Superparamagnetic Thermoresponsive Composite Latex via W/O Miniemulsion Polymerization

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ABSTRACT: In this research, the thermoresponsive composite latex particles were prepared via W/O miniemulsion polymerization. Fe_3O_4 nanoparticles were homogeneously dispersed inside the poly(NIPAAm-*co*-MAA) latex particles. In the first step, PAA oligomers were used as stabilizers to produce a stable water-based Fe_3O_4 ferrofluid, which could mix well with the water-soluble monomers. In the second step, the Fe_3O_4/poly(NIPAAm-*co*-MAA) composite latex particles were synthesized via W/O miniemulsion polymerization. This polymerization proceeded in cyclohexane at room temperature, with Span80 as the emulsifier, NIPAAm as the thermoresponsive monomer, MAA as a comonomer with —COOH functional groups, and APS/SMBS as the redox initiator system. The distribution of Fe_3O_4 nanoparticles inside the composite latex particles was expected to be homogeneous. The nucleation and morphology of the composite latex particles were mainly controlled by the concentration of the surfactant, Span80, in cyclohexane. The properties of the composite latex were examined with several instruments such as DSC and TGA. Finally, the superparamagnetic and thermoresponsive characteristics of this functional composite latex were also investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3987–3996, 2006

Key words: thermoresponsive; superparamagnetic; *N*-isopropylacrylamide; inverse miniemulsion

INTRODUCTION

More and more attentions have been drawn to the preparation of different kinds of magnetic polymeric particles in the past decades because of the applications of magnetism to various fields, such as cell separation,[1–4] protein purification,[5] targeting drug delivery,[6,7] environment and food analyses,[8] organic and biochemical syntheses,[9] and industrial water treatment.[10]

Several methodologies on the preparation of magnetic polymeric latices have been investigated as reported.[11–16] Emulsion and emulsifier-free emulsion polymerization are the most frequently used methods for the encapsulation of minerals with polymers, in which the magnetite nanoparticles are coated by a surfactant double layer, to enhance the encapsulation. Yanase et al.[11] synthesized the magnetic latex by a batch emulsion polymerization of styrene in the presence of ferrofluid. Xie et al.[12] investigated the effects of polymerization parameters on the magnetic poly(styrene–butyl acrylate–methacrylic acid) latex via emulsifier-free emulsion polymerization. By using the similar method, Kondo and coworkers[17,18] prepared the core–shell magnetic latex particles, with poly(styrene) in the core and PNIPAAm in the shell. In our previous study, the poly(methyl methacrylate) latex containing magnetite nanoparticles were also synthesized by using soapless dispersion polymerization, in which the lauric acid was used to coat the magnetite nanoparticles to form a surfactant double layer.[4,19] Although the methods based on emulsion or emulsifier-free emulsion polymerization have the potential to yield composite latex containing more than 20 wt % magnetite, they also might cause latex coagulation, or incomplete and nonuniform encapsulation, depending on the composition and synthesis conditions, with respect to the nucleation mechanism discussed in our previous work.[19]

Recently, direct or inverse miniemulsion polymerization has been applied to encapsulate inorganic nanoparticles in the polymer matrix. This method potentially assures the uniform loading of magnetic particles into the latex particles, in which the magnetic particles are directly dispersed into the monomers of interest, and then the monomer droplets with magnetic nanoparticles dispersed in the continuous phase would act as "nanoreactors" to form the magnetic polymeric particles in situ. For O/W system, recently, Ramirez and Landfester[16] encapsulated magnetic particles by polystyrene successfully by using a new three-step preparation route, including two miniemulsion processes. On the other hand, Wormuth[13] used a

W/O miniemulsion polymerization to encapsulate the magnetic nanoparticles, which was stabilized by poly-(ethylene-*co*-butylene)-*b*-poly(ethylene oxide) diblock copolymer, by 2-hydroxyethylmethacrylate and methacrylic acid (MAA) in decane continuous phase. The superparamagnetic polymeric particles thus prepared have the average diameter between 140 and 220 nm, with uniform encapsulation and contain 18 wt % of magnetic iron oxide.

