

Interfacially Confined RAFT Miniemulsion Copolymerization of Styrene and Butadiene

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ABSTRACT: In this study, ammonolyzed poly(styrene-*alt*-maleic anhydride) terminated with dithioester group can be self-assembled into an amphiphilic macro-reversible addition-fragmentation chain transfer (RAFT) agent, and RAFT group will be located in the interface of oil and water. RAFT polymerization of styrene (S) and butadiene (B) will be confined in the interface. The main work is to study the effect of degree of aminolysis, reaction temperature, and ratio of S/B on the polymerization kinetics and living characters. The experimental results revealed that aminolysis of dithioester group would lead to retardation and loss of living characters under higher degree of aminolysis. Interfacially confined RAFT miniemulsion polymerizations were of relatively good controlled/living characters under lower degree of aminolysis before gelation. Increase of reaction temperature and ratio of S/B will accelerate the formation of gelation. Finally, styrene/butadiene copolymer nanoparticles with uniform particle size were formed, and because of micro-phase segregation “core-shell” morphology with polybutadiene core and polystyrene shell was seen obviously. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: living polymerization; gel permeation chromatography; TEM; interfacially confined RAFT miniemulsion polymerization; styrene/butadiene copolymer

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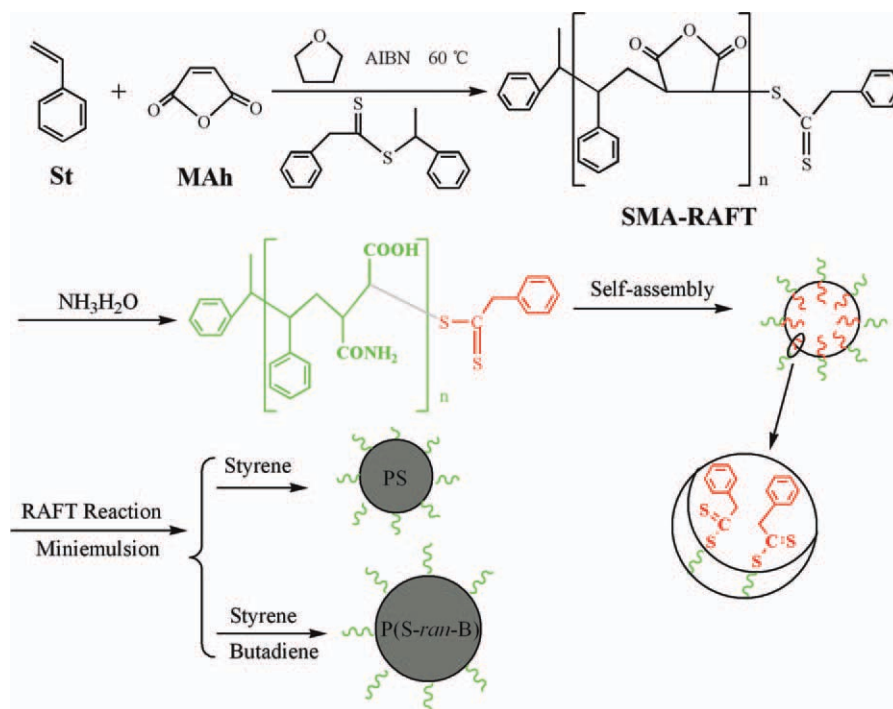
INTRODUCTION

Free radical polymerization has been an important research in the preparation of synthetic polymers over the last 100 years. Many different methods exist to produce polymers but free radical polymerizations have been dominated the field, accounting for the production of more than 50% of all commercially made polymers. The main shortcoming of free radical polymerization is its inability to control polymer structure and functionality. The technique is unable to control molecular weight and produces polymers with high polydispersity indexes (PDIs) and is not capable of producing complex architectures such as block copolymers, stars, and graft polymers. The advent of controlled/living radical polymerization techniques [nitroxide-mediated polymerization,¹ atom transfer radical polymerization,² and reversible addition-fragmentation chain transfer (RAFT) radical polymerization³] opens a new domain of polymer chemistry. Of these controlled/living radical polymerization techniques, RAFT polymerization can be easily applicable to a wide range of monomers at the facile temperature in homogeneous^{4–7} and heterogeneous systems.^{8–12} Especially, in the miniemulsion poly-

merization system with droplet nucleation mechanism, the polymer particles are converted from monomer droplets directly, and polymerization rate is faster than conventional emulsion polymerization. Besides, miniemulsion polymerization provides environmental friendly processes, remove the reaction heat easily during polymerization, and assure the feasible handling of the final product having a low viscosity.

In the RAFT radical polymerization system, the RAFT agent (oil-soluble, water-soluble, and amphiphilic) is a highly efficient transfer agent with a general structure $Z-C(=S)-SR$. Of these different kinds of RAFT agents, an amphiphilic RAFT agent will self-assemble to form stable micelles in miniemulsion system.^{13–16} The hydrophobic group, RAFT functional group, is located at the interface of oil and water, and the hydrophilic group will be capable of stabilizing the particles. When the polymerization begins, the RAFT polymerization is confined in the interface of oil and water. The polymer chains will grow inward gradually, leading to the formation of the polymer shell.^{11,16,17} Theoretically, such a principle will allow forming homopolymer and copolymer nanoparticles with functionality on the particle surface, and

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Scheme 1. Schematic illustration of interfacially confined RAFT miniemulsion copolymerization of styrene and butadiene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the thickness of polymer shell can be tuned by simply choosing RAFT agent bearing different hydrophilic group and controlling conversion.

