFT agent) and 5 styrene units (6.9 ppm, 25 H). The yield of macro-RAFT agent was 79% calculated by ^{1}H NMR and gravimetric analysis.

pH Value Monitor. The pH value of the aqueous phase was detected by a pH-meter (LEICI PHS-2C). The electrode type was E201-4.

GPC Analysis. Number-average molecular weight (M_n), weight-average moleculaer weight (M_w), and PDI (M_w/M_n) were measured by gel permeation chromatography (Waters 1525 binary HPLC pump, Waters 2414 refractive index detector, Waters 717 autosampler). UV 311 signals were detected by Waters 2487 dual λ absorbance detector. The samples were dried in a vacuum oven at 120 °C for 2 h and then dissolved in tetrahydrofuran, which contained 2 wt % 1 M sulfate aqueous solution to mask COOH group interactions with GPC columns.[31] The eluent was tetrahydrofuran with a flow rate of 1.0 mL/min, and the measured temperature was 30 °C. Depending on the molecular weight, two sets of Waters Styragel column (HR 4, 3, 1 (the measure range is 500 000−100) and HR 5, 4, 3 (the measure range is 4 000 000−500)) were used. The molecular weights and PDI were derived from a calibration curve based on narrow polystyrene standards.

Particle Size Analysis. The number-average particle size D_n, volume average particle size D_v, and distributions were measured by a Malvern ZETASIZER 3000 HAS at 25 °C. The samples were dried in vacuum at 30 °C for 2 h to remove residual monomer. The number of particles, N_p, was calculated by $N_p = 6m/\pi D_v^3 d_p$, in which m is the polymer mass in gram (g_{latex}^{-1}), d_p is polystyrene density, 1.05 g cm^{-3}, and D_v is the particle diameter measured by Malvern.

Potentiometric Titration. Potentiometric titration was measured as in ref 32. The titration was operated with stirring at 25 °C in a vessel containing 100 mL of 0.09 wt % macro-RAFT agent solution. NaOH 1.00 M solution was used. pH-meter (LEICI PHS-2C) with an electrode (E201-4) was used to monitor pH value. A period of 45 s was allowed to ensure equilibrium before recording pH value. The degree of neutralization of $-COOH$ group was calculated by the follow equation:

$$\alpha = \frac{[NaOH]+[H^+]-[OH^-]}{C_{COOH}}$$

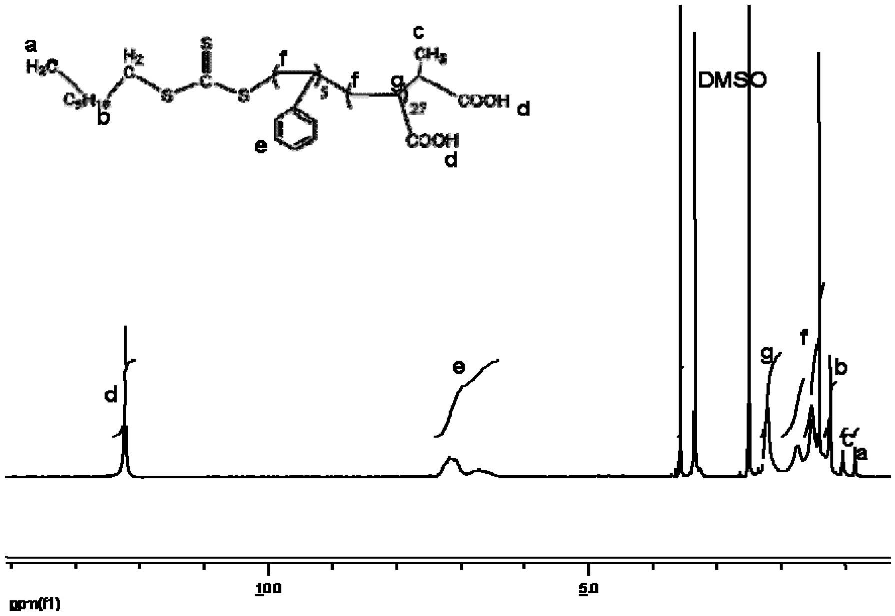


Figure 1. ^{1}H NMR spectrum of poly(acrylic acid-*b*-styrene) macro-RAFT agent.

in which α is the degree of neutralization and [NaOH], [H^+], and [OH^-] are the molar concentrations of added NaOH, H^+, and OH^-. C_{COOH} is the total concentration of acrylic acid groups of macro-RAFT. [H^+] and [OH^-] were calculated from pH value.

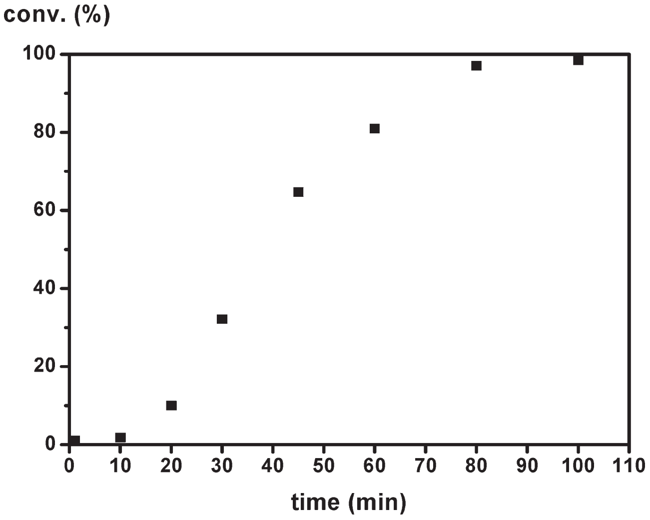


Figure 2. Conversion versus polymerization time plot in Exp 1. [KPS]:[RAFT] was 1:5, pH value of aqueous phase was 2.80, solid content was 20%, and the reaction temperature was 70 °C.

