

Comparison of Styrene Reversible Addition–Fragmentation Chain-Transfer Polymerization in a Miniemulsion System Stabilized by Ammonolysis Poly(styrene-*alt*-maleic anhydride) and Sodium Dodecyl Sulfate

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ABSTRACT: In this study, we conducted the reversible addition–fragmentation chain-transfer (RAFT) polymerization of styrene (St) in a miniemulsion system stabilized by two different stabilizers, ammonolysis poly(styrene-*alt*-maleic anhydride) (SMA) and sodium dodecyl sulfate (SDS), with identical reaction conditions. The main objective was to compare the polymerization kinetics, living character, latex stability, and particle morphology. The macro-RAFT agent used in both systems was SMA, which was obtained by RAFT solution polymerization mediated by 1-phenylethyl phenyl-dithioacetate. The experimental results show that the St RAFT miniemulsion polymerization stabilized by SDS

exhibited a better living character than that stabilized by ammonolysis SMA. The final latices were very stable in two systems, but different stabilizers had an obvious effect on the polymerization kinetics, living character, and particle morphology. All of the particles obtained by RAFT miniemulsion polymerization stabilized by SDS were solid, but an obvious core–shell structure was observed in the miniemulsion system stabilized by ammonolysis SMA. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4249–4258, 2012

Key words: core–shell polymers; gel permeation chromatography (GPC); self-assembly

INTRODUCTION

Studies of living/controlled free-radical polymerizations, including nitroxide-mediated polymerization,¹ atom-transfer radical polymerization,^{2–4} and reversible addition–fragmentation chain-transfer (RAFT) radical polymerization,⁵ have increased significantly during recent years.^{6–10} The advent of living/controlled free-radical polymerization techniques opens a new era in the domain of polymer chemistry. One of the main advantages is the possibility of designing more polymers with well-defined structures, such as block, graft, and star polymers, which are not accessible by other polymerization methods. Compared with other living/controlled free-radical polymerization methods, RAFT polymerization can be easily applicable to a wide range of monomers at the facile temperature.^{11–13} Moreover, studies of RAFT polymerization in miniemulsion systems have been more successful than other living/controlled polymerizations. RAFT miniemulsion polymeriza-

tions are of great importance in industrial applications as they provide environmental friendly processes, remove the reaction heat easily during polymerization, and ensure feasible handling of the final product with a low viscosity.¹⁴ So many studies have been concentrated on RAFT miniemulsion polymerizations.^{15–26}

With that definition, RAFT miniemulsion polymerization involves at least five ingredients: the continuous phase, the dispersed phase, the RAFT agent, the costabilizer, which is often dissolved in the dispersed phase, and the surfactant. The surfactant is a surface-active compound generally dissolved in the continuous phase and responsible for the stability of the latex through the prevention of droplet coalescence during the emulsification step and coagulation between particles. Among the ingredients, the surfactant has a direct effect on the polymerization kinetics and colloidal stability of the final latex. The added amount of surfactant should be adjusted to prevent micellar nucleation. Moreover, when low-molecular-weight surfactants are used with a RAFT agent in miniemulsion, the presence of relatively large amounts of surfactants reduce the quality and usefulness of the final product latex.

Therefore, intense research has been focused on finding alternative stabilizers instead of on the surfactant.^{27–34} Macromolecular surfactants are potential

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stabilizers to replace low-molecular-weight surfactants for several reasons, which are related to the characteristics of the resulting latices. First, the use of a macromolecular stabilizer during miniemulsion polymerization is an efficient, one-pot strategy for synthesizing nanoparticles. Second, a macromolecular stabilizer can act not only as a stabilizer but also as a chain-transfer agent and so on; thus, it replaces some molecular reactants. For example, pham et al.¹⁸ devised a new approach to carry out miniemulsion polymerization wherein amphiphilic RAFT agents are used to emulsify the dispersed phase, stabilize the particles, and control the molecular weight of the polymer produced. A wide variety of chemical structures of macromolecular surfactants has been used in (mini)emulsion systems. Of these macromolecular surfactants, the ammonolysis copolymer of styrene (St) and maleic anhydride (MAh), poly(styrene-*alt*-maleic anhydride) (SMA), can be used as an amphiphilic surfactant to stabilize particles in aqueous phase by electrostatic interactions. Luo and Gu³⁵ published a method for encapsulating oil droplets by a polymer shell to form nanosized, liquid-filled particles with ammonolysis copolymer of St and MAh. However, the effects of ammonia on the polymerization kinetics and living character and comparison with different surfactants have not been studied yet.

So in this work, we mainly synthesized a diblock copolymer having alternating segments via RAFT polymerization in miniemulsion systems stabilized by different surfactants with identical reaction conditions. On the other hand, we compared the polymerization kinetics, living character, latex stability, and particle morphology in two RAFT miniemulsion systems. One was regulated by sodium dodecyl sulfate (SDS), and the other was regulated by ammonolysis SMA.

EXPERIMENTAL

Materials

St was distilled under reduced pressure before use. The initiator, 2,2'-azoisobutyronitrile (AIBN), was recrystallized twice from methanol. MAh, hexadecane (HD), SDS, and potassium persulfate (KPS), which were analytical-reagent grade, were used as received without further purification. Solvents used for the synthesis of the polymers and the RAFT agent were freshly distilled with sodium. Ammonia solution (25 wt % in water) was used without any purification. Hydroquinone was used to quench the samples withdrawn during the experiments.