To our best knowledge, RAFT copolymerization of maleic anhydride (MAh) and styrene (St) can synthesize alternating copolymer, poly(styrene-*alt*-maleic anhydride) (SMA), terminated with dithioester group.⁷ Anhydride group can be ammonolyzed to form hydrophilic group, acting as an amphiphilic RAFT agent to mediate the formation of nanoencapsulation.¹⁷ The use of macromolecular stabilizer during miniemulsion polymerization is an efficient strategy for synthesizing nanoencapsulations.^{16–18} Moreover, macromolecular stabilizer can act not only as stabilizers but also as chain transfer agents.^{14,19–21} In our previous study, it was found that SMA macro-RAFT agent could mediate the styrene and butyl acrylate to synthesize triblock copolymer, SMA-*b*-polystyrene-*b*-poly(butyl acrylate), via RAFT miniemulsion polymerizations.²² RAFT miniemulsion polymerization technique was also used to produce block copolymer of styrene and butadiene.²³ In the recent research, we found that ammonolyzed SMA can successfully mediate the copolymerization of styrene and butadiene in surfactant-free system. However, the effects of degree of aminolysis, reaction temperature, and ratio of S/B on the polymerization kinetics and living characters have not studied. Therefore, in this study, our main work, on one hand, was to choose ammonolyzed SMA as an amphiphilic RAFT agent and styrene and butadiene as monomers to demonstrate interfacially confined miniemulsion copolymerization of styrene and butadiene nanoparticles illustrated in Scheme 1. On the other hand, the effects of degree of aminolysis, reaction temperature, and ratio of S/B were studied in detail.

EXPERIMENTAL

Materials

Styrene was distilled under reduced pressure before use. The initiator, 2,2'-azoisobutyronitrile, was recrystallized twice from methanol. MAh, hexadecane (HD), and potassium persulfate (KPS), which were analytical agent grade, were used as received without further purification. Solvents used for the synthesis of polymers and RAFT agent, such as tetrahydrofuran (THF), methanol, and acetone, were freshly distilled using sodium. Butadiene (B) was distilled directly from a 3-L storage vessel into a cooling steel container. Ammonia solution (25 wt % in water) was used without any purification. Hydroquinone was used to quench the samples withdrawn during the experiment.

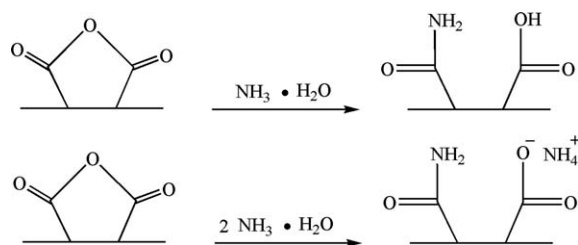
Synthesis of Poly(styrene-*alt*-maleic anhydride), SMA-RAFT

First, the RAFT agent, 1-phenylethyl phenyldithioacetate, was synthesized as described in the literature.²⁴ Macro-RAFT agent, poly(styrene-*alt*-maleic anhydride) (SMA-RAFT), was synthesized according to the literature.⁷

Interfacially Confined Styrene RAFT

Miniemulsion Polymerization

SMA-RAFT ($M_n = 3560 \text{ g mol}^{-1}$ and PDI = 1.14), styrene, HD, and a little acetone were first thoroughly mixed by magnetic stirring until homogeneous, and ammonia (25 wt % in water) was added to 100 g of deionized water. Then, the diluted ammonia solution was added dropwise to the oil phase under stirring. After pre-emulsification by magnetic stirring, the crude emulsion was ultrasonicated for 60 times with the lifetime of 3 s. The obtained miniemulsion was transferred to a 250-mL four-necked, round-bottomed flask. After purging N_2 for



Scheme 2. The aminolysis process of SMA RAFT agent (SMA-RAFT).

30 min, the initiator KPS was added into the miniemulsion, which was then heated to 70°C to start the polymerization. Samples were taken at regular time intervals throughout the reaction for analysis.

Interfacially Confined Styrene/Butadiene RAFT Miniemulsion Copolymerization

A styrene precursor miniemulsion was first prepared according to the method described above. Then, the obtained miniemulsion was transferred to a 1-L autoclave with a two-blade skewed propeller. The autoclave was first purged with highly pure nitrogen for 30 min. The distilled butadiene was then pumped into the autoclave. After swelling for 5 h in the emulsion, the polymerization was carried out at different temperatures. The samples were taken with a home-made sampler at regular time intervals and quenched by drops of 1 wt % hydroquinone aqueous solution.

Polymer Characterization

Conversion Measurement. The conversions of the monomers to the polymer were determined by a gravimetric method. Samples were drawn from the reactor at different times, immediately quenched with hydroquinone in a bath of ice water, and then dried under pressure.

