Ab Initio RAFT Emulsion Copolymerization of Styrene and Acrylonitrile

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ABSTRACT: Ab initio RAFT emulsion copolymerization of styrene (St) and acrylonitrile (AN) was investigated by using poly(acrylic acid)$_{20}$-b-polystyrene$_5$ trithiocarbonate as surfactant and RAFT agent. The well-controlled polymerization in terms of linear growth of molecular weight, low PDI, and little coagulum could be achieved only when the mass ratio m(St)/m(AN) was greater than 1:1 and suitable polymerization temperature depending on the monomer ratios. A significant amount of coagulum was formed when more AN was used. The gel effect, which led to the diffusion-controlled RAFT addition reactions in the late stage of the polymerization, played a significant influence on the PDI, the degree of which was highly dependent on the targeted molecular weight and monomer compositions. For the copolymerization of styrene and acrylonitrile with the azeotropic composition (75 wt % styrene), the gel effect could be relieved by increasing the reaction temperature from 70 to 90 °C after the nucleation period, resulting in PDI as low as 1.20. However, in the cases of the higher AN composition, the gel effect was still pronounced. Unexpectedly, the particle number was insensitive to the RAFT agent concentrations.

■ INTRODUCTION

Controlled/living radical polymerization (CLRP), including nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition–fragmentation chain transfer radical polymerization (RAFT), being an important breakthrough in polymer chemistry over the past few decades, provides a powerful tool to synthesize complex polymers like block copolymer and gradient copolymer with predetermined molecular weight and finely tuned microstructures.[1−4] Copolymers of styrene and acrylonitrile (SAN) possess outstanding chemical and mechanical properties such as solvent resistance, heat resistance, transparency, and processability and are used primarily as transparent structural materials or blend components for polymer alloying.[5]

SAN was mainly synthesized via conventional radical emulsion polymerization, and the relevant research of mechanism was reported in the early 1940s.[6,7] CLRP would allow us to synthesize SAN block copolymer, which could be of interest as compatiblizer, high impact plastics, and elastomer. Among CLRPs, nitroxide-mediated free radical polymerization was first applied to the copolymerization of azeotropic mixtures of styrene and acrylonitrile.[8] Since then, the CLRP of styrene and acrylonitrile has received more and more attentions. Detrembleur et al. synthesized SAN copolymer successfully via controlled nitroxide-mediated radical polymerization in the presence of N-tert-butyl-α-isopropylnitrone, which was easily synthesized from cheap reagents.[9] Matyjaszewski et al. successfully prepared SAN copolymers with high molecular weight ($M_n \sim 200000$) and low polydispersity ($M_w/M_n < 1.3$) and with different chain architectures by ARGET ATRP.[10] Al-Harthi et al. investigated the effect of monofunctional and bifunctional initiators on the ATRP of styrene and acrylonitrile, and the results showed that under different polymerization procedures, simultaneous and sequential polymerizations, monofunctional and bifunctional initiators affected the

polymerization differently, and the composition drift of copolymer was more pronounced when the bifunctional initiator was used.[11] Fan et al. synthesized a series of SAN copolymer with various ratios of styrene and acrylonitrile via RAFT polymerization, investigated polymerization kinetics, molecular weight and its distribution and composition drift during the polymerization, and further prepared various SAN-containing block copolymers successfully.[12]

So far, almost all of the CLRPs for synthesizing SAN copolymer were carried out in homogeneous bulk or solution polymerization. Many hours were needed to reach a relatively high conversion. By contrast, RAFT emulsion polymerization is more desirable in the context of commercial applications and offers an effective method to suppress the irreversible termination reactions with little cost of the polymerization rate,[13−18] which is particularly important in the synthesis of a high molecular weight polymer.[19,20] Bozovic-Vukic et al. synthesized poly(4-vinylpyridine)-b-SAN (P4VP-b- SAN) copolymer by RAFT polymerization in solution and emulsion and made a comparison. The results showed that P4VP-b-SAN block copolymers were synthesized successfully by solution polymerization with high molecular weight ($M_n \sim 77800$) and low distribution (PDI < 1.35), but, in emulsion process, the GPC chromatograms showed high PDI of the final product (PDI = 4).[21]

Ab initio emulsion RAFT polymerization is far more complicated than one thought. Colloidal instability and losing control over molecular weight and molecular weight distribution were often reported.[22,23] Successful ab initio emulsion RAFT polymerization was achieved only recently after the

continuous efforts of several groups.[20,24−28] In the previous work of our lab, we have demonstrated that using poly(acrylic acid)-b-polystyrene (PAA-b-PSt) trithiocarbonate with relatively more acrylic acid units and less styrene units would be a good strategy to achieve a successful RAFT emulsion polymerization in terms of little coagulum, predicted molecular weight, and relatively low PDI. The relative more acrylic acid units in the PAA-b-PSt trithiocarbonate make the RAFT agent water-soluble even without neutralization. The neutralization in the particle nucleation period was found to lead to the loss control in molecular weight and need to avoid. Once the particle nucleation period was finished, the acrylic acid units could be neutralized to prevent from the possible coagulation which was observed in the synthesis of high molecular weight polymer.[20,29−32]

In this work, we explored RAFT ab initio emulsion polymerization of styrene and acrylonitrile by using PAA_{20}-b-PSt_5 trithiocarbonate as surfactant and RAFT agent. The polymerization kinetics, particle number N_p, colloidal stability, molecular weight, and molecular weight distribution were investigated.