Synthesis of 1-phenylethyl phenyldithioacetate (PEPDTA)

The RAFT agent, PEPDTA, was synthesized according to the literature.³⁶

St and MAh RAFT polymerization in a solution system

The SMA-RAFT agent, which is shown in Scheme 1, was synthesized according to a previously described method.³⁷ In a 250-mL, round-bottom flask equipped with a stirring bar, a nitrogen purge, and reflux condenser, MAh (19.60 g, 0.20 mol), St (20.80 g, 0.20 mol), PEPDTA (2.722 g, 10.00 mmol), and AIBN (0.163 g, 1.00 mmol) were dissolved in 100 mL of dried tetrahydrofuran and then deoxygenated via purging with N₂ gas under stirring. The reaction mixture was then put into a 60°C water bath and left stirring for 4 h under an N₂ atmosphere. Precipitation in 500 mL of methanol yielded 36.2 g of polymer after drying in a vacuum oven at 40°C.

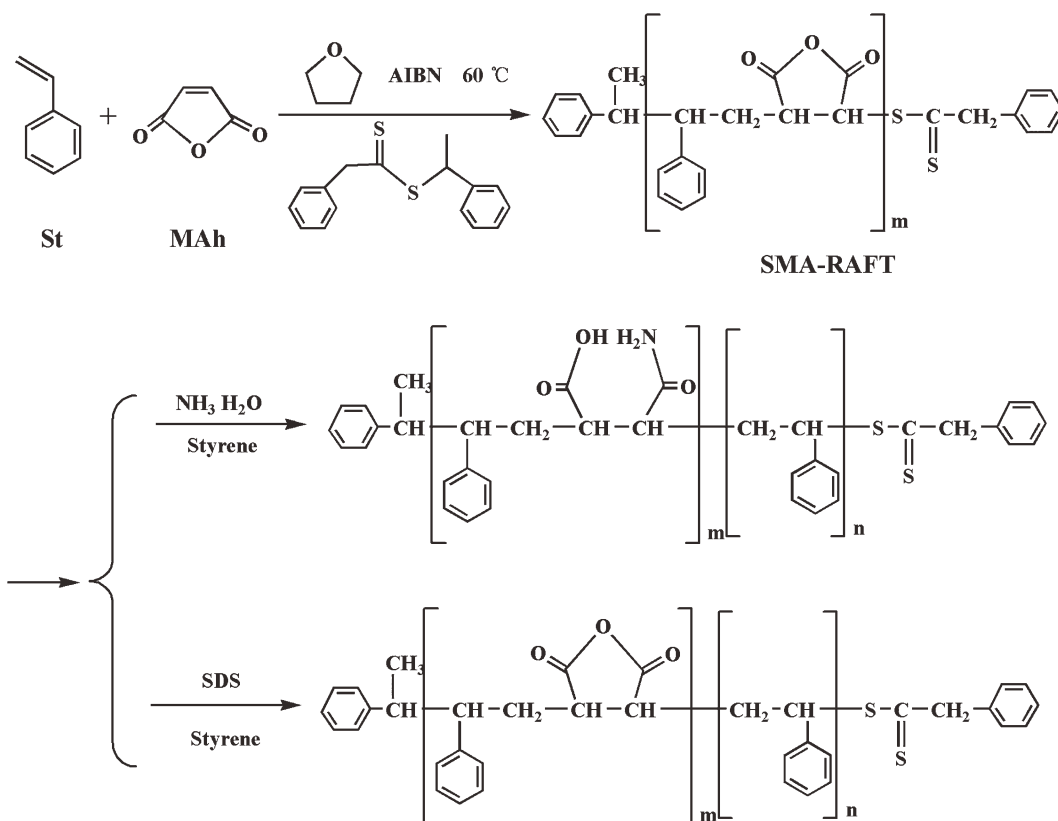
¹H-NMR (Fig. 1; CDCl₃, δ, ppm, tetramethylsilane): 5.85–7.62 (benzyl ring), 1.02–3.58 (anhydride unit and –CH₂–CHPh). Fourier transform infrared (FTIR) spectroscopy (cm⁻¹): ν_{C=O} 1790 and 1850. Gel permeation chromatography (GPC) number-average molecular weight (M_n): 3560 g/mol. Polydispersity index (PDI): 1.13.

St RAFT polymerization in a miniemulsion system stabilized by SDS

The SMA-RAFT agent (3.00 g, 0.843 mmol), St (20.00 g, 0.192 mol), initiator (if AIBN was used), HD (0.45 g, 1.99 mmol), and acetone (15 mL) were first thoroughly mixed by magnetic stirring until homogeneous, and then, the oil phase was slowly added to 90 g of an aqueous solution, which dissolved SDS. After pre-emulsification by magnetic stirring, the crude emulsion was ultrasonicated by a probe 60 times with a lifetime of 3 s. The obtained miniemulsion was transferred to a 250-mL, four-necked, round-bottom flask. After N₂ was purged for 30 min, the initiator (if KPS was used) was added to the miniemulsion, which was then heated to the reaction temperature to start the polymerization. Samples were taken at regular time intervals throughout the reaction for analysis. The solid content of the emulsions was kept at 20%. The reaction scheme is depicted in Scheme 1. To study the effect of initiator and reaction temperature on the polymerization kinetics, five experiments were carried out, and the recipes are listed in Table I.

St RAFT polymerization in a miniemulsion system stabilized by ammonolysis SMA

A typical procedure for St RAFT polymerization in a miniemulsion system stabilized by the ammonolysis SMA-RAFT agent (Scheme 1) was as follows. The SMA-RAFT agent (3.00 g, 0.843 mmol), St (20.00 g, 0.192 mol), HD (0.45 g, 1.99 mmol), and acetone (15 mL) were first thoroughly mixed by magnetic stirring until homogeneous, and then, the diluted



Scheme 1 Reaction scheme for the St RAFT polymerizations in the miniemulsion systems stabilized by ammonolyzed SMA and SDS.

ammonia solution (90.0 g) was added dropwise to the oil phase under stirring. After pre-emulsification by magnetic stirring, the crude emulsion was ultrasonicated for 6 min in an ice-water bath. The obtained miniemulsion was transferred to a 500-mL, four-necked, round-bottom flask. After N₂ was purged for 30 min, the initiator KPS (0.06 g, 0.22 mmol) was added to 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. To study the effect of ammonia on the

polymerization kinetics, experiments 6–10 were carried out, and the recipes are listed in Table II.