Gel Permeation Chromatography Analysis. The molecular weight and PDI of the dried polymers were recorded on a Waters 1525 gel permeation chromatography (GPC) instrument with three gel columns (7.8 mm × 300 mm) and a differential refractive index detector and ultraviolet (UV) detector. The eluent was THF at 35°C with a flow rate of 1.0 mL min⁻¹. The molecular weights and PDI of dried polymer samples were calibrated using narrow polystyrene standards with molecular weight from 1200 to 3,940,000 g mol⁻¹.

Gel Fraction and Gel Point Measurement. The dried styrene/butadiene random copolymer (w_1) was dissolved in 100 mL THF with moderate agitation for 48 h. Then, the solution was subjected to filtration and the filtrate was dried until constant weight (w_2). The gel fraction was calculated by the equation: gel fraction = w_2/w_1 . The gel point was determined from the relationship between gel fraction and conversion.

Fourier Transform Infrared Spectroscopy Analysis. Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet 5700 FTIR spectrometer (KBr), and samples of the alternating copolymer were dried in a vacuum oven at 50°C for 6 h.

Nuclear Magnetic Resonance Spectroscopy Analysis. ¹H-nuclear magnetic resonance (NMR) analyses were performed on a

Bruker DMX-500 nuclear resonance instrument with chloroform-*d* as solvent and tetramethylsilane (TMS) as an internal standard at room temperature.

Transmission Electron Microscopy Analysis. The morphology and size of the latex particles were examined by transmission electron microscopy (TEM, JEOL JEM-1230). The samples were prepared as follows: the latex samples were diluted to 0.03% and was mounted on 400-mesh carbon-coated copper grids and dried at room temperature. After 24 h, the TEM samples were stained with osmium tetroxide (OsO₄) vapor at room temperature for 1 h, which led to a selective staining of the double bonds in the PB fraction of the copolymer. TEM was operated at 80 kV.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was carried out with a DSCQ1000 instrument. The glass transition temperature (T_g) was reported at the inflection point of the heat capacity jump with a heating rate of 20°C min⁻¹.

RESULTS AND DISCUSSION

Interfacially Confined Styrene RAFT Miniemulsion Polymerization

MAH group in the SMA-RAFT chains can be ammonolyzed to form hydrophilic group to stabilize particles, which is illustrated as Scheme 2. During the aminolysis and ultrasonication, the formed hydrophilic group stabilizing the particles was located in the particle surface, and hydrophobic group was located inside the particles and RAFT group was anchored in the interface of oil and water. Therefore, when polymerization started, the RAFT polymerization was confined in the interface. However, as some literatures described,^{19,20} RAFT group, dithioester group, can be ammonolyzed to form thioamide and thiol (Scheme 3). As we know, thiol is a chain transfer agent without living character. Degree of aminolysis will have an effect on the interfacially confined RAFT miniemulsion polymerization. Therefore, we designed two experiments of styrene RAFT miniemulsion polymerization stabilized by ammonolyzed SMA with lower (30%) and higher (80%) degree of aminolysis to study the effect of degree of aminolysis on the polymerization kinetics.

Figure 1 shows the polymerization kinetics of interfacially confined styrene RAFT miniemulsion polymerization under lower and higher degree of aminolysis. From the results, we found that under higher degree of aminolysis, the retardation time was about 120 min, whereas there was no retardation time under lower degree of aminolysis. The reason was that the aminolysis of dithioester group was ammonolyzed to form thiol, leading to the retardation.^{25,26} Another evidence of aminolysis of dithioester group was the appearance of absorbance peak with elution time at 30.96 min assigning to thiol formed in the GPC chromatography determined by UV detector [Figure 2(b)].²⁷



Scheme 3. Schematic presentation of aminolysis of dithioester group and ammonia.

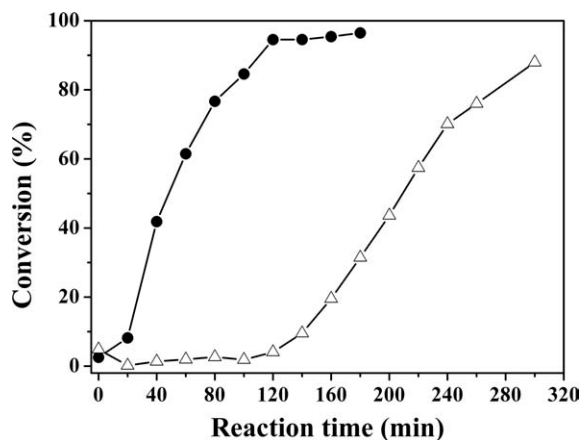


Figure 1. Conversion versus reaction time for interfacially confined RAFT miniemulsion polymerization of styrene using ammonolyzed SMA macro-RAFT agent with different degree of aminolysis as a mediator (●: 30% and △: 80%).

However, thiol absorbance peak in the GPC of polystyrene obtained under lower degree of aminolysis was not seen [Figure 2(a)]. This accounted for the fact that aminolysis of MAh was easier than that of dithioester group. Also, we found that a shoulder peak in the higher molecular weight section appeared from Figure 2(b). To our best knowledge, thiol could be coupled to form coupling compound with about double molecular weight. From the elution time of shoulder peak, its molecular weight was about double that of polystyrene peak with elution time at 23.82 min. This accounted for the fact that aminolysis of dithioester group resulted in retardation and loss of living character under higher degree of aminolysis. However, for styrene RAFT miniemulsion polymerization under lower degree of aminolysis, there was no obvious retardation and GPC peaks shifted toward the region of higher molecular weight with the increase of conversion [Figure 3(a)], and this was also illustrated the linear growth of the molecular weight with increase of conversion and the values of PDI were narrow [Figure 3(b)]. This verified the relatively good controlled/living characters under lower degree of aminolysis.