■ EXPERIMENTAL SECTION

Materials. Acrylic acid and styrene were distilled under reduced pressure at 30 °C. Acrylonitrile was distilled under normal pressure at 100 °C. 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 (DSCTSPA), was synthesized and purified as described in the literature.[24]

Synthesis of PAA_{20}-b-PSt_5 Trithiocarbonate Macro-RAFT Agent. First, a solution containing 1.500 g (4.29×10^{-3} mol) of the small RAFT agent, 0.100 g (3.57×10^{-4} mol) of V501, 6.178 g (8.57×10^{-2} mol) of acrylic acid, and 35.001 g of dioxane was introduced to a flask, and the reaction proceeded with stirring at 80 °C for 2 h. The flask was then cooled to room temperature, and another solution containing 4.463 g (4.29×10^{-2} mol) of styrene, 0.100 g (3.57×10^{-4} mol) of V501, and 15.039 g of dioxane was added. The mixture was deoxygenated and reacted for a 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 40 °C. The calculated macro-RAFT structure by NMR agrees well with the theoretical value, and PDI as low as 1.17 and the GPC curves of RI and UV 311 signals were almost overlapped, demonstrating the good control on the block copolymerization of acrylic acid and styrene with very few dead chains by DSCTSPA.

Synthesis of SAN Copolymers via RAFT Ab Initio Emulsion Polymerization. Taking the experiment of [St]: [AN] = 3:1 and the theoretical molecular weight 30000 g/mol as an example, 1.670 g (7.22×10^{-4} mol) of the macro-RAFT agent was dissolved in 77.091 g of deionized water. Then, 15.057 g (1.45×10^{-1} mol) of styrene and 5.052 g (9.52×10^{-2} mol) of acrylonitrile (20% solid content based on the total latex) were mixed with the previous aqueous solution in a 250 mL flask. During 30 min deoxygenation by nitrogen purge, the temperature was increased to 70 °C (or further increased to 90 °C after 20 min in the indicated cases). The initiator potassium persulfate (KPS, 0.039 g, 1.44×10^{-4} mol, in 2.891 g of deionized water) was injected to start the emulsion polymer-

ization. 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. The structural derivation of macro-RAFT agents was according to the literature.[20]

GPC Analysis. Number-average molecular weight (M_n), weight-average molecular 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. For SAN samples, before analysis, the polymers were modified by methylation of the carboxylic acid groups using trimethylsilyl diazomethane to eliminate COOH group interactions with GPC columns.[34] The eluent was tetrahydrofuran with a flow rate of 1.0 mL/min, and measured temperature was 30 °C. Waters Styragel column (HR 4, 3, 1, the measure range is 500000−100) was utilized. 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 latex samples were placed in vacuum at 40 °C for 2 h to removed residual monomer. The particle number, N_p, was calculated by

$$N_p = \frac{6m}{\pi D_v^{\,3} d_p} \tag{4}$$

where m is the polymer mass (including macroRAFT) in grams (g_{latex}^{-1}), D_v is the particle diameter measured by Malvern, and the density of polymer, d_p, was calculated by

$$d_p = d_{PSt}W_{St} + d_{PAN}W_{AN} \tag{2}$$

where the density of polystyrene, d_{PSt}, is 1.05g/mL,[35] while the density of polyacrylonitrile, d_{PAN}, is 1.15g/mL,[35] and W_{St} and W_{AN} represent the mass fractions of styrene and acrylonitrile, respectively.

■ RESULTS AND DISCUSSION

A series of ab initio RAFT emulsion polymerization of styrene and acrylonitrile was carried out with various molecular weights and various molar ratios. The experimental conditions are shown in Table 1. The results are summarized as follows.

Ab Initio RAFT Emulsion Polymerization of Styrene and Acrylonitrile with Various Molecular Weights. Exps. 1−3 were carried out with the azeotropic mixture of styrene and acrylonitrile (75 wt % styrene), and the polymerization kinetics are plotted in Figure 1. All the polymerizations proceeded very fast, finished within 60 min. The polymerization rate decreases with the increase of theoretical M_n of SAN copolymers. The reason is that the theoretical M_ns of SAN copolymers were set by changing [RAFT], and poly(acrylic acid)$_{20}$-b-polystyrene$_5$ trithiocarbonate was used not only as the RAFT agent but also as the surfactant. To increase the theoretical M_n, we reduced the surfactant concentration, as well as initiator concentration, which would decrease the polymerization rate.

Table 1. Conditions for Ab Initio RAFT Emulsion Polymerization of Styrene and Acrylonitrile

exp.[a]	m(S):m(AN)	$M_{n,theo}$[b]	solid content (%)	time (min)
1	3:1	30 000	20.0	60
2	3:1	45 000	20.0	60
3	3:1	60 000	20.0	60
4	3:1	30 000	20.0	40
5	3:1	45 000	20.0	40
6	3:1	60 000	20.0	40
7	1:0	30 000	20.0	80
8	3:2	30 000	20.0	40
9	1:1	30 000	20.0	40
10	0:1	30 000	20.0	40

[a]All the experiments (Exp. 1−10) used KPS (1:5[RAFT]) as initiator. In Exp. 1−3 and Exp. 7, the reaction temperature were kept at 70 °C, while in other experiments, the reaction temperature were further increased to 90 °C after the nucleation period. In Exp. 2−3 and Exp. 5−6, NaOH was injected slowly to partly neutralized the macro-RAFT agent (the molar ratio of the added NaOH over acrylic acid of macro-RAFT was 10:20) to suppress the possible particle coalescence.[20,33] [b]The theoretical M_n values were calculated from $M_{n,theo} = M_{n,RAFT} + M_{n,mon}[M]x/[RAFT]$, where $[M]$ and $[RAFT]$ represent the monomer and macro-RAFT agent concentrations, $M_{n,mon}$ is the average molecular weight of the monomer mixture, and x is the conversion.
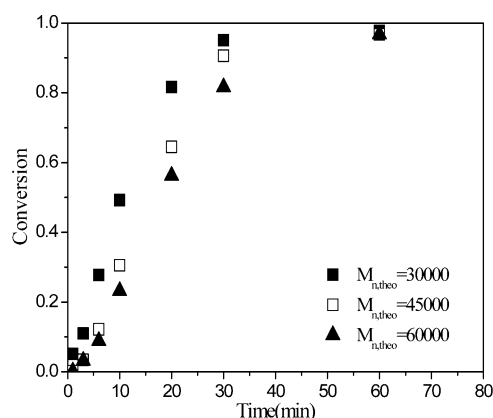