Results and Discussion

Emulsion Polymerization of Styrene Mediated by the Macro-RAFT Agent. The amphiphilic macro-RAFT agent reported in the literature, for example AA_5-*b*-BA_{20}[24,25] (AA for acrylic acid and BA for butyl acrylate), was often hydrophobic and required neutralization with NaOH in order to dissolve in aqueous phase prior to polymerization. The hydrophilic head of the macro-RAFT molecule is fully ionized and is thus large in size due to strong electrostatic repulsion. A low number of such amphiphilic surfactant molecules is required to form a micelle, and therefore a high number of micelles is generated which possibly prolongs the nucleation period. In the present, the structure of macro-RAFT agent was designed as AA_{27}-*b*-St_5 macro-RAFT (St for styrene). Because of the high AA/St ratio, the macro-RAFT agent readily dissolved in aqueous phase without neutralization.

In Exp 1, styrene, the RAFT agent, and initiator were charged in one pot, and no AA units of the macro-RAFT agent was neutralized. At the completion of polymerization, a stable latex was obtained with negligible amount of coagulum. As shown in Figure 2, the complete conversion was achieved within 80 min, including a 15 min inhibition period. The inhibition was probably caused by radical transfer to poly(acrylic acid)[33] or termination of radicals derived from R group in the aqueous phase. After the inhibition period, the polymerization rate rapidly increased, remained constant in the 20%–65% conversion range, and then decreased, similar to conventional emulsion polymerization. After polymerization, the final particle diameter was about 100 nm, and the particle number (N_p) was estimated 3.7×10^{17} /L, as shown in Figure 3. The number of particles decreased at the early stage of polymerization and leveled off at 32% conversion. Considering that the first sample had the particle diameter about 14 nm, similar to that prior to the addition of initiator, they were most likely actual micelles. It must be pointed out that due to hydrophilic shell of the RAFT agents, N_p data of the first two points could be significant underestimated. During the nucleation process, some micelles were disassociated to stabilize the growth of particles, leading to the decrease in their number (the total of micelles and particles). Different from high molecular weight amphiphilic block polymer, the cmc values of the current RAFT agents without neutralization are high, experimentally estimated as 0.25 mM/L. The nucleated particles could therefore remain stable by absorbing the RAFT agent surfactant, as in a conventional emulsion polymerization of styrene. The nucleation period was long last until 30% conversion, and N_p remained constant after 30 min. Figure 4 presents the number-fraction and volume-fraction particle size distributions. It is clear that the distribution was narrow, and no small size particles (< 20 nm) were observed.

The polymerization of styrene was well controlled as shown in Figure 5. The PDI experienced an initial increase followed by a decrease at high conversion, reaching 1.28 at 100% conversion. This observation was in excellent

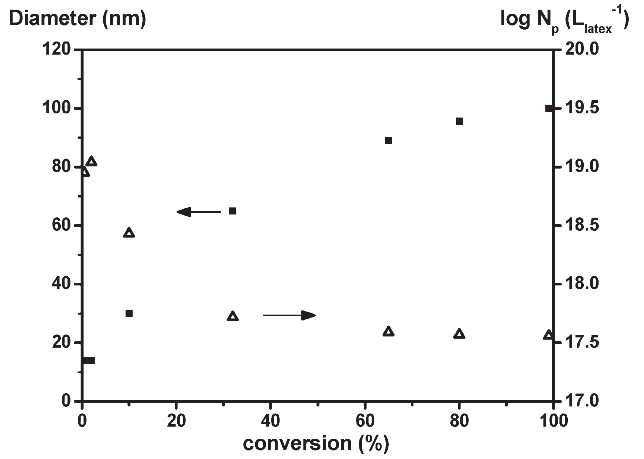


Figure 3. Particle diameter determined by Malvern ZETASIZER and particle number vs conversion in Exp 1. [KPS]:[RAFT] was 1:5, pH value of aqueous phase was 2.80, solid content was 20%, and the reaction temperature was 70 °C.