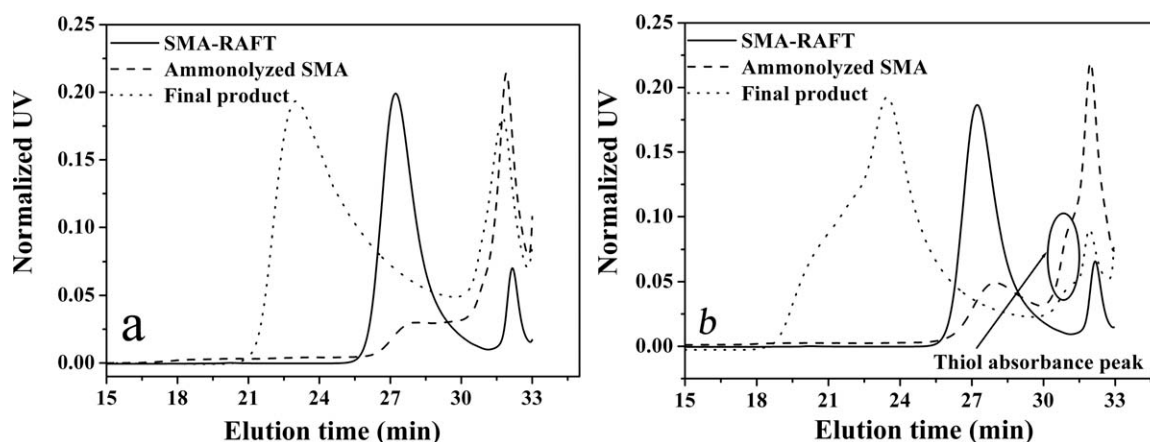


Figure 2. GPC curves from UV detector for interfacially confined styrene RAFT miniemulsion polymerization under lower (a) and higher (b) degree of aminolysis.

As for stability of emulsion, the polystyrene emulsion obtained via interfacially confined RAFT miniemulsion polymerization was very stable without visible phase separation for several months. The polystyrene particles obtained under lower degree of aminolysis were subjected to TEM analysis, which is illustrated in Figure 4. Uniform polystyrene nanoparticles with particle size of about 59 nm were seen distinctly. From those analyses, we could conclude that interfacially confined RAFT miniemulsion polymerization is a useful tool for synthesizing homopolymer nanoparticles with uniform particle size.

Interfacially Confined Styrene/Butadiene RAFT Miniemulsion Copolymerization

From the analyses, interfacially confined RAFT miniemulsion polymerization mediated by ammonolyzed SMA with lower degree of aminolysis (30%) is of relatively good controlled/living character. Therefore, we carried out the RAFT miniemulsion copolymerization of styrene and butadiene with the same degree of aminolysis, avoiding the effect of aminolysis of dithioester group on the copolymerization of styrene and butadiene. For all the copolymer emulsions obtained by RAFT polymerization mediated by ammonolyzed SMA, they were very stable without visible phase separation for several months. After RAFT miniemulsion copolymerization of styrene and butadiene, the emulsion was demulsified to obtain styrene/butadiene random copolymer and then subjected to FTIR and H-NMR analyses. Figure 5 shows the FTIR and H-NMR spectra of SMA-RAFT agent, polystyrene, and styrene/butadiene random copolymer. The split peaks at 1760 and 1870 cm^{-1} were assigned to anhydride quaternary ring in the SMA-RAFT agent. After aminolysis, the stretching vibrations of carbonyl group (1710 cm^{-1}) appeared, revealing that amphiphilic group formed in the process of aminolysis. For random copolymer of styrene and butadiene, the bands at 966 and 1720 cm^{-1} represented the C–H bending of *trans*-1,4-polybutadiene units and C=C double bonds, respectively. Because of the overlapping of a polystyrene peak, the absorption bands of *cis*-1,4-polybutadiene and 1,2-polybutadiene were not obvious. The results of H-NMR spectra showed that the peaks appearing at 4.85–5.05 ppm indicate the few content of 1,2-