Polymer characterization

Conversion analyses

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.

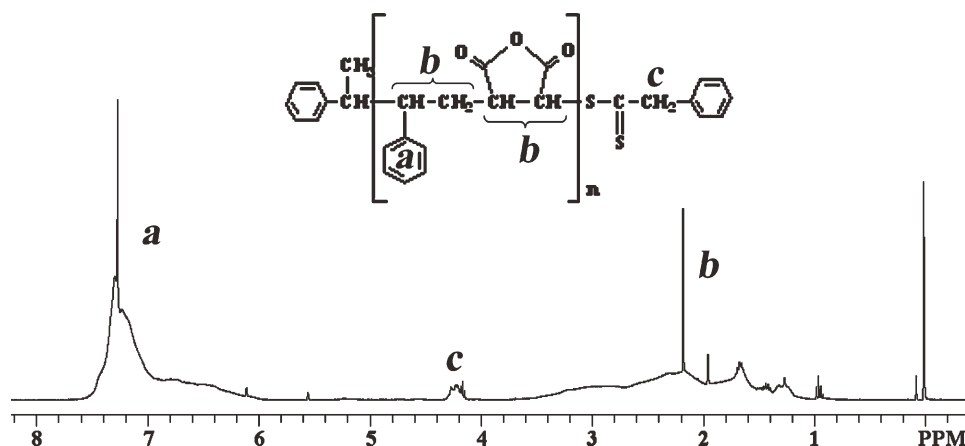


Figure 1 ¹H-NMR spectrum of SMA.

TABLE I
Reaction Conditions of the St RAFT Polymerization in the Miniemulsion System Stabilized by SDS

Experiment	AIBN (%)	KPS (%)	Reaction temperature (°C)
1	20	0	60
2	20	0	70
3	40	0	70
4	0	20	60
5	0	40	70

GPC analyses

The M_n and PDI values of the dried polymers were recorded on a Waters 1525 GPC instrument (Kansas, Missouri, USA) with three gel columns ($7.8 \times 300 \text{ mm}^2$) and a differential refractive-index (RI) detector. The eluent was tetrahydrofuran at 35°C with a flow rate of 1.0 mL/min . The molecular weights of the dried polymer samples were determined with standard polystyrene calibration.

FTIR spectroscopy analysis

FTIR measurements were performed on a Nicolet 5700 FTIR (Madison, Wisconsin, USA) spectrometer (KBr). The polymer samples were dried in a vacuum oven at 50°C for 6 h.

NMR analysis

NMR analyses were performed on a Bruker DMX-500 nuclear resonance (Fälladen, Switzerland) instrument with chloroform- d as a solvent and tetramethylsilane as an internal standard at ambient temperature.

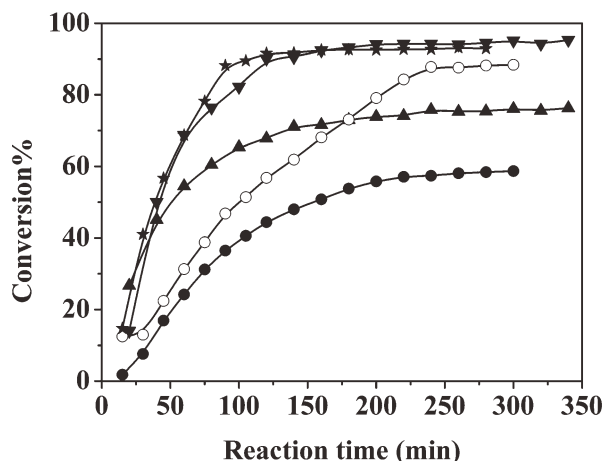


TABLE II
Reaction Conditions of the St RAFT Polymerization in the Miniemulsion System Stabilized by Ammonolyzed SMA at 70°C

Experiment	Degree of aminolysis (%)	Time (min)	Conversion (%)
6	30	180	96.5
7	40	140	94.4
8	60	180	62.6
9	80	300	87.9
10	100	360	89.4

Transmission electron microscopy (TEM) analysis

The morphologies of the latex particles were examined by TEM (JEOL, JEM-1200) (Tokyo, Japan). For the measurement, the samples were diluted to a solid content of 0.005 g/g of latex. The dilution was dipped onto carbon-coated copper grids and dried at room temperature. TEM was done at 80 kV .

Dynamic light scattering measurement

Dynamic light scattering was performed with a 90 plus particle size analyzer (Brookhaven Instruments Corp.) (Holtville, New York, USA) equipped with an He-Ne laser (633 nm). The measurements were made at the scattering angle ($\theta = 90^\circ$) at room temperature.