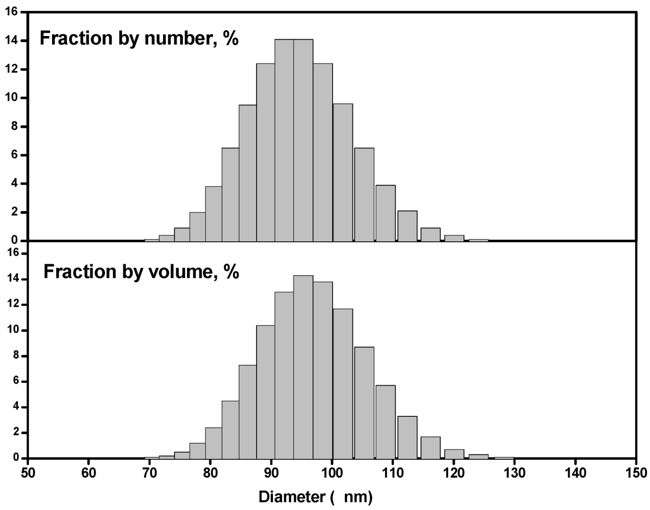


Figure 4. Histograms by number and volume for final sample in Exp 1. [KPS]:[RAFT] was 1:5, pH value of aqueous phase was 2.80, solid content was 20%, and the reaction temperature was 70 °C.

agreement with the nucleation process. As evident in Figure 6, during the nucleation process (< 32%), only those polymer chains in the nucleated particles were able to grow, which broadened the molecular weight distribution. Upon completion of the nucleation period, the growth of polymer chains in later-born particles was faster than that in earlier-born counterparts due to the compartmentalization effect.[8] As a result, PDI decreased continuously. Exp 1 clearly followed the mechanism of ab initio emulsion polymerization.

In Exp 2, NaOH equivalent of 14 out of 27 carboxylic units of the macro-RAFT agent was added to neutralize −COOH groups prior to polymerization. Stable latex was obtained at the completion of polymerization. As shown in Figure 7, the complete conversion was achieved within 100 min, and the inhibition period was extended to 30 min. The inhibition period lasted longer than that without neutralization because charge repulsion significantly increased with neutralization, which might increase the possibility of radical transfer to poly(acrylic acid).[33] In contrast to the case without neutralization, the polymerization rate steadily increased all the time, indicating that new particles were continuously generated during the whole course of polymerization. However, Figure 8 shows that N_p decreased very slowly during the whole polymerization process, in sharp contrast to that of Figure 3. It is very likely that the un-nucleated micelles also contributed to the measured N_p value. The final particle size was about 45 nm, smaller than 100 nm in Exp 1 and, the final

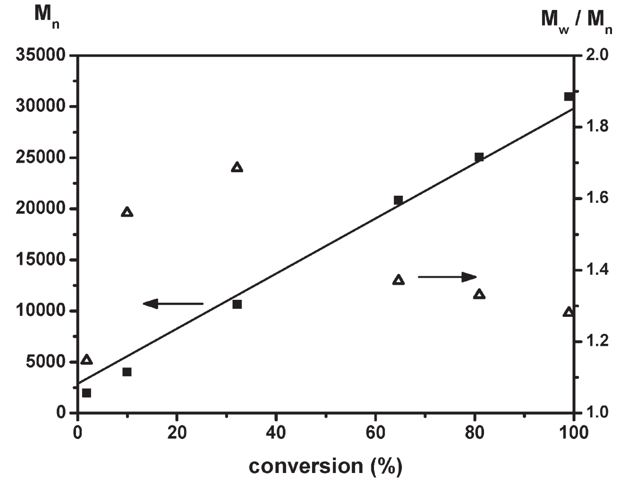


Figure 5. M_n and PDI determined by GPC (relative to styrene standards) with conversion in Exp 1. The straight line corresponds to the theoretical M_n with conversion. [KPS]:[RAFT] was 1:5, pH value of aqueous phase was 2.80, solid content was 20%, and the reaction temperature was 70 °C.

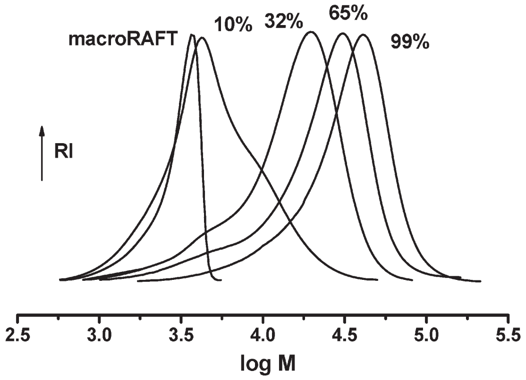


Figure 6. GPC curve evolution of the polymer samples collected at different conversions in Exp 1. [KPS]:[RAFT] was 1:5, pH value of aqueous phase was 2.80, solid content was 20%, and the reaction temperature was 70 °C.

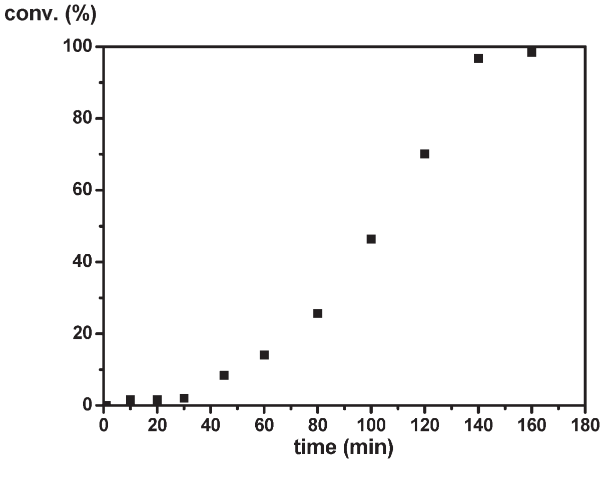


Figure 7. Conversion versus polymerization time plot in Exp 2. [KPS]:[RAFT] was 1:5, initial pH value of aqueous phase was 6.29, solid content was 20%, and the reaction temperature was 70 °C.