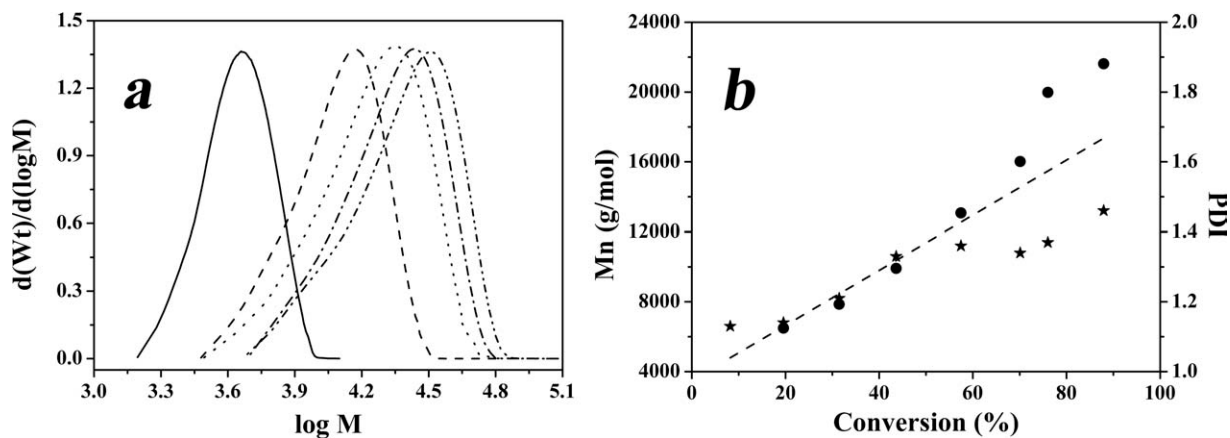


Figure 3. (a) Evolution of molecular weight distributions for interfacially confined RAFT miniemulsion polymerization under lower degree of aminolysis and (b) varieties of molecular weights (●) and PDI (★) with conversion.

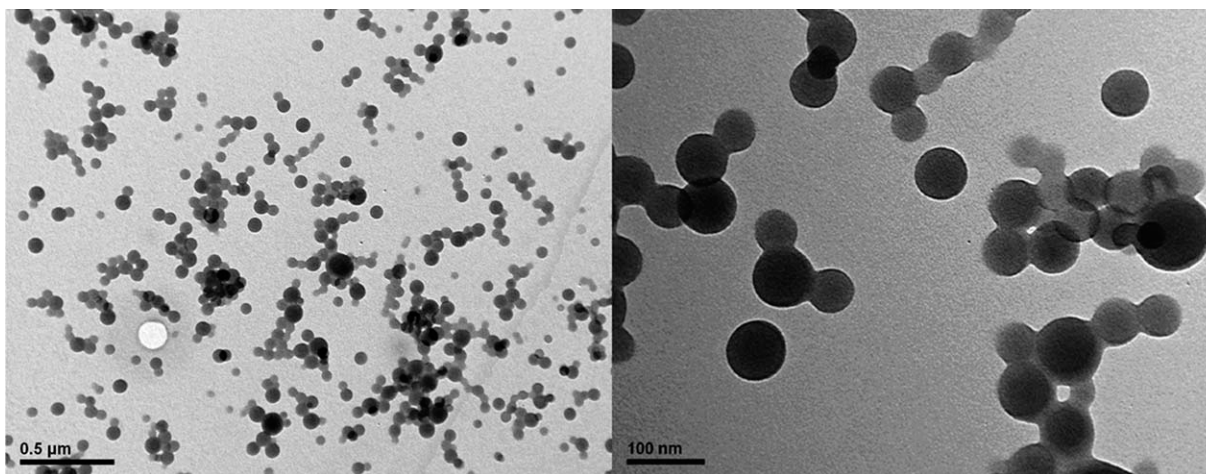


Figure 4. TEM images of polystyrene particles obtained by interfacially confined RAFT miniemulsion polymerization.

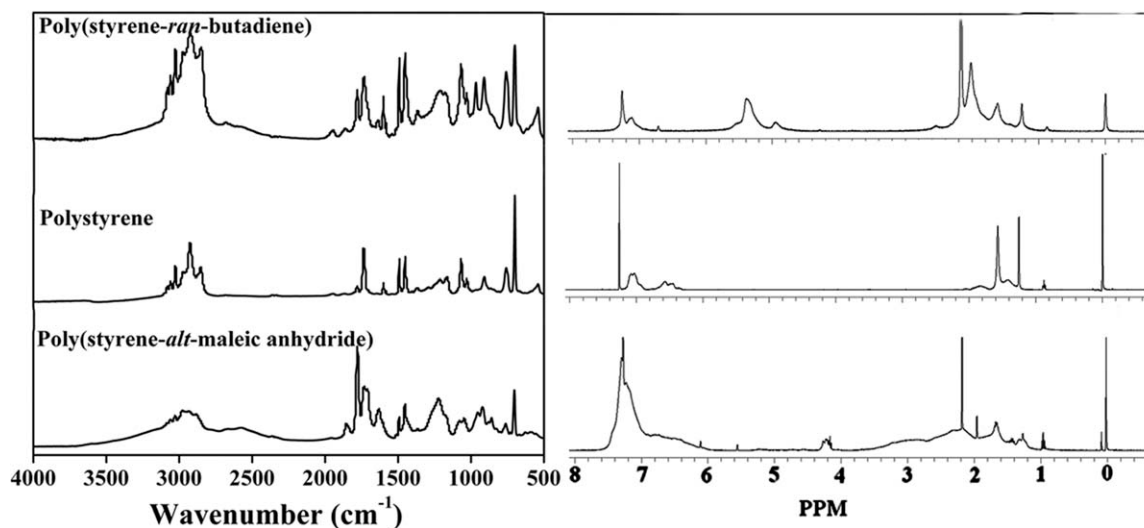


Figure 5. FTIR and H-NMR spectra of SMA, polystyrene, and random copolymer of styrene and butadiene.