RESULTS AND DISCUSSION

Comparison of polymerization kinetics in miniemulsion systems stabilized by different stabilizers

In the miniemulsion system stabilized by SDS, to study the effects of different factors on St miniemulsion polymerizations, a series of experiments were carried out under different experimental conditions,

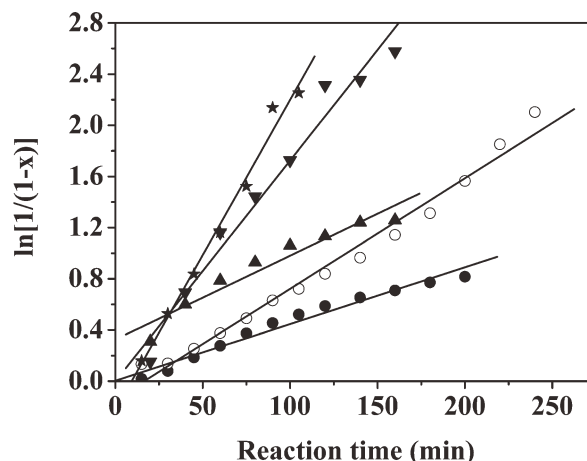


Figure 2 Polymerization kinetics of the St RAFT polymerization in the miniemulsion system stabilized by SDS with different reaction conditions: (●) experiment 1 in Table I, (▲) experiment 2 in Table I, (▼) experiment 3 in Table I, (○) experiment 4 in Table I, and (★) experiment 5 in Table I.

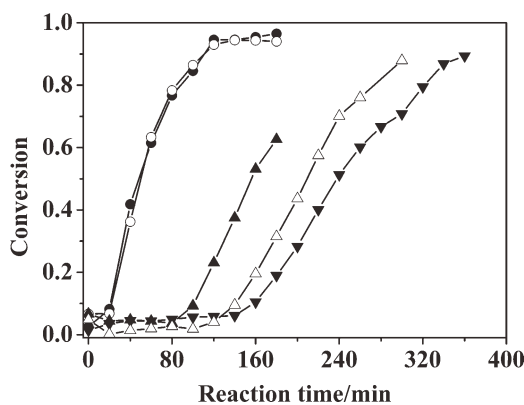


Figure 3 Polymerization kinetics of the St RAFT polymerization in the miniemulsion system stabilized by ammonolyzed SMA with different degrees of aminolysis: (○) 30% (experiment 6 in Table II), (●) 40% (experiment 7 in Table II), (▲) 60% (experiment 8 in Table II), (△) 80% (experiment 9 in Table II), and (▼) 100% (experiment 10 in Table II).

with variations in the reaction temperature and the amount and type of initiator (Table I), and the polymerization kinetics are depicted in Figure 2.

From the polymerization kinetic plots [Fig. 2(a)], it was found that the reaction temperature and the type and amount of initiator had an obvious influence on the polymerization kinetics. The conversion of St increased when the reaction temperature or the amount of initiator was increased. On the other hand, the water-soluble initiator (KPS) had better initiator ability than the oil-soluble initiator (AIBN). For experiment 4, because of the better entry ability of the radical from KPS compared to AIBN, the polymerization rate was faster than for experiment 1. However, compared with experiment 2, the reaction temperature obviously affected the polymerization rate. However, the half-life of AIBN was shorter than that of KPS, so the final conversion of experiment 4 was higher. As shown from the mechanism of the RAFT polymerization, the radical concentration remained almost constant. Figure 2(b) shows the results of the study of the relationship between $\ln[1/(1-x)]$ and the polymerization time in different polymerization conditions, where x is the conversion of monomer. The straight line plotting $\ln[1/(1-x)]$ versus the polymerization time indicated that the chain radical concentra-

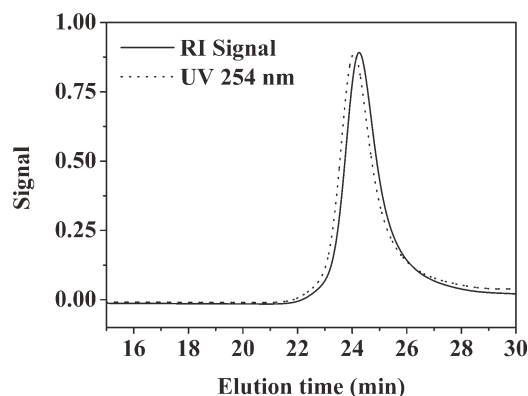
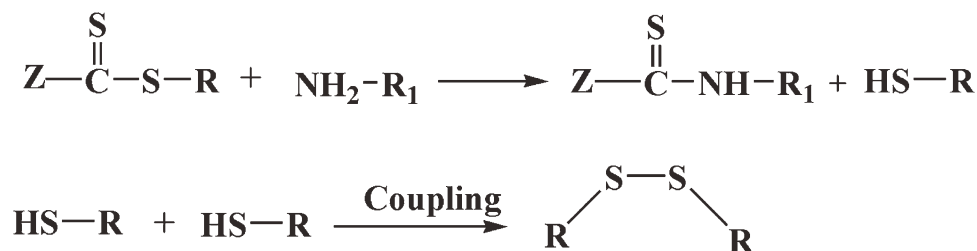


Figure 4 Overlays of polystyrene molecular weight distributions obtained from the (—) RI detector of GPC and (···) UV detector operated at 254 nm for the RAFT polymerization in a miniemulsion stabilized by SDS.

tion remained constant in the process of the miniemulsion polymerization.

For the miniemulsion system stabilized by ammonolysis SMA, ammonolysis SMA could form the hydrophilic group, which could stabilize the latex. So in the St RAFT polymerization in the miniemulsion system stabilized by ammonolysis SMA, we studied the effect of ammonia on the St RAFT miniemulsion polymerization kinetics. As shown in Figure 3, which reveals the relationship between the conversion and reaction time, it was found that significant retardation was observed with an increase in the amount of ammonia. The greater the amount of ammonia was, the longer the retardation time was. For the St RAFT polymerization in the miniemulsion system stabilized by ammonolysis SMA with a higher degree of aminolysis, although the radical might have been consumed by thiol formed by the aminolysis of the dithioester group, the residual radical from KPS was still able to initiate the polymerization and to achieve a higher conversion.