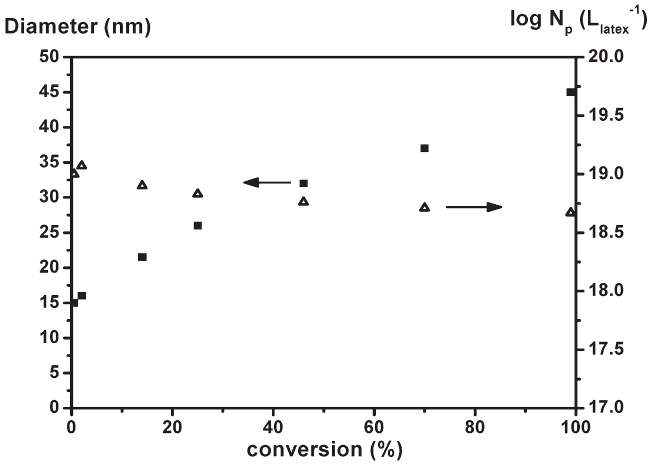


Figure 8. Particle diameter determined by Malvern ZETASIZER and particle number vs conversion in Exp 2. [KPS]:[RAFT] was 1:5, initial pH value of aqueous phase was 6.29, solid content was 20%, and the reaction temperature was 70 °C.

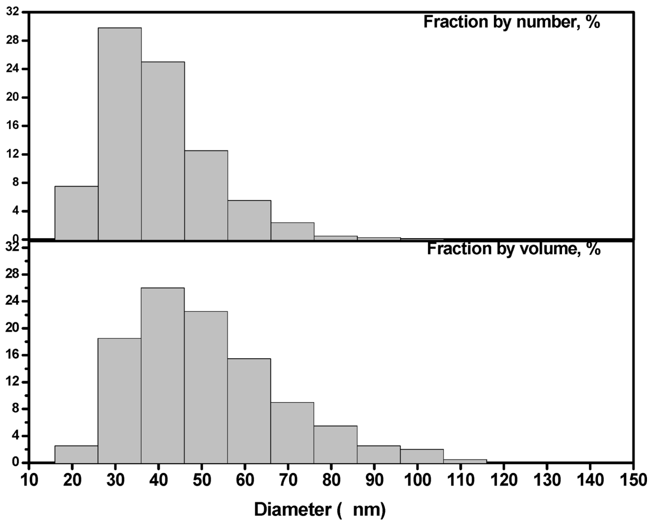


Figure 9. Histogram by number and volume for final sample in Exp 2. [KPS]:[RAFT] was 1:5, initial pH value of aqueous phase was 6.29, solid content was 20%, and the reaction temperature was 70 °C.

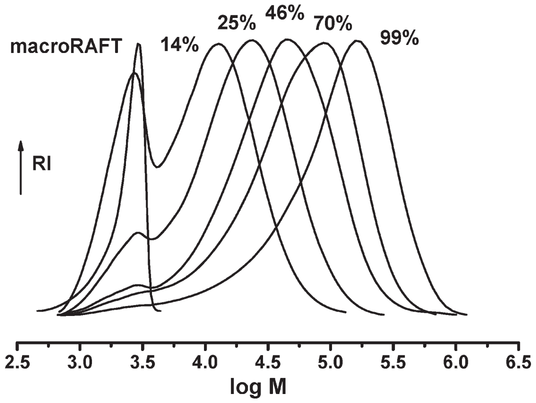


Figure 10. GPC curve evolution of polymer formed at different conversions in Exp 2. [KPS]:[RAFT] was 1:5, initial pH value of aqueous phase was 6.29, solid content was 20%, and the reaction temperature was 70 °C.

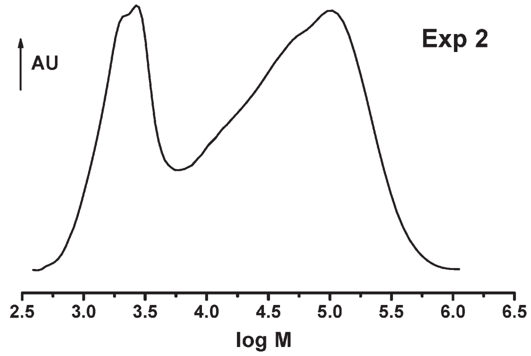


Figure 11. UV 311 GPC chromatogram of the polymer from Exp 2 at complete conversion. [KPS]:[RAFT] was 1:5, initial pH value of aqueous phase was 6.29, solid content was 20%, and the reaction temperature was 70 °C.