Table I. Different Experimental Conditions and GPC Results for Styrene/Butadiene Interfacially Confined Miniemulsion Polymerization

| Exp | Ratio of S/B (w/w) | Temperature (°C) | Reaction time (h) | Conversion (%) | GPC | |
|-----|--------------------|------------------|-------------------|----------------|------------------------------|----------|
| | | | | | M_n (g mol ⁻¹) | PDI |
| 1 | 2 : 3 | 60 | 10 | 38.3 | 35,970 | 2.20 |
| 2 | 2 : 3 | 70 | 9 | 71.0 | Gelation | Gelation |
| 3 | 3 : 2 | 60 | 10 | 45.5 | 40,482 | 2.71 |
| 4 | 3 : 2 | 70 | 9 | 86.1 | Gelation | gelation |

polybutadiene units, and the peaks appearing at 5.35–5.41 ppm indicate the high content of 1,4-polybutadiene units.²⁸

Comparing with polymerization kinetics of styrene RAFT miniemulsion polymerization, copolymerization kinetics of RAFT miniemulsion polymerization of styrene and butadiene proceeded slowly because of the lower propagating rate constant of butadiene.²⁹ To study the effect of reaction temperature and ratio of styrene and butadiene (S/B) on the polymerization kinetics, four experiments listed in Table I were carried out. From the relationship between conversion and reaction time (Figure 6), it was found that reaction temperature had an obvious influence on the copolymerization kinetics with the same ratio of S/B. The reason was that higher temperature would accelerate polymerization. According to Arrhenius equation, the faster the polymerization rate was, the higher the reaction temperature was. Therefore, the polymerization rates at 70°C were faster than those at 60°C. However, at different reaction temperatures, the ratio of S/B had different effects on the polymerization kinetics. First, at 60°C, the ratio of S/B had no effect on the polymerization kinetics. The polymerization rate might be determined by propagating rate constant, which was affected by reaction temperature. Although the propagating rate constant of styrene was larger than that of butadiene, the reaction temperature became the main factor affecting the polymerization rate. However, at higher temperature, the more the styrene percentage was, the faster the polymerization rate was. Therefore, the polymerization rate of experiment 4 was faster than that of experiment 2 at 70°C.

One of the advantages of RAFT polymerization is a good control over the molecular weights (M_n s) and PDI of the polymers. Because of carbon–carbon double bonds of butadiene, branching or crosslinking reaction would happen during the copolymerization of styrene and butadiene to form insoluble gelation, leading to being difficult to obtain the molecular weight of copolymer. Therefore, before forming gelation, the molecular weights of random copolymer with different conversions were subjected to GPC analyses, which are shown in Figure 7. For all the polymerizations (before gelation), the GPC peaks shifted toward the region of higher molecular weight with the increase of the conversions, and this is also illustrated the linear growth of the molecular weight with increase of conversion. Because of large majority of polymer chains having a dithioester end group, the content of dead polymer is very few. Therefore, the PDI values were lower than 1.5 at lower conversion and molecular weights were in good agreement with theoretical prediction.

With increase of conversion, because of the residual carbon–carbon double bonds, microgel and branching reaction would happen, leading to the increase of PDI values. However, microgel or branching reaction will have more obvious effect on the PDI values than on the molecular weights. Therefore, the number molecular weight increases linearly with conversion, whereas the experimental molecular weights became larger than theoretical prediction approaching gel point and the PDI values of copolymer become higher than 1.5. The reason was that the branching and crosslinking reaction with increase of conversion. In addition, according to the literature,³⁰ gelation is attributed to the higher ratio of polymer/butadiene. The content of butadiene within the particles will have an influence on the gelation. With the progress of copolymerization, the content of butadiene will decrease gradually and crosslinking or branching reaction will happen, leading to the higher PDI values. Therefore, under the same experimental conditions, the PDI values are higher at S/B ratio of 3 : 2. From all the analyses above, we could conclude that random copolymer of styrene and butadiene could be synthesized by interfacially confined RAFT miniemulsion polymerization, and reaction temperature had an obvious effect on the gelation, which was easier to be formed at higher temperature than at lower temperature. For all the polymerizations, before gelation the polymerization is of relatively good controlled/living characters.

Figure 8 shows the DSC trace of the final copolymer of styrene and butadiene. For polystyrene, there was only one glass

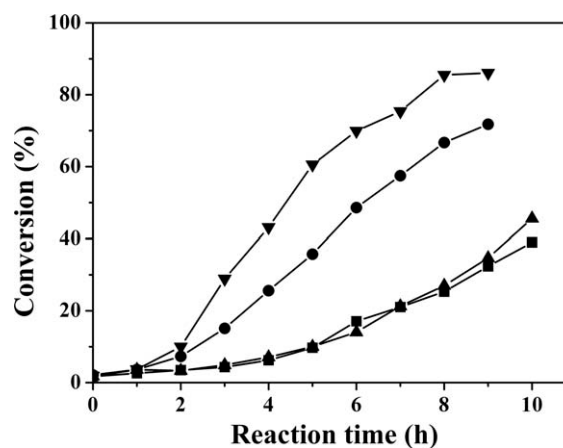


Figure 6. Conversion versus reaction time for interfacially confined miniemulsion copolymerization of styrene and butadiene with different ratios of S/B and reaction temperature. 60°C (S/B = 2 : 3, ■); 70°C (S/B = 2 : 3, ●); 60°C (S/B = 3 : 2, ▲); and 70°C (S/B = 3 : 2, ▼).