Figure 1. Conversion versus polymerization time in Exp. 1−3. [KPS]: [RAFT] = 1:5, solid content: 20% and the reaction temperature: 70 °C.
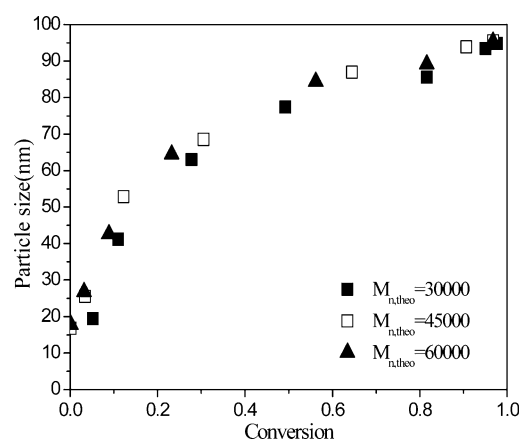
The development of the particle size and particle number with conversion is presented in Figure 2. In the beginning of the polymerization, the particle size quickly increases with monomer conversion. At about 20% monomer conversion, a turning point is reached, after which the particle size becomes to steadily increase. Accordingly, the particle number decreases very fast in the beginning of the polymerization and levels off after 20% monomer conversion, as seen in Figure 2. As pointed out previously,[20] both the micelles of macro-RAFT agent and nucleated particles were measured by DLS. So, the quick decrease of the number of "particles" actually reflects that many micelles were dissociated to protect the new born particles. The nucleation period seems finished at about 20% monomer conversion. Quite surprisingly, the particle number is actually not so different when [RAFT] was changed to target the various molecular weights. It must be noted that according to the Smith-Ewart equation

$$N_p = k\left(\frac{k_d[I]}{K}\right)^{0.4}(a_s[S])^{0.6} \tag{3}$$

where k_d represents the initiator decomposition rate, K represents volume growth rate per particle, a_s represents area of a surfactant molecule when the surface is saturated, $[I]$ and $[S]$ represent the initiator and surfactant concentration, and k is the constant, respectively. $N_p \propto [RAFT]$ since the ratio of [KPS] and [RAFT] was set to be constant. It seems that the efficiency of the particle nucleation should increase with the increase of theoretical M_n of SAN copolymer.

Figure 3 represents the plots of M_n and PDI values against monomer conversions in Exps. 1−3. The experimental molecular weights increase linearly with monomer conversion, but the experimental M_n looks deviated significantly from the theoretical values, which could be ascribed to the reported molecular weights are not true values but relative to the polystyrene standards. The PDI increases initially and then decreases with the conversion, which is very similar to styrene RAFT emulsion polymerization.[20] During the nucleation period (<20%, as suggested by Figure 2), PDI increases with more and more macro-RAFT agent reactivated, and after the nucleation period was over, those polymer chains in the later-born particles would grow faster due to the so-called compartmentalization effect. Interestingly, at the late stage of polymerization (>80%), PDI increases dramatically again. GPC curves, as
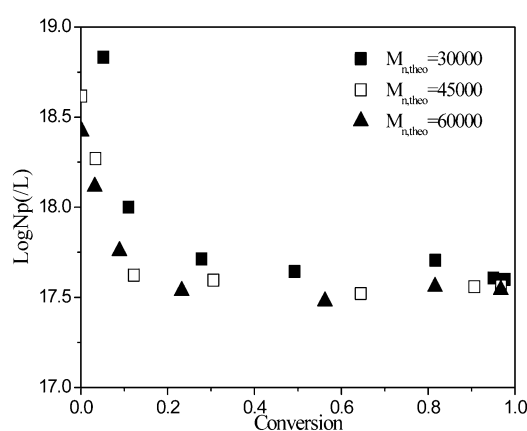