Significant retardation was observed in the St RAFT polymerization in the miniemulsion stabilized by ammonolysis SMA with an increase of ammonia. To our knowledge, ammonia can react with anhydride groups to form hydrophilic groups. However, according to some studies, the dithioester group in the RAFT agent is rather apt to be hydrolyzed^{38,39} and ammonolysis.^{40,41} It is more easily ammonolysis than hydrolyzed. For example, as shown in Scheme 2,



Scheme 2 Schematic presentation of the aminolysis and coupling reaction.

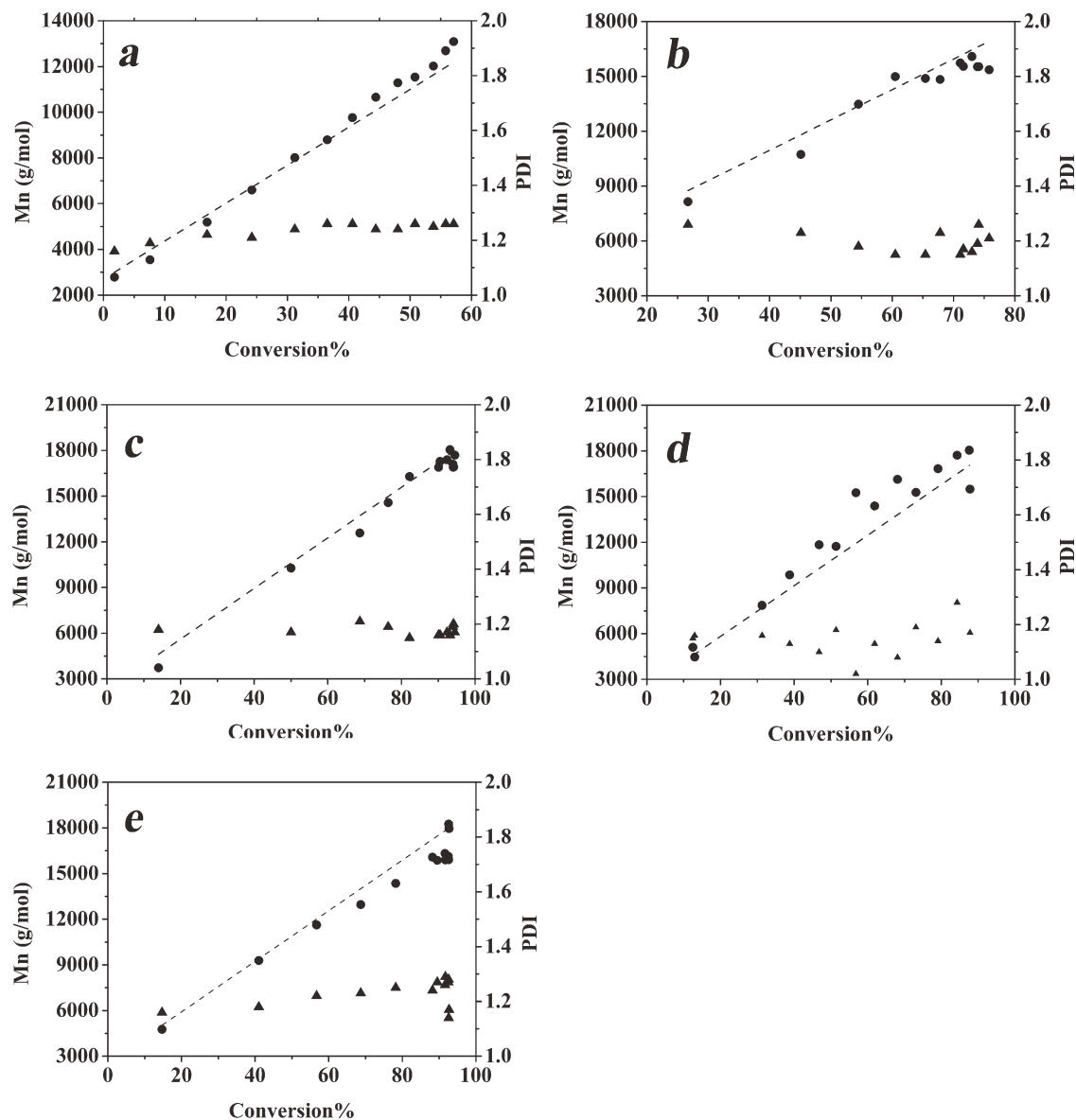


Figure 5 Plots of (●) M_n and (▲) PDI and (---) theoretical values against conversions for the St polymerizations in the miniemulsions stabilized by SDS: experiments (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5.

the dithioester group can be ammonolysis to form thioamide and thiol. On one hand, thiol will still act as a chain-transfer agent without living character and may still form some block copolymer; this results in a broadening of the PDIs of the final polymers. On the other hand, thiol can be coupled to form another polymer with double the molecular weight. Therefore, during the aminolysis of the anhydride group, the dithioester group might be fractured by ammonia; this leads to the appearance of retardation.

Comparison of the living characters in miniemulsion systems stabilized by different stabilizers

According to the mechanism of RAFT polymerization, most of the polymer chains were terminated by

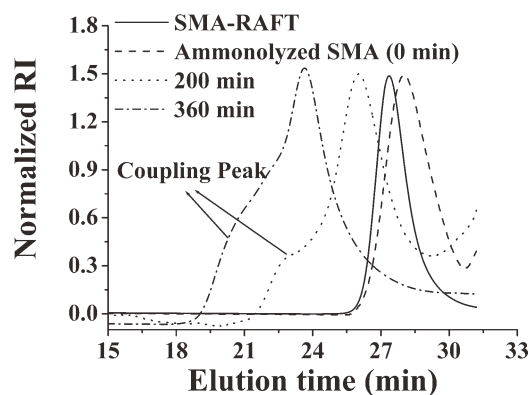


Figure 6 Gel permeation chromatograms with the RI detector of SMA, ammonolyzed SMA, and polymers with different reaction times in experiment 10 with fully ammonolyzed SMA as a stabilizer at 70°C.