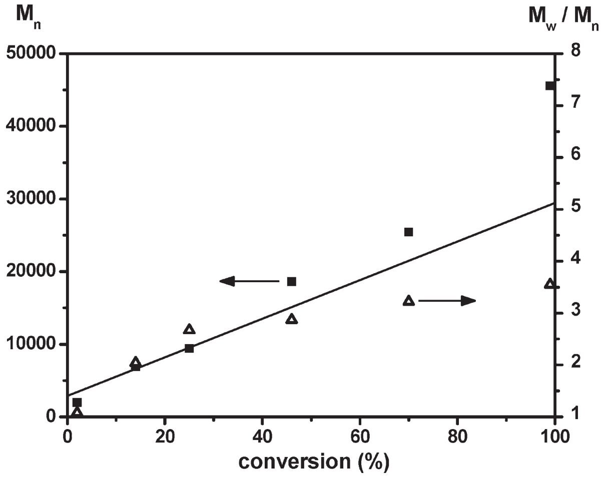


Figure 12. M_n and PDI determined by GPC (relative to styrene standards) with conversion in Exp 2. The straight line represents the theoretical M_n. [KPS]:[RAFT] was 1:5, initial pH value of aqueous phase was 6.29, solid content was 20%, and the reaction temperature was 70 °C.

N_p value was estimated 4.3×10^{18}/L, 10 times higher than that in Exp 1 (3.7×10^{17} /L). The number-fraction and volume-fraction histograms of the final sample are shown in Figure 9. Unlike Exp 1, the particle size distributions were broad, and there still existed a small fraction of "particles" with diameters about 20 nm. It is evident from the GPC chromatograms in Figure 10 that the original macro-RAFT agent peak disappeared gradually, and a small shoulder peak remained until the complete conversion. Figure 11 shows the GPC curves collected from a UV 311 nm detector, providing some insight into the trithiocarbonate RAFT group distribution. The data revealed that a noticeable fraction of the macro-RAFT agents were not involved in the polymerization even in the final sample, suggesting the presence of some micelles consistent with the particle size distribution data shown in Figure 9. It is estimated from N_p data that only about half of the original micelles disappeared during the polymerization, which was contrary to the situation without neutralization. As observed in Figure 12, the molecular weight became increasingly higher than the theoretical M_n value with conversion. PDI was much higher than that without neutralization, increased steadily during the whole course of polymerization, and finally reached 3.55 at the complete conversion.

Figure 13 compares the GPC curves of the final polymer samples obtained in Exp 1 and Exp 2. They were very different. The molecular weight of the main peak in Exp2 was higher than in Exp1. An observable shoulder peak of the

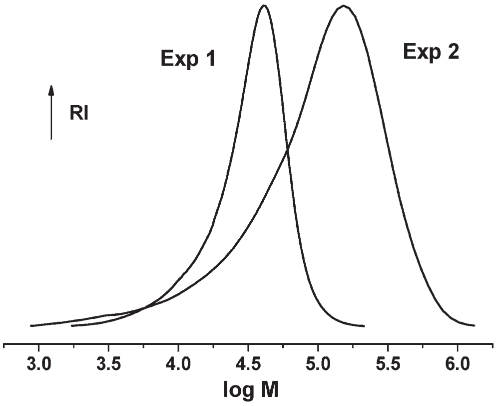
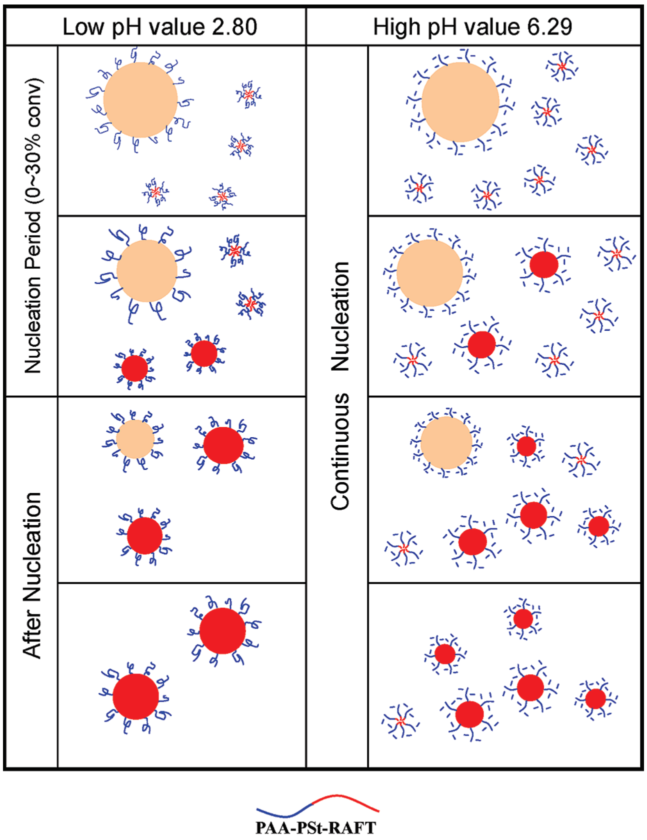


Figure 13. GPC chromatograms of the polymers at complete conversion from Exp1 and Exp2. Exp1: initial pH value of aqueous phase was 2.80. Exp2: initial pH value of aqueous phase was 6.29.

Scheme 2. Initial pH Value Effect on Polymerization[a]



[a] The particle size in this scheme was inconsistent with the actual size.