Figure 2. Particle size determined by Malvern ZETASIZER and particle number versus conversion in Exp. 1−3. [KPS]:[RAFT] = 1:5, solid content: 20% and the reaction temperature: 70 °C.
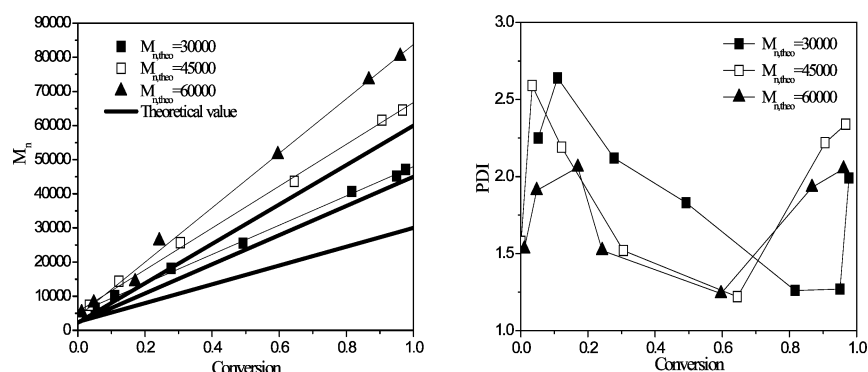
Figure 3. M_n and PDI determined by GPC (relative to polystyrene standards) versus conversion in Exp. 1−3. [KPS]:[RAFT] = 1:5, solid content: 20% and the reaction temperature: 70 °C.
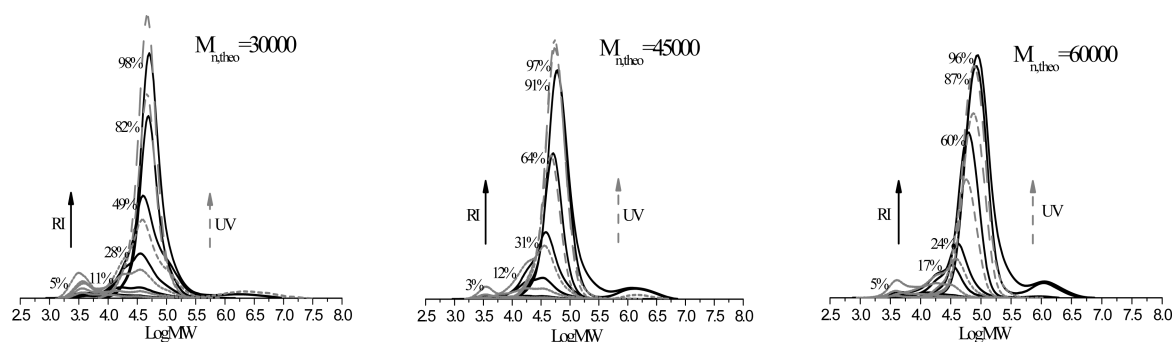
Figure 4. The GPC curve evolution of the polymer samples collected at different conversions in Exp. 1−3. [KPS]:[RAFT] = 1:5, solid content: 20% and the reaction temperature: 70 °C.
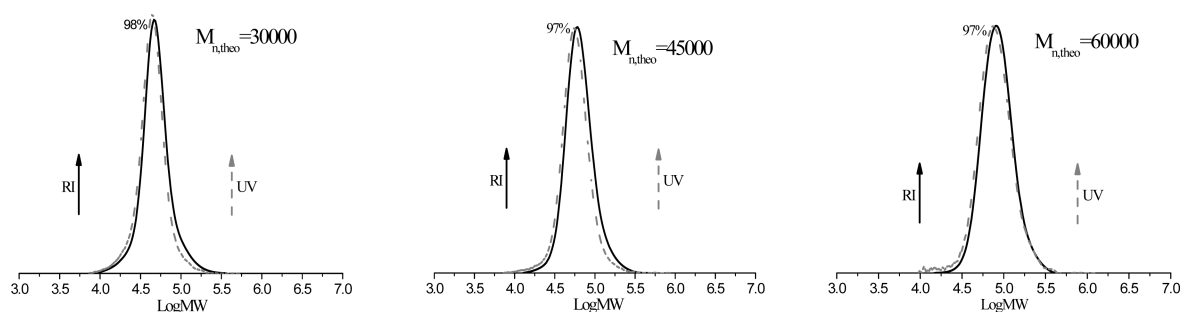
Figure 5. The GPC curve of the polymer samples collected at high conversions in Exp. 4−6. [KPS]:[RAFT] = 1:5, solid content: 20% and the reaction temperature: 70 °C, further increased to 90 °C after the nucleation period.

Table 2. Effect of Postincreasing Temperature on Ab Initio RAFT Emulsion Polymerization of Styrene and Acrylonitrile with Various Molecular Weights

Exp.[a]	conv.[b] (%)	D_v[c] (nm)	log N_p (/L$_{latex}$)	PSD (D_v/D_n)	$M_{n,theo}$[d] (g/mol)	$M_{n,exp}$[e] (g/mol)	PDI (M_w/M_n)
1	98	95	17.6	1.07	29 400	47 100	1.99
2	97	96	17.6	1.10	43 600	64 600	2.34
3	97	95	17.5	1.12	58 100	80 300	2.05
4	98	92	17.6	1.11	29 500	42 800	1.20
5	97	95	17.6	1.10	43 800	57 300	1.18
6	97	96	17.5	1.08	58 000	74 300	1.20

[a]All the experiments (Exp. 1−6) used KPS (1:5[RAFT]) as initiator, and with the azeotropic composition of styrene and acrylonitrile. [b]The monomer conversion was measured by gravimetry, according to conversion = m$_{polymer}$/m$_{monomer}$, where m$_{polymer}$ and m$_{monomer}$ represent the masses of polymer (except for macroRAFT) and monomer, respectively. [c]D_v is volume-average particle diameter measured by Malvern. [d]The theoretical M_n values were calculated from $M_{n,theo} = M_{n,RAFT} + M_{n,monomer}x$[M]/[RAFT], where [M] and [RAFT] represent the monomer and macro-RAFT agent concentrations and x is the conversion. [e]The experimental M_n values were derived from a calibration curve based on narrow polystyrene standards.

shown in Figure 4, reveal that a peak of the higher molecular weight than that of the main peak appears, and thus results in a

quick increase of PDI. As seen in Figure 2, no additional particles formed at this stage of the polymerization. UV 311

signals, which are from the thioester groups, also suggest that the polymer of the minor peak actually should possess RAFT groups. So, it is inferred that at the late stage of polymerization, the RAFT addition reaction might become diffusion-controlled due to the gel effect. It should be noticed that no autoacceleration in polymerization rate was observed since the monomer concentration also decreased very fast at this stage. The very similar results have been reported in RAFT (mini)emulsion of methyl methacrylate.[36−38] In order to relieve the diffusion-controlled effect, we increased polymerization temperature from 70 to 90 °C after the nucleation period (about 20 min, and reached to 90 °C in 5 min) in Exps. 4−6. The shoulder peaks disappear at high conversion (>95%), as shown in Figure 5, which is consistent with the assumption that the bimodal GPC peaks were caused by the diffusion-controlled RAFT addition reactions. PDIs are as low as 1.20 (Table 2) in the end of the polymerization, and the colloidal stability of the final latex was very excellent without any coagulum.

**Ab Initio RAFT Emulsion Polymerization of Styrene and Acrylonitrile with Various Monomer Compositions.** A series of ab initio RAFT emulsion polymerization was carried out with various ratios of styrene and acrylonitrile in Exp. 4 and Exps. 7−10; the initial reaction temperature was 70 °C and further increased to 90 °C after the nucleation period to relieve the gel effect. The polymerization kinetics is plotted in Figure 6.
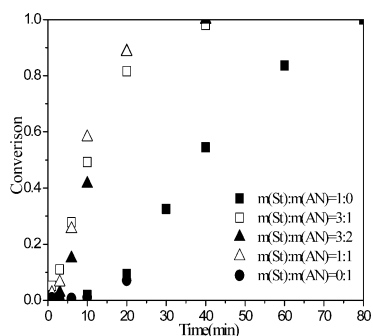
Figure 6. Conversion versus polymerization time in Exp. 4 and Exps. 7−10. [KPS]:[RAFT] = 1:5, solid content: 20% and the reaction temperature: 70 °C, further increased to 90 °C after the nucleation period.