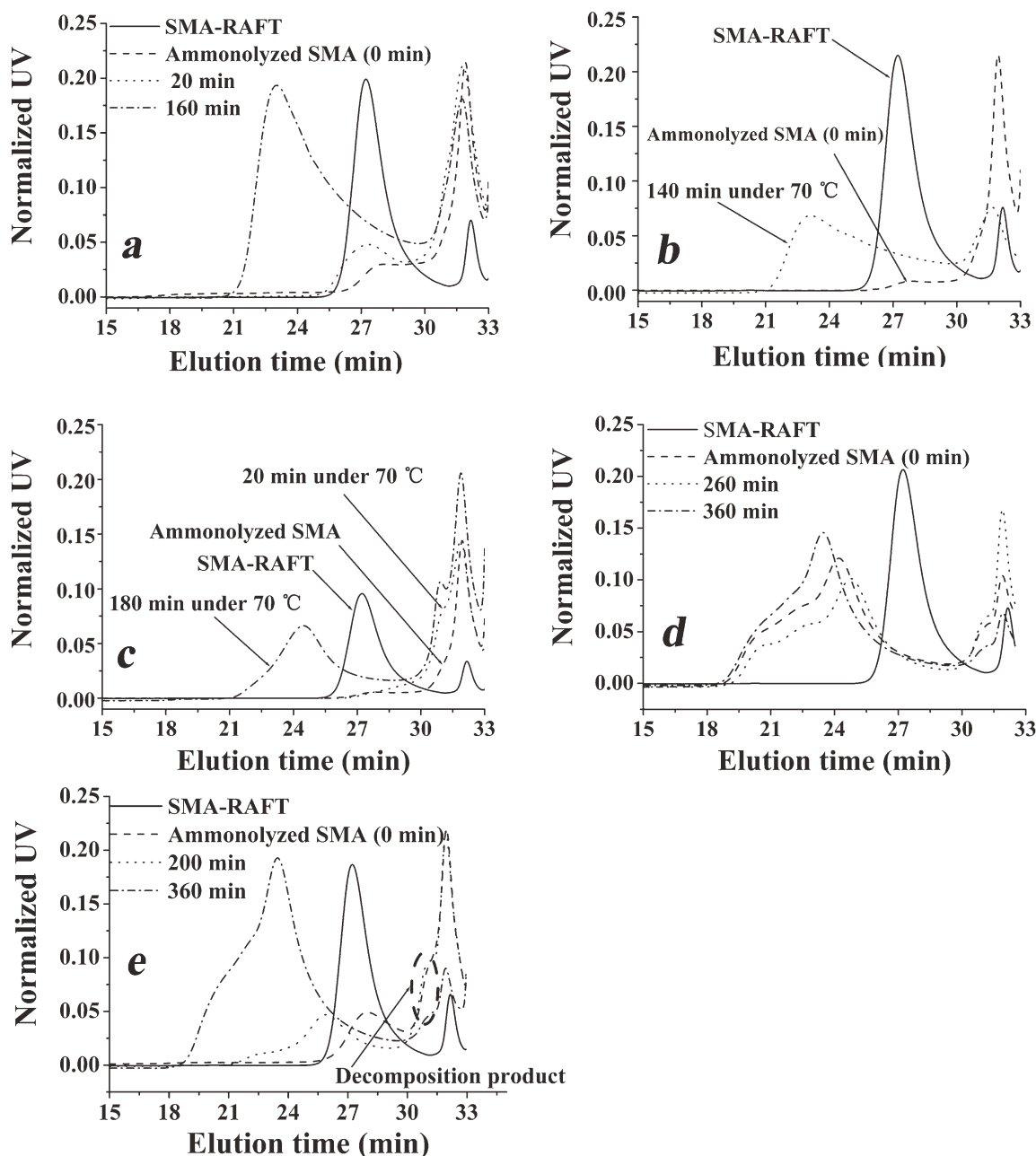


Figure 7 Gel permeation chromatograms with the UV detector of SMA, ammonolyzed SMA, and the polymers of experiments (a) 6, (b) 7, (c) 8, (d) 9, and (e) 10 with different degrees of aminolysis.

RAFT end groups after the polymerization was finished. To investigate whether the dithioester end group was homogeneously distributed throughout the distribution, a dual RI-UV detector system was used for GPC (the UV detector was set at 254 nm, which corresponded to the UV absorption wavelength of the dithioester RAFT agent). For all of the miniemulsion polymerization systems stabilized by SDS, the RI-UV perfect overlay of the final polymers' molecular weight distributions for the miniemulsion polymerizations (Fig. 4) indicated that a large majority of chains had a dithioester end group.

Figure 5 shows that the variations of the molecular weight and PDI of all of the products with different conversions of the miniemulsion polymerization stabilized by SDS. For all of the polymerizations, the GPC peaks shifted toward the region of higher molecular weight with increasing conversion, and this was also illustrated by the linear growth of the molecular weight with increasing conversion. Because the large majority of polymer chains had a dithioester end group, the content of dead polymer was very low. Therefore, the PDI values were very low and were independent of the experiment.