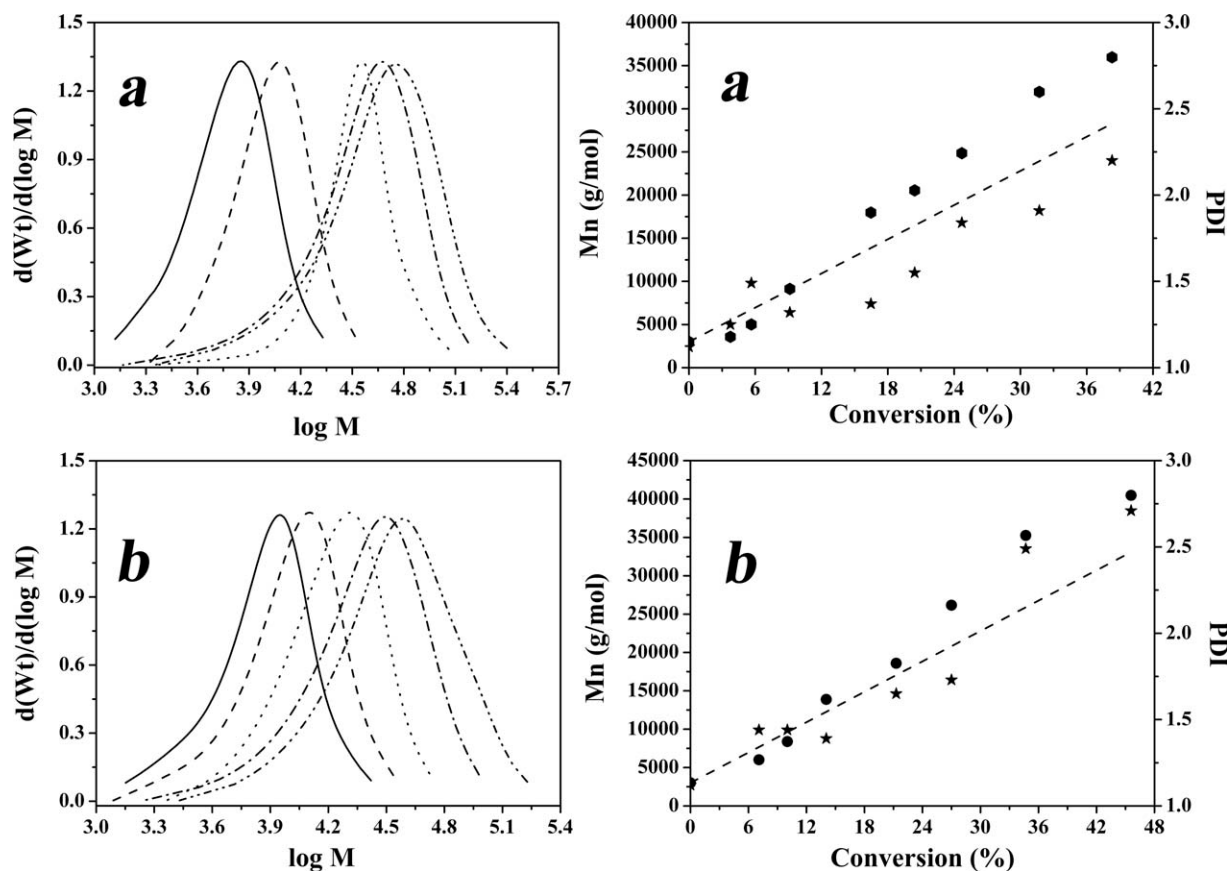


Figure 7. Evolution of molecular weight distributions of random copolymer with conversion and varieties of molecular weights (●) and PDI (★) against conversion [a: 60°C (S/B = 2 : 3) and b: 60°C (S/B = 3 : 2)].

transition temperature at 101°C. For random copolymer of styrene and butadiene, an obvious glass transition temperature (T_g) at -36°C assigned to the copolymer segment could be seen clearly. There was no transition temperature peak assigning to homopolymers of styrene or butadiene. This accounted for the fact that ammonolyzed SMA can efficiently mediate styrene and

butadiene RAFT miniemulsion polymerization to synthesize random copolymer.

Copolymer nanoparticles of styrene and butadiene are prone to microphase segregation.³¹ Therefore, the final nanoparticles were carried out to TEM analysis. Figure 9 shows the TEM images of styrene/butadiene copolymer nanoparticles obtained by interfacially confined miniemulsion polymerization. The obtained copolymer nanoparticles had uniform particle size. Because the residual double bonds could be stained with OsO_4 , the butadiene-rich microdomains appeared dark and the styrene-rich microdomains appeared light. From the TEM images, microphase segregation was obvious and “core-shell” copolymer nanoparticles with polybutadiene core (dark) and polystyrene shell (light) could be seen clearly.