As shown in Figure 6, the copolymerization rate of styrene and acrylonitrile is much faster than that of styrene homopolymerization, just as the conventional radical copolymerization. Interestingly, the obvious inhibition periods of 10 min are seen in both styrene and acrylonitrile homopolymerization, but no inhibition period is observed in the copolymerization of styrene and acrylonitrile. The possible reason might be related to the character of the copolymerization of styrene and acrylonitrile. It is believed that the inhibition period should be related to the exit of R radicals which release from the macro-RAFT agent added by a radical,[13] as seen in Scheme 1. It should be noticed that the hydrophilicity of the R radical should be higher than the macroRAFT agent since the Z group of the macroRAFT

**Scheme 1. Mechanism of the Exit of R Radicals of the RAFT Agent**
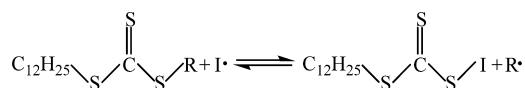
agent was the dodecyl chain. Once the R radical is released, it could exit out to water phase before it is added by a monomer molecule. The exit probability is related to its hydrophobicity and k_p value. For homopolymerization of styrene, $k_{p,St}$ is so low that the R radical could exit to the aqueous phase before a monmer is added. For homopolymerization of acrylonitrile, though $k_{p,AN}$ is much higher than $k_{p,St}$, more acrylonitrile molecules should be added to produce a radical with enough hydrophobicity. In the cases of the copolymerization of styrene and acrylonitrile, the radical prefers to cross-propagate according to the monomer reactivity ratios ($r_{St} = 0.41$, $r_{AN} = 0.03$[7]) and the cross-propagation rate constants are much higher than the self-propagation rate constants,[39] and thus the radical could quickly increase chain length and hydrophobicity before exiting, leading to the disappearance of the inhibition period.

The development of the particle size and particle number with conversion in the copolymerization is presented in Figure 7. The particle sizes increased with conversion, and the particle numbers decreased at the early stage of polymerization quickly and leveled off after the nucleation period, as the same as those of homopolymerization of styrene.

The curves of M_n and PDI versus conversion in RAFT emulsion polymerization of styrene and acrylonitrile with various molar ratios are plotted in Figure 8. The experimental molecular weights increase linearly with conversion in all cases. It is noticed that the gel effect is more pronounced with more acrylonitrile added. The peaks of much higher molecular weight are still seen in the GPC curves of Exp. 8 (m(St):m(AN) = 3:2) and Exp. 9 (m(St):m(AN) = 1:1) even with postincreasing the reaction temperature from 70 to 90 °C after the nucleation period, as shown in Figure 9.

Little coagulum was observed in the homopolymerization of styrene. No coagulum was observed in the cases of styrene and acrylonitrile copolymerization with the azeotropic composition, as seen in Table 3. However, further increasing acrylonitrile ratios led to the formation of the coagulum. In the case of Exp. 8 (m(St):m(AN) = 3:2), the coagulum appeared at about 80% conversion, while in the case of Exp. 9 (m(St):m(AN) = 1:1), the coagulum was observed at around 60%. No open report was found about the colloidal instability in the conventional emulsion copolymerization of styrene and high level of acrylonitrile. In the case of Exp. 10 (homopolymerization of acrylonitrile), the system totally lost colloidal stability after 10% conversion. In Figure 10, the theoretical copolymer and monomer instantaneous compositions are plotted against monomer conversions according to the Mayo−Lewis equation. Though the theoretical calculation was based on a homogeneous system, it still can be seen that the conversion where the coagulum occurred agrees very well with the dramatic decreases in styrene composition. The agreement seems to suggest that once the copolymer with very rich acrylonitrile was formed, the colloidal system would be unstable. The solubility parameters δ of the monomer mixtures and the formed copolymer in the beginning of polymerization and at the conversions where styrene consumed completely were estimated and summarized in Table 4. In Exp. 8 and Exp. 9, the solubility parameter values of the copolymer and monomer mixtures were close at the beginning of polymerization, suggesting that the polymer could be well swollen by monomer mixtures. The co-oligomer radicals formed in the water phase could dissolve in the particles. With an increase of monomer conversion, St composition in the monomer mixture decreased first steadily
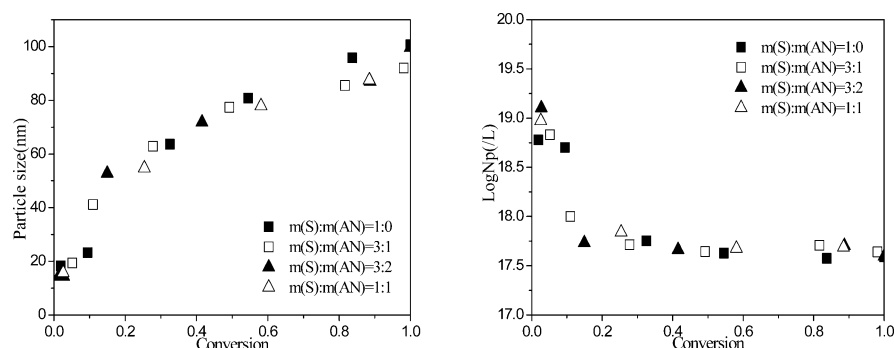
Figure 7. Particle size determined by Malvern ZETASIZER and particle number versus conversion in Exp. 4 and Exp. 7−9. [KPS]:[RAFT] = 1:5, solid content: 20% and the reaction temperature: 70 °C, further increased to 90 °C after the nucleation period.
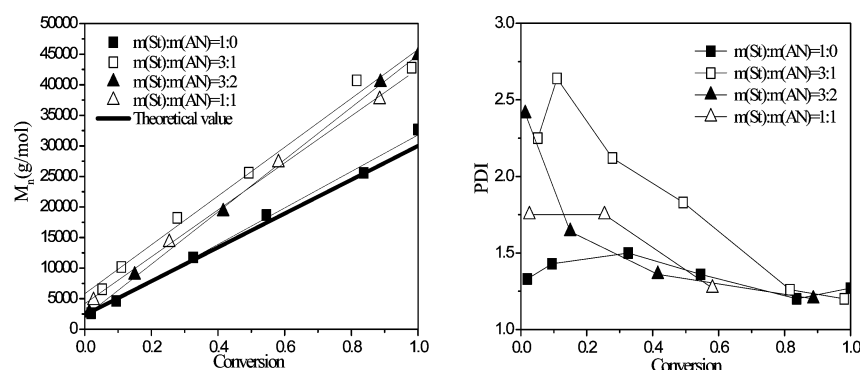
Figure 8. M_n and PDI determined by GPC (relative to polystyrene standards) versus conversion in Exp. 4 and Exp. 7−9. [KPS]:[RAFT] = 1:5, solid content: 20% and the reaction temperature: 70 °C, further increased to 90 °C after the nucleation period.
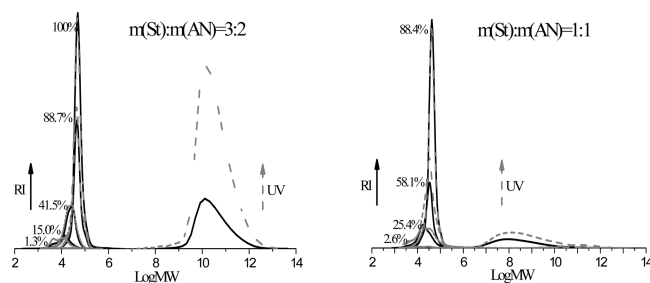
Figure 9. The GPC curve evolution of the polymer samples collected at different conversions in Exp. 8−9. [KPS]:[RAFT] = 1:5, solid content: 20% and the reaction temperature: 70 °C, further increased to 90 °C after the nucleation period.