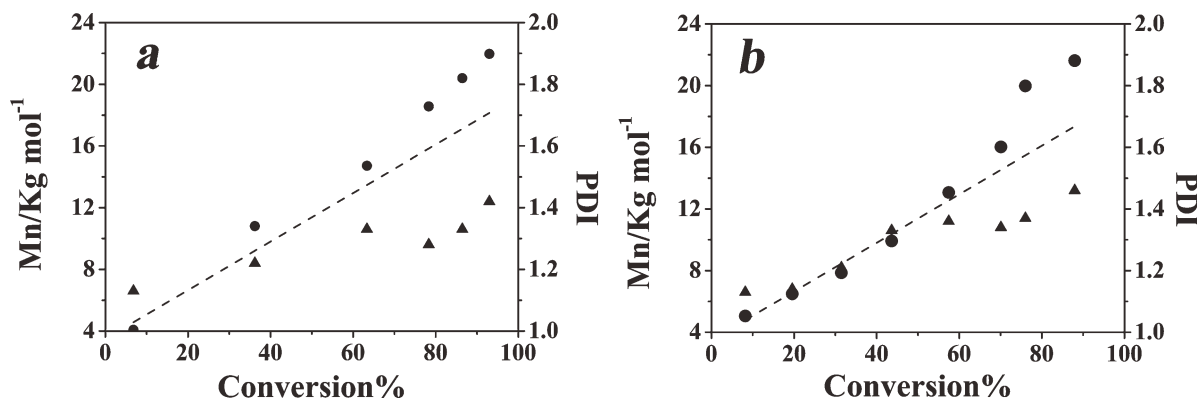


Figure 8 Molecular weight and PDI against the conversion of experiments 6 (left) and 7 (right).

However, for the miniemulsion polymerizations stabilized by ammonolysis SMA, we found that the amount of ammonia played a crucial role and had an obvious effect on the living character in the miniemulsion polymerization system from the polymerization kinetics. So we first compared the GPC changes in SMA and ammonolysis SMA, and the products with different reaction times with the RI detector for experiment 10 with full ammonolysis. The chromatograms obtained with the RI detector (Fig. 6) displayed a small change in the molecular weights of SMA and ammonolysis SMA. After aminolysis, the retention time of strong absorption shifted from 27.31 to 27.99 min and indicated that the dithioester group had been fractured. This was one piece of evidence of the fracture of the dithioester group and loss of living character. The peaks appeared at about double the molecular weight. So we concluded that a shoulder peak was caused by the coupling of thiol formed by aminolysis. This accounted for the fact that ammonia reacted with the dithioester group during the polymerization.

Because the changes in the chromatograms of SMA before and after aminolysis obtained with the RI detector were not very obvious, the UV detector at 254 nm detected the more obvious change that a shoulder peak with an elution time of 30.96 min appeared after aminolysis (Fig. 7). This was more evidence of the fracture of the dithioester group and loss of living character.⁴²

However, for experiment 8, it was found that there was no decomposition product peak at an elution time of 30.9 min before and after aminolysis. However, after polymerization began, this shoulder peak appeared [Fig. 7(c)]. The possible reason was that it was easier for the dithioester group to be fractured by ammonia at 70°C than at room temperature.

However, for experiments 6 and 7, the ratios of ammonia concentration to anhydride concentration were about 30 and 40%, respectively, and the final latices obtained were very stable, without visible phase separation

for several months. From the kinetic plots, there was no retardation, either. The results of M_n and PDI determined by GPC showed that the polymerizations of experiments 6 and 7 exhibited relatively good controlled/living nature, as shown in Figure 8. From the results of the molecular weight and PDI, the St miniemulsion polymerizations stabilized by ammonolysis SMA with a lower degree of aminolysis (<40%) exhibited a relatively good controlled/living nature.

Comparison of the latex stability and particle morphology in miniemulsion systems stabilized by different stabilizers

Anhydride groups in the SMA chain could be hydrolyzed and ammonolysis to form hydrophilic groups, carboxylic acid, which could stabilize the latex. With the purpose of comparing the stability of the final latices, three parallel polymerizations of St were carried out at 70°C, with one regulated by SMA, one regulated by ammonolysis SMA, and the

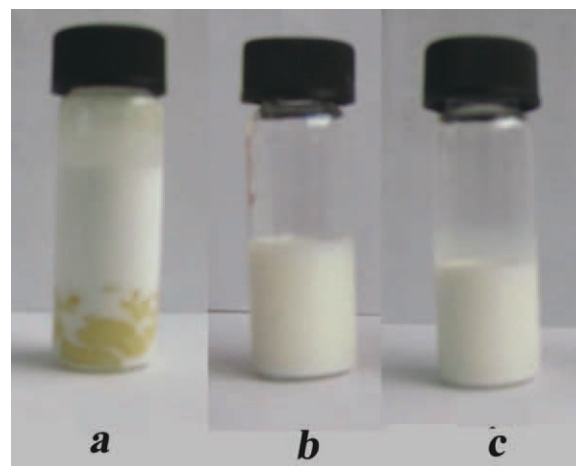


Figure 9 Photographs of the final latices stabilized by (a) unammonolyzed SMA, (b) ammonolyzed SMA, and (c) SDS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

other regulated by SDS under identical reaction conditions. Figure 9 shows the photographs of the final latices with different stabilizer systems.

In the St RAFT polymerization in the miniemulsion stabilized by unammonolysis SMA, although the carboxylic acid group could be formed in the process of the hydrolysis of SMA, a small amount of coagulum could be observed during storage. This indicated that the hydrophilic group formed from the hydrolysis of anhydride was not efficiently capable to stabilize the latex. However, for experiments 6–10, the latices were very stable, without visible phase separation. Also, the latex obtained and stabilized by SDS was very stable.