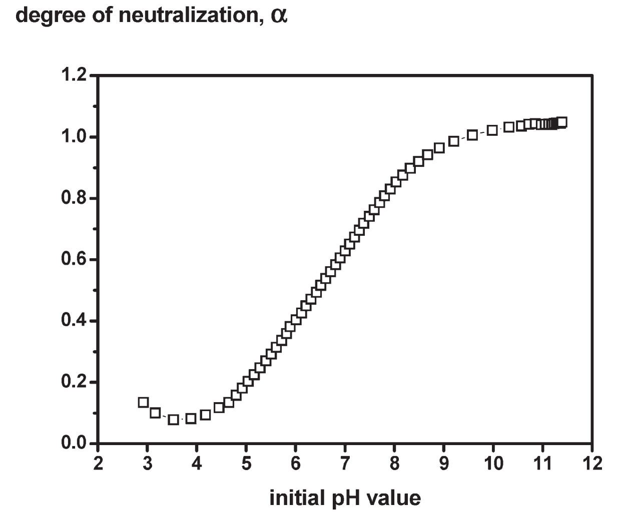


Figure 14. Degree of neutralization, α, vs initial pH value for 0.1 wt % AA−St−macro-RAFT agent solution.

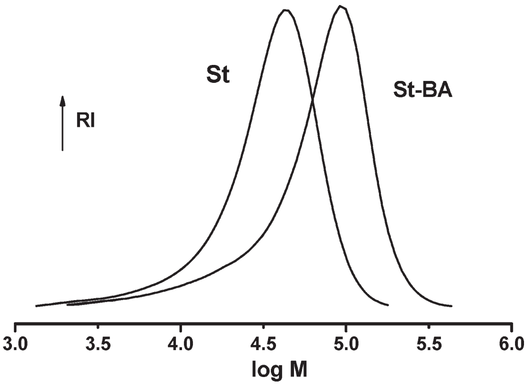


Figure 15. GPC chromatograms of the polymers in Exp 11. Left: latex before BA addition. Right: latex after BA addition. [KPS]:[RAFT] was 1:5, initial pH value of aqueous phase was 2.80, solid content was 20%, and the reaction temperature was 70 °C.

original macro-RAFT agent appeared in the Exp2 GPC curve.

Scheme 2 illustrates how the initial pH value affects the polymerization process. The polymerization mediated by poly(acrylic acid-*b*-styrene) trithiocarbonate without neutralization proceeded in a manner typical of emulsion polymerization. However, with neutralization, the surface area covered by the macro-RAFT agent molecules increased greatly due to the strong static electronic repulsion caused by the dissociation of −COOH groups in the hydrophilic corona. Each micelle was composed of fewer macro-RAFT agent molecules. The neutralized system contained more micelles and thus higher N_p. The number of micelles was so large that the micelles could not be totally consumed in the polymerization, as in the case of microemulsion polymerization. This led to a very broad molecular weight distribution and molecular weight higher than the theoretically predicted, as reported in the literature.[25]

Three more experiments were designed to further study the effect of neutralization with different NaOH amounts added prior to polymerization (Exp 3−5, referred to Table 1). Different levels of coagulation occurred in Exp 3 and Exp 4, but the molecular weights agreed with their theoretical values and PDI remained low. Stable latex of small particle diameter (46 nm) and large N_p (4.4×10^{18} /L) was obtained in Exp 5, but with unpredicted molecular weight and broad PDI observed as in Exp 2. The pH values after neutralization were recorded in Table 1. Figure 14 shows the relationship between the degree of neutralization and the initial pH values, obtained by pH titration. When pH $<$ 5, as in Exp 3 and Exp 4, the degree of neutralization did not increase significantly as the pH value increased. The situations of Exp 3 and 4 were similar to that of Exp 1, as suggested by the molecular weight and PDI data. Different from the colloidal instability we often observed in RAFT emulsion polymerization, the formation of coagulum in Exp 3 and 4 was probably due to the coalescence caused by NaOH addition (electrolyte effect). To test this hypothesis, NaCl (equivalent to NaOH in mole in Exp 4) was added in Exp 6. Exp 4 and Exp 6 gave almost the same results. When pH $>$ 5, the degree

Table 1. Effect of the Initial pH Values on ab Initio Emulsion Polymerization of Styrene Mediated by AA_{27}−St_5−Macro-RAFT Agent

experiment[a]	initial pH values	NaOH:AA[b]	time (min)	conv[c] (%)	$M_{n,th}$[d] (g mol^{-1})	$M_{n,exp}$ (g mol^{-1})	PDI (M_w/M_n)	coagulum[e] (%)
Exp 1	2.80	0:27	80	98	29 800	30 900	1.28	
Exp 2	6.29	14:27	100	99	30 000	45 500	3.55	
Exp 3	3.90	1:27	80	98	30 500	32 800	1.32	1.06
Exp 4	4.21	2:27	100	99	30 200	31 500	1.33	2.58
Exp 5	5.30	7:27	100	95	28 500	43 200	3.50	
Exp 6[f]	2.80	0:27	80	96	28 900	27 900	1.25	2.80

[a] All the experiments (Exp 1−6) used KPS (1:5 [RAFT]) as initiator, and the theoretical M_n was about 30 000 g/mol. The reaction temperature was kept at 70 °C. In Exp 2−5, NaOH was added to the aqueous phase to adjust pH value before polymerization. [b] The molar ratio of added NaOH over acrylic acid of macro-RAFT agent. [c] The monomer conversion was measured by gravimetry. [d] The theoretical M_n values were calculated from $M_{n,theo} = M_{n,RAFT} + M_{n,monomer} \cdot x[M]/[RAFT]$, where [M] and [RAFT] represent the monomer and macro-RAFT agent concentrations, and x is the conversion. [e] The percent coagulum in Exp 3, Exp 4, and Exp 6 was calculated based on the total polymer mass. [f] In Exp 6, NaCl (the mole concentration of NaCl was kept as the same as NaOH used in Exp 4) was added to the aqueous phase before polymerization.