and then quickly to zero at monomer conversion 83% for Exp. 8 and 70% for Exp. 9, as theoretically predicted in Figure 10 b.

Accordingly, the monomer mixture became a more and more less effective solvent for the copolymer. When the polymerization proceeded close to the conversion where St was fully converted, the left acrylonitrile should be a poor solvent of the copolymer as indicated by their solubility parameters. Considering the relative high solubility of acrylonitrile in aqueous phase (11.0 ± 0.1 g AN/100g H_2O, at 60.3 °C),[7] it is very likely that the left acrylonitrile mainly dissolved in the water in these cases. As a result, homo-oligomer of acrylonitrile was formed in the aqueous phase and precipitated out on the surface of the particles. So, the latex lost stability since the protecting acrylic acid groups covalently bonded to the polymer were buried by polyacrylonitrile. In Exp. 10, the coagulum formed at very low monomer conversion since polyacrylonitrile cannot dissolve in acrylonitrile at all. To synthesize the SAN latex of higher content of acrylonitrile, semibatch emulsion

Table 3. Ab Initio RAFT Emulsion Polymerization of Styrene and Acrylonitrile with Various Molar Ratios

exp.[a]	conv.[b] (%)	D_v[c] (nm)	PSD (D_v/D_n)	log N_p (/L_{latex})	$M_{n,theo}$[d] (g/mol)	$M_{n,exp}$[e] (g/mol)	PDI (M_w/M_n)	coag.[f] (%)
7	100	101	1.05	17.6	30 000	32 700	1.27	1.17
4	98.1	92	1.11	17.6	29 500	42 800	1.20	
8	100	100	1.08	17.6	30 000			1.96
9		bimodal						44.72
10								100

[a]All the experiments (Exp. 4 and Exp. 7−10) used KPS (1:5[RAFT]) as initiator, and the theoretical M_n was about 30000 g/mol. [b]The monomer conversion was measured by gravimetry, according to conversion = $m_{polymer}/m_{monomer}$, where $m_{polymer}$ and $m_{monomer}$ represent the masses of polymer (except for macroRAFT) and monomer, respectively. [c]D_v is volume-average particle diameter measured by Malvern. [d]The theoretical M_n values were calculated from $M_{n,theo} = M_{n,RAFT} + M_{n,monomer}x[M]/[RAFT]$, where [M] and [RAFT] represent the monomer and macro-RAFT agent concentrations and x is the conversion. [e]The experimental M_n values were derived from a calibration curve based on narrow polystyrene standards. [f]The percent coagulum in Exp. 7−10 was calculated based on the total polymer mass.

a: copolymer composition　　　　　　　b: monomer composition
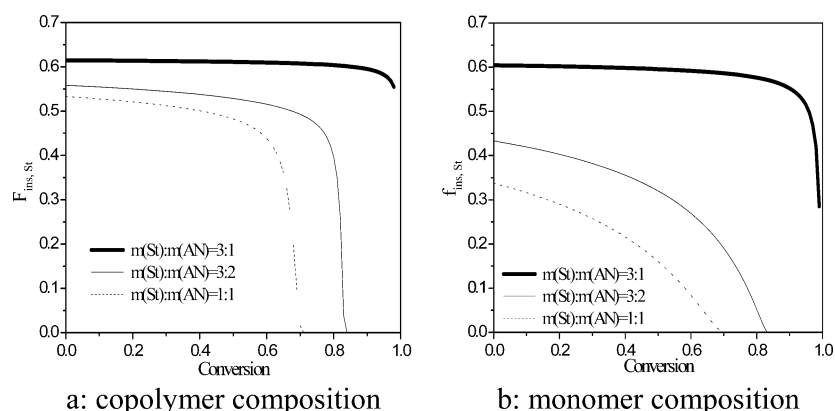
Figure 10. Instantaneous styrene mole fraction in copolymer and monomer mixture as a function of conversion in Exp. 4 and Exp. 8−9 calculated by Mayo−Lewis equation with r_{St} = 0.41, r_{AN} = 0.03.