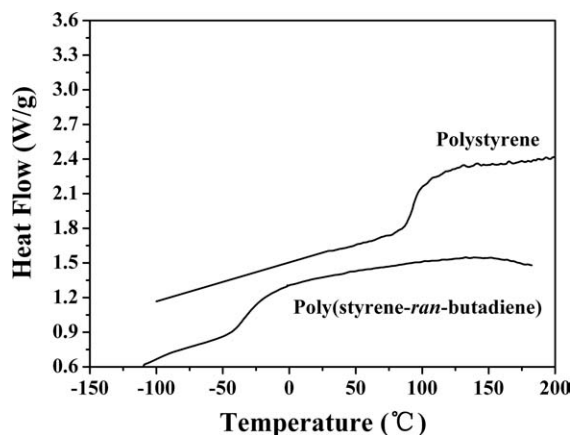


Figure 8. DSC trace of polystyrene and random copolymer of styrene and butadiene obtained by interfacially confined RAFT miniemulsion polymerization.

CONCLUSIONS

Ammonolyzed SMA macro-RAFT agent can be used as an amphiphilic RAFT agent to mediate styrene/butadiene interfacially confined RAFT miniemulsion polymerization to synthesize stable nanoparticles. First, aminolysis reaction between dithioester group and ammonia will result in retardation and loss of living characters. Interfacially confined RAFT miniemulsion polymerization is of relatively good controlled/living characters under lower degree of aminolysis and obtained emulsions are stable without phase separation for several months. The

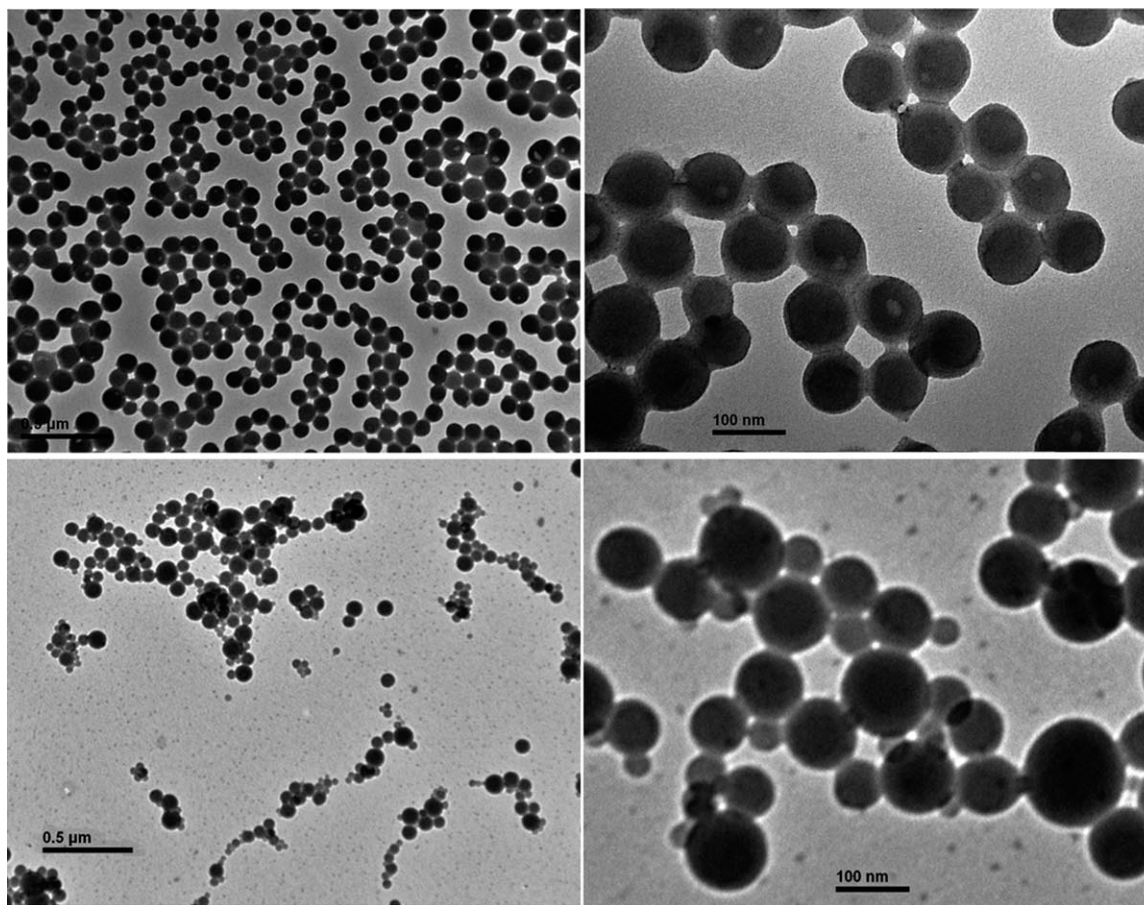


Figure 9. TEM images of styrene/butadiene copolymer nanoparticles obtained by interfacially confined RAFT miniemulsion polymerization.

reaction temperature and ratio of S/B had an effect on the polymerization kinetics, living characters, and gelation. The increase of reaction temperature and ratio of S/B could accelerate the formation of gelation. In the aspect of nanoparticle morphology, the styrene/butadiene copolymer nanoparticles obtained by interfacially confined RAFT miniemulsion polymerization possessed “core-shell” morphology with polybutadiene core and polystyrene shell because of microphase segregation.

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