Table 2. Synthesis of High Molecular Weight Polystyrene by ab Initio Emulsion Polymerization Mediated by AA−St−Macro-RAFT Agent with and without Postaddition of NaOH Solution

experiment[a]	time (min)	conv[b] (%)	time (conv) of postaddition of NaOH (min (%))	$M_{n,th}$[c] (g mol^{-1})	$M_{n,exp}$ (g mol^{-1})	PDI (M_w/M_n)	coagulum[d] (%)
Exp 7	105	99		62 500	63 900	1.38	3.69
Exp 8	100	99	30 (13)	63 000	68 700	1.41	
Exp 9	135	73[e]		89 176[e]	128 400	1.43	27.30
Exp 10	100	99	37 (15)	121 200	127 000	1.45	

[a] All the experiments (Exp 7−10) used KPS (1:5 [RAFT]) as initiator, and all the initial pH values were about 2.80 without neutralization. The reaction temperature was kept at 70 °C. The theoretical M_n was about 60 kg/mol in Exp 7 and Exp 8 and 120 kg/mol in Exp 9 and Exp 10. In Exp 8 and Exp 10, postaddition of NaOH solution was used. [b] The monomer conversion was measured by gravimetry. [c] Theoretical M_n at the obtained monomer conversion. [d] The percent coagulum in Exp 7 and Exp 9 was calculated based on the total polymer mass. [e] In Exp 9, 27.30 wt % coagulum was collected at the complete conversion (such a large amount of coagulum probably affected gravimetry and contributed to the large deviation of M_n).

of neutralization increased quickly with the initial pH value. Therefore, Exp 5 gave good colloidal stability because of high charge repulsion, and the resulting molecular weight and PDI were similar to those of Exp 2.

Synthesis of High Molecular Weight Polystyrene. Another challenge of CRP is to prepare high molecular weight polymer samples. We raised the targeted molecular weight to 60 kg/mol in Exp 7 and 120 kg/mol in Exp 9. As summarized in Table 2, without neutralization, a significant amount of coagulum (3.8 wt % in Exp 7 and 27.3 wt % in Exp 9) was observed, though the molecular weight agreed with theoretical values and PDI was low. Similar to Exp 3 and 4, the coagulum was caused by the coalescence because of the high styrene to macro-RAFT agent ratio. Postaddition of NaOH aqueous solution was employed to solve this problem. After the polymerization proceeded for some time and reached certain conversion (13% in Exp 8 and 15% in Exp 10), a syringe of NaOH aqueous solution (equivalent of 6 −COOH units of macro-RAFT) was added to the system to increase the surface charge of particles. Good colloidal stability was achieved in Exp 8 and Exp 10 with controlled molecular weight and low PDI.

Synthesis of Styrene−Butyl Acrylate Block Copolymer. Styrene−butyl acrylate (BA) diblock copolymer was synthesized in Exp 11, as shown in Table 3. The first block polystyrene was synthesized as in Exp 1. When the polymerization proceeded to 70 min, NaOH solution (the molar ratio of added NaOH over acrylic acid of macro-RAFT agent was 6:27) was added, and the second monomer BA was added at 16.8 mL/h rate for 20 min. The polymerization reacted for another 40 min to reach complete conversion. Figure 15 shows the GPC chromatograms of polystyrene and polystyrene−poly(butyl acrylate) copolymer. The block copolymer was synthesized as designed.

Table 3. Synthesis of Polystyrene−Poly(butyl acrylate) Diblock Copolymer by ab Initio Emulsion Polymerization Mediated by AA−St−Macro-RAFT Agent

experiment	time (min)	conv (%)	$M_{n,th}$[d] (g mol^{-1})	$M_{n,exp}$ (g mol^{-1})	PDI (M_w/M_n)
Exp 11[a]	70	98[b]	31 500	33 000	1.33
	130	97[c]	61 000	65 500	1.41

[a] Exp 11 used KPS (1:5 [RAFT]) as initiator and the initial pH value was about 2.80 without neutralization. The reaction temperature was kept at 70 °C. Final solid content was kept at 20%. At 70 min, a syringe of NaOH solution was inserted and the second monomer BA was added at 16.8 mL/h for 20 min. [b] Styrene conversion. [c] Total monomer conversion. [d] Theoretical M_n.