Table 4. Solubility Parameters of Copolymer and Monomer Mixtures during Copolymerization of Styrene and Acrylonitrile

Exp.		δ_0 $((J/cm^3)^{1/2})$	δ_1 $((J/cm^3)^{1/2})$
8	SAN[a]	18.7	18.6
	monomer mixture[b]	19.1	21.4
9	SAN[a]	18.8	18.6
	monomer mixture[b]	19.5	21.4
10	PAN[40]	26.0−31.5	26.0−31.5
	AN[40]	21.4	21.4

[a]The solubility parameter δ values of SAN were estimated by the group contributions method of Small,[39] and δ_0 and δ_1 represent the solubility parameter at the times of polymerization beginning and styrene consumed completely. [b]The solubility parameter values of monomer mixture were calculated by $\delta_{mix} = \Phi_{St}\delta_{St} + \Phi_{AN}\delta_{AN}$, where Φ_{St} and Φ_{AN} represent the volume fraction of styrene and acrylonitrile, and δ_{St} ($17.7(J/cm^3)^{1/2}$) and δ_{AN} ($21.4(J/cm^3)^{1/2}$) represent the solubility parameter of styrene and acrylonitrile, respectively.[39]

polymerization might be an effective method by feeding styrene or monomer mixture.

CONCLUSIONS

Ab initio RAFT emulsion polymerization of styrene and acrylonitrile was carried out by using PAA_{20}-b-PS_5 trithiocarbonate as a surfactant and RAFT agent with various monomer compositions and targeted molecular weight from 30 to 60 kg/mol. The following conclusions are drawn:

(1) Monomer compositions play a significant influence on the formation of coagulum. Little coagulum was formed in the cases of m(St)/m(AN) = 3/1 and 3/2. However, in the cases of monomer mass ratio 1:1 and homopolymerization of AN, a significant amount of coagulum was formed. It is suggested that very rich AN copolymer would bury the colloid-protecting groups, resulting in the coalescence.

(2) In those colloidal stable systems, the polymerization could be well controlled as indicated by linear growth of molecular weight and low PDI. However, the RAFT addition reaction could become diffusion-controlled at the late stage of polymerization (>80%) and thus resulted in a quick increase of PDI. With an increase of the targeted molecular weight and AN levels, the gel effect became more pronounced. PDIs could reduce to about 1.20 at the complete monomer conversion by increasing the reaction temperature from 70 to 90 °C after the nucleation period in the case of m(St)/m(AN) = 3/1. For

m(St)/m(AN) = 3/1 and 3/2, the gel effect still led to the appearance of a minor GPC peak in the end of the higher molecular weight in the very late stage of the polymerization.

(3) The particle number was insensitive to RAFT agent (surfactant) concentrations, which is unexpected from the classic Smith-Ewart equation.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Chiefari, J.; Chong, Y.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G. Living free-radical polymerization by reversible addition-fragmentation chain transfer: the RAFT process. *Macromolecules* **1998**, *31* (16), 5559.

(2) Hawker, C. J.; Bosman, A. W.; Harth, E. New polymer synthesis by nitroxide mediated living radical polymerizations. *Chem. Rev.* **2001**, *101* (12), 3661.

(3) Kamigaito, M.; Ando, T.; Sawamoto, M. Metal-catalyzed living radical polymerization. *Chem. Rev.* **2001**, *101* (12), 3689.

(4) Matyjaszewski, K.; Xia, J. Atom transfer radical polymerization. *Chem. Rev.* **2001**, *101* (9), 2921.

(5) Scheirs, J.; Priddy, D. *Modern styrenic polymers: polystyrenes and styrenic copolymers*. Wiley: New York, 2003.

(6) Fordyce, R. G. Copolymerization. III. The Mechanism of Emulsion Copolymerization of Styrene and Acrylonitrile. *J. Am. Chem. Soc.* **1947**, *69* (8), 1903.

(7) Fordyce, R. G.; Chapin, E. C. Copolymerization. I. The mechanism of emulsion copolymerization of styrene and acrylonitrile. *J. Am. Chem. Soc.* **1947**, *69* (3), 581.

(8) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. Mechanisms and kinetics of nitroxide-controlled free radical polymerization. *Macromolecules* **1996**, *29* (20), 6393.

(9) Detrembleur, C.; Sciannamea, V.; Koulic, C.; Claes, M.; Hoebeke, M.; Jérôme, R. Controlled nitroxide-mediated radical polymerization

of styrene, styrene/acrylonitrile mixtures, and dienes using a nitrone. *Macromolecules* **2002**, *35* (19), 7214.

(10) Pietrasik, J.; Dong, H.; Matyjaszewski, K. Synthesis of high molecular weight poly(styrene-co-acrylonitrile) copolymers with controlled architecture. *Macromolecules* **2006**, *39* (19), 6384.

(11) Al-Harthi, M.; Sardashti, A.; Soares, J. B.; Simon, L. C. Atom transfer radical polymerization (ATRP) of styrene and acrylonitrile with monofunctional and bifunctional initiators. *Polymer* **2007**, *48* (7), 1954.

(12) Fan, D.; He, J.; Xu, J.; Tang, W.; Liu, Y.; Yang, Y. Synthesis of SAN-containing block copolymers using RAFT polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (7), 2260.

(13) Butté, A.; Storti, G.; Morbidelli, M. Miniemulsion living free radical polymerization by RAFT. *Macromolecules* **2001**, *34* (17), 5885.

(14) Luo, Y.; Wang, R.; Yang, L.; Yu, B.; Li, B.; Zhu, S. Effect of reversible addition-fragmentation transfer (RAFT) reactions on (mini)emulsion polymerization kinetics and estimate of RAFT equilibrium constant. *Macromolecules* **2006**, *39* (4), 1328.

(15) Maehata, H.; Buragina, C.; Cunningham, M.; Keoshkerian, B. Compartmentalization in TEMPO-mediated styrene miniemulsion polymerization. *Macromolecules* **2007**, *40* (20), 7126.