Miniemulsion polymerization with a droplet nucleation mechanism can be a versatile tool for the synthesis of nanoparticles. The particles obtained by the RAFT miniemulsion polymerizations stabilized by SDS and ammonolysis SMA were subjected to TEM analyses. A typical TEM graph of particles stabilized by SDS is shown in Figure 10. Particles with a homogeneous size were observed clearly, and all of the particles were solid.

However, for the St miniemulsion polymerization stabilized by ammonolysis SMA, the amphiphilic RAFT agent self-assembled into micelles, where the RAFT end group was located in the interface of oil and water, and when the polymerization happened, St grew inward, and polystyrene particles with ammonolysis SMA on the surface of shells may have formed. The particles should have possessed a core-shell structure with a hydrophobic core and a hydrophilic shell. Therefore, we studied the effect of ammonia on the morphologies of particles with different degrees of aminolysis. All of the TEM graphs are presented in Figure 11. It was found that the core-shell morphology was not obvious under a lower degree of aminolysis [<40 mol %, Fig. 11(a,b)]. A

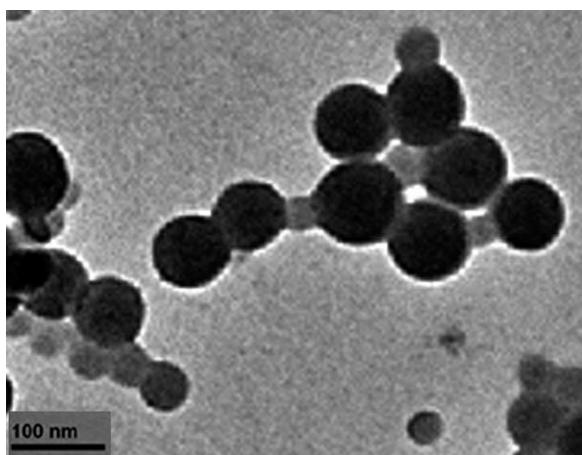


Figure 10 Typical TEM graph of the particles obtained by the St RAFT polymerization in the miniemulsion stabilized by SDS (experiment 5).

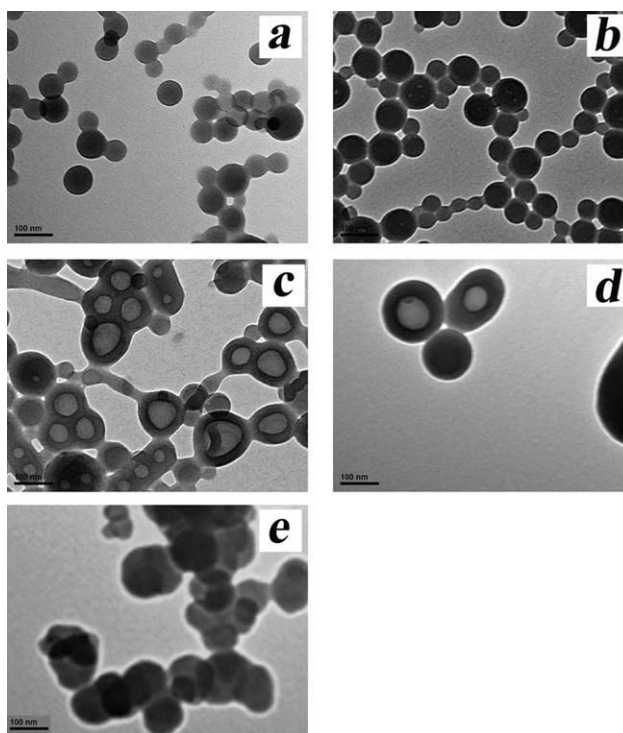


Figure 11 TEM graphs of all of the final particles obtained by the RAFT polymerization in the miniemulsion system stabilized by ammonolyzed SMA with different degrees of aminolysis: experiments (a) 6, (b) 7, (c) 8, (d) 9, and (e) 10.

possible reason was that the interfacial tension was still high, and the RAFT end group could not be located fully in the interface of oil and water so that the polymerization could not occur in the interface of oil and water. The final nanoparticles existed in the form of solid particles. With increasing amount of ammonia, a well-defined core-shell morphology became more and more obvious [Fig. 11(c,d)]. However, the core-shell morphology of the resultant particles of experiment 10 was not observed, and a possible reason was that the aminolysis of the macro-RAFT agent led to more coupling product solid particles [Fig. 11(e)]. On the other hand, fully ammonolysis SMA became soluble in water, and when the polymerization began, homogeneous nucleation happened to form solid particles.

CONCLUSIONS

SDS and ammonolysis SMA as different stabilizers were used to stabilize miniemulsions of St. However, different stabilizers had different effects on the polymerization kinetics, living character, and particle morphology. In the SDS system, the St RAFT miniemulsion polymerization exhibited a good controlled nature, with a narrow PDI and controlled molecular weight. However, for the miniemulsion polymerization system stabilized by ammonolysis SMA, when

less than 60 mol % of all anhydride was ammonolysis by ammonia, the polymerizations exhibited a relatively good controlled/living nature. When more than 60 mol % of all anhydride was ammonolysis by ammonia, the polymerizations showed a loss of living character because of the formation of thiol from the aminolysis of dithioester groups. Stable latices were obtained by RAFT polymerization in the miniemulsion system stabilized by SDS or ammonolysis SMA. Particles obtained by the RAFT miniemulsion polymerization stabilized by SDS were solid particles, except for the St miniemulsion polymerization stabilized by ammonolysis SMA, where an obvious core-shell structure was seen clearly with a certain degree of aminolysis. A core-shell structure was not obvious under a lower or higher degree of aminolysis.

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