Conclusion

We demonstrated a successful ab initio RAFT emulsion polymerization of styrene using poly(acrylic acid-*b*-styrene) trithiocarbonate as both surfactant and RAFT agent. pH value was found to play a critical role for a success. The influence of pH was twofold: A high-degree dissociation of poly(acrylic acid-*b*-styrene) trithiocarbonate was helpful to protect colloids from coalescence. However, it also extended duration of the nucleation process, leading to a broad molecular weight distribution and deviation of molecular weight from the theoretically predicted. With a targeted molecular weight of 30 kg/mol, the polymerization mediated by poly(acrylic acid-*b*-styrene) trithiocarbonate without neutralization was very successful in terms of high polymerization rate, predicted molecular weight, narrow molecular weight distribution, and little coagulum. The polymerization proceeded in a manner typical of emulsion polymerization with the nucleation ended at 30% conversion. The PDI increased significantly in the nucleation stage but decreased quickly to 1.28 at the end of the stage. However, when pH was increased to 3.9 and 4.2, some coagulum appeared, though molecular weight agreed with the theoretical and PDI remained low, due to colloidal coalescence caused by NaOH addition. When pH was further increased to 5.3, no coagulum was formed but molecular weight became much higher than the theoretical and PDI reached 3.5. The nucleation process appeared to last for the entire course of polymerization. At the end of polymerization, there were still some original RAFT agent molecules left unreacted. When the target molecular weight was >60 kg/mol, the amount of coagulum increase dramatically. Postadding NaOH was effective in limiting the coagulum and stabilizing the latex system.

Polystyrene with molecular weight as high as 120 kg/mol and block copolymer of styrene and butyl acrylate with well-controlled block lengths were also synthesized. This simple approach developed in the present work yielded surfactant-free and stable latex products. The short chain AA content accounted for only 1.5 wt % of the total polymer in Exp 10. The approach could be extended to other monomers. This approach has good promise for commercial applications of RAFT polymerization.

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References and Notes

(1) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688.
(2) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990.
(3) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3745.
(4) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.
(5) Sun, X.; Luo, Y.; Wang, R.; Li, B.; Liu, B.; Zhu, S. *Macromolecules* **2007**, *40*, 849–859.
(6) Oh, J. K. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6983–7001.
(7) Butte, A.; Storti, G.; Morbidelli, M. *Macromolecules* **2001**, *34*, 5885–5896.
(8) Luo, Y.; Wang, R.; Yang, L.; Yu, B.; Li, B.; Zhu, S. *Macromolecules* **2006**, *39*, 1328–1337.
(9) Zetterlund, P. B.; Kagawa, Y.; Okubo, M. *Chem. Rev.* **2008**, *108*, 3747–3794.
(10) Zetterlund, P. B.; Okubo, M. *Macromolecules* **2006**, *39*, 8959–8967.
(11) Kagawa, Y.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromol. Theory Simul.* **2006**, *15*, 608–613.
(12) Maehata, H.; Buragina, C.; Cunningham, M.; Keoshkerian, B. *Macromolecules* **2007**, *40*, 7126–7131.
(13) Delaittre, G.; Charleux, B. *Macromolecules* **2008**, *41*, 2361–2367.
(14) Simms, R. W.; Cunningham, M. F. *Macromolecules* **2008**, *41*, 5148–5155.
(15) Monteiro, M. J.; Hodgson, M.; De Brouwer, H. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2837–2847.
(16) Cunningham, M. F. *Prog. Polym. Sci.* **2008**, *33*, 365–398.
(17) Luo, Y.; Tsavalas, J.; Schork, F. J. *Macromolecules* **2001**, *34*, 5501–5507.
(18) Luo, Y.; Cui, X. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2837–2847.
(19) De Brouwer, H.; Tsavalas, J. G.; Schork, F. J.; Monteiro, M. J. *Macromolecules* **2000**, *33*, 9239–9246.
(20) Monteiro, M. J.; De Barbeyrac, J. *Macromolecules* **2001**, *34*, 4416–4423.
(21) Monteiro, M. J.; Hodgson, M.; De Brouwer, H. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3864–3874.
(22) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2002**, *35*, 5417–5425.
(23) Save, M.; Guillaneuf, Y.; Gilbert, R. G. *Aust. J. Chem.* **2006**, *59*, 693–711.
(24) Ferguson, C. J.; Hughes, R. J.; Pham, B. T. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2002**, *35*, 9243–9245.
(25) 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.
(26) Rieger, J.; Stoffelbach, F.; Bui, C.; Alaimo, D.; Jerome, C.; Charleux, B. *Macromolecules* **2008**, *41*, 4065–4068.
(27) Urbani, C. N.; Monteiro, M. J. *Macromolecules* **2009**, *42*, 3884−3886.
(28) Save, M.; Manguian, M.; Chassenieux, C.; Charleux, B. *Macromolecules* **2005**, *38*, 280–289.
(29) Manguian, M.; Save, M.; Charleux, B. *Macromol. Rapid Commun.* **2006**, *27*, 399–404.
(30) Dos Santos, A. M.; Pohn, J.; Lansalot, M.; D'Agosto, F. *Macromol. Rapid Commun.* **2007**, *28*, 1325–1332.
(31) Barner-Kowollik, C.; Heuts, J. P. A.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 656–664.
(32) Ravi, P.; Wang, C.; Tam, K. C.; Gan, L. H. *Macromolecules* **2003**, *36*, 173–179.
(33) Thickett, S. C.; Gilbert, R. G. *Macromolecules* **2006**, *39*, 6495–6504.