(16) Delaittre, G.; Charleux, B. Kinetics of in-situ formation of poly(acrylic acid)-b-polystyrene amphiphilic block copolymers via nitroxide-mediated controlled free-radical emulsion polymerization. discussion on the effect of compartmentalization on the polymerization rate. *Macromolecules* **2008**, *41* (7), 2361.

(17) Simms, R. W.; Cunningham, M. F. Compartmentalization of reverse atom transfer radical polymerization in miniemulsion. *Macromolecules* **2008**, *41* (14), 5148.

(18) Zetterlund, P. B.; Kagawa, Y.; Okubo, M. Controlled/living radical polymerization in dispersed systems. *Chem. Rev.* **2008**, *108* (9), 3747.

(19) Yang, L.; Luo, Y.; Li, B. RAFT miniemulsion polymerization targeting to polymer of higher molecular weight. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43* (20), 4972.

(20) Wang, X.; Luo, Y.; Li, B.; Zhu, S. Ab initio batch emulsion RAFT polymerization of styrene mediated by poly(acrylic acid-b-styrene) trithiocarbonate. *Macromolecules* **2009**, *42* (17), 6414.

(21) Bozovic-Vukic, J.; Mañon, H. T.; Meuldijk, J.; Koning, C.; Klumperman, B. SAN-b-P4VP block copolymer synthesis by chain extension from RAFT-functional poly(4-vinylpyridine) in solution and in emulsion. *Macromolecules* **2007**, *40* (20), 7132.

(22) Monteiro, M. J.; Hodgson, M.; De Brouwer, H. The influence of RAFT on the rates and molecular weight distributions of styrene in seeded emulsion polymerizations. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (21), 3864.

(23) Cunningham, M. F. Controlled/living radical polymerization in aqueous dispersed systems. *Prog. Polym. Sci.* **2008**, *33* (4), 365.

(24) Ferguson, C. J.; Hughes, R. J.; Nguyen, D.; Pham, B. T.; Gilbert, R. G.; Serelis, A. K.; Such, C. H.; Hawkett, B. S. Ab Initio Emulsion Polymerization by RAFT-Controlled Self-Assembly. *Macromolecules* **2005**, *38* (6), 2191.

(25) Rieger, J.; Stoffelbach, F.; Bui, C.; Alaimo, D.; Jérôme, C.; Charleux, B. Amphiphilic poly(ethylene oxide) macromolecular RAFT agent as a stabilizer and control agent in ab initio batch emulsion polymerization. *Macromolecules* **2008**, *41* (12), 4065.

(26) Urbani, C. N.; Monteiro, M. J. Nanoreactors for aqueous RAFT-mediated polymerizations. *Macromolecules* **2009**, *42* (12), 3884.

(27) Chaduc, I.; Girod, M.; Antoine, R.; Charleux, B.; D'Agosto, F.; Lansalot, M. Batch emulsion polymerization mediated by poly-(methacrylic acid) macroRAFT agents: one-pot synthesis of self-stabilized particles. *Macromolecules* **2012**, *45* (15), 5881.

(28) Ferguson, C. J.; Hughes, R. J.; Pham, B. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. Effective ab initio emulsion polymerization under RAFT control. *Macromolecules* **2002**, *35* (25), 9243.

(29) Luo, Y.; Wang, X.; Zhu, Y.; Li, B.; Zhu, S. Polystyrene-block-poly(n-butyl acrylate)-block-polystyrene triblock copolymer thermo-plastic elastomer synthesized via RAFT emulsion polymerization. *Macromolecules* **2010**, *43* (18), 7472.

(30) Wei, R.; Luo, Y.; Xu, P. Ab initio RAFT emulsion polymerization of butadiene using the amphiphilic poly(acrylic acid-b-styrene) trithiocarbonate as both surfactant and mediator. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49* (13), 2980.

(31) Luo, Y.; Guo, Y.; Gao, X.; Li, B.; Xie, T. A General Approach Towards Thermoplastic Multishape-Memory Polymers via Sequence Structure Design. *Adv. Mater.* **2012**, *25* (5), 743.

(32) Xu, S.; Huang, J.; Xu, S.; Luo, Y. RAFT ab initio emulsion copolymerization of γ-methyl- α-methylene-γ-butyrolactone and styrene. *Polymer* **2013**, *54* (7), 1779.

(33) Luo, Y.; Wang, X.; Li, B.; Zhu, S. Toward well-controlled ab initio RAFT emulsion polymerization of styrene mediated by 2-(((dodecylsulfanyl) carbonothioyl) sulfanyl) propanoic acid. *Macromolecules* **2010**, *44* (2), 221.

(34) Couvreur, L.; Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. First nitroxide-mediated controlled free-radical polymerization of acrylic acid. *Macromolecules* **2003**, *36* (22), 8260.

(35) Grulke, E. A.; Brandrup, J.; Immergut, E. H. *Polymer handbook*. Wiley: New York, 1999.

(36) Peklak, A. D.; Butté, A.; Storti, G.; Morbidelli, M. Gel effect in the bulk reversible addition—fragmentation chain transfer polymerization of methyl methacrylate: Modeling and experiments. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (3), 1071.

(37) Yang, L.; Luo, Y.; Liu, X.; Li, B. RAFT miniemulsion polymerization of methyl methacrylate. *Polymer* **2009**, *50* (18), 4334.

(38) Zhang, W.; D'Agosto, F.; Dugas, P. Y.; Rieger, J.; Charleux, B. RAFT-mediated one-pot aqueous emulsion polymerization of methyl methacrylate in presence of poly (methacrylic acid-co-poly(ethylene oxide) methacrylate) trithiocarbonate macro- molecular chain transfer agent. *Polymer* **2013**, *54* (8), 2011.

(39) Pan, Z. *Macromolecular chemistry*. Chemical Industry Press: Beijing, 2007.

(40) He, M.; Chen, W.; Dong, X. *Polymer physics*. Chemical Industry Press: Beijing, 1990.