However, when these magnetic polymeric particles are applied in the biological field, the small size of the latex particles could provide larger surface area for functional purposes, but the magnetic separation becomes much more difficult.[17,18] To circumvent this problem, thermoresponsive and superparamagnetic hydrogel microspheres, based on PNIPAAm, containing magnetite nanoparticles were synthesized in this study. MAA was added to introduce carboxylic acid groups into microgels, for further applications. These microgels were expected to show a reversible transition between dispersion and flocculation as a function of temperature because of the thermoresponsive property of PNIPAAm. The thermoflocculation of these composite particles could improve the magnetic separation efficiently.[17,18] In this study, a two-step inverse miniemulsion polymerization was adopted to synthesize the Fe_3O_4/poly(NIPAAm-*co*-MAA) composite particles using Span80 as the emulsifier. The superparamagnetic and thermoresponsive characteristics of this functional composite latex were investigated.

EXPERIMENTAL

Material

Iron(II) chloride tetrahydrate (99%), Iron(III) chloride hexahydrate (97%), ammonium hydroxide (28% NH_3 in water, w/w), monomers NIPAAm and MAA, crosslinking agent *N,N*'-methylenebisacrylamide (MBA), initiator ammonium persulfate (APS), accelerator sodium metabisulfite (SMBS), and cyclohexane were purchased from Acros and used as supplied. Poly(acrylic acid) (PAA oligomer: $M_w \sim 2000$) was purchased from Aldrich. The cyclohexane-soluble surfactant, Span80 (sorbitane monooleate), which is commonly used in inverse emulsion (HLB = 4.3) was purchased from Showa. The structure of Span80 and its surface tension measurement in cyclohexane are shown in Figure 1. Distilled and deionized water was used throughout the work.

Synthesis and stability of ferrofluid

The method of coprecipitation of Fe(II) and Fe(III) salts in the presence of PAA oligomer ($M_w \sim 2000$) was used to produce stable Fe_3O_4 ferrofluid. In this process, 1 g of PAA oligomer (MW, 2000), 4.75 g of
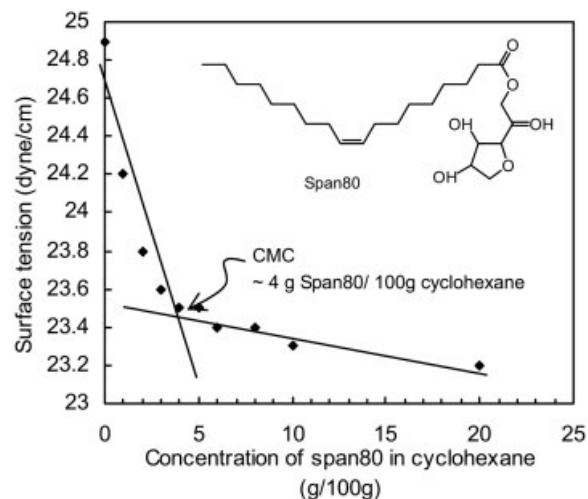

Figure 1 The surface tension of Span80 in cyclohexane solution with different concentrations at 25°C.

$FeCl_3 \cdot 6H_2O$, and 1.75 g of $FeCl_2 \cdot 4H_2O$ were dissolved in 80 mL water with vigorous stirring at 60°C, under N_2 atmosphere. Then, 7.5 mL of 28% (w/w) NH_4OH was added, and the stirring was continued at 400 rpm for 30 min. Once the ammonium solution was added into the reactor, the color of the mixture turned from orange to black immediately. After the ferrofluid was synthesized, MAA was used as titrant to titrate the ferrofluid after 1 or 2 mL of 28% (w/w) ammonium solution was added in the ferrofluid. The pH value of the fluid was measured, and the stability of the particles suspended in the fluid was observed visually during the titration.

Synthesis of magnetic polymeric particles

The magnetic polymeric particles were prepared by using a two-step miniemulsion polymerization, which means two types of miniemulsions (i.e., monomer miniemulsion and initiator miniemulsion) should be prepared with respect to the ingredients shown in Tables I and II. The sample code, for example 2/8–3%-F1.8, of the composite copolymer latex represents the composition of the feed mixture, where 2/8 is the molar ratio of MAA/NIPAAm (total amount of monomers is 0.023 mol), 3% is the concentration of crosslinking agent in MBA (mole)/total monomers (MAA + NIPAAm) (mole), and F1.8 means that the magnetic nanoparticles (1.8 wt %) were incorporated in the composite latex.

In the preparation of monomer miniemulsion, a suitable proportion of monomers and crosslinker, according to the sample code, was dissolved in deionized water homogenously at first to form the monomer solution. Then, the ammonium solution, whose volume was the same as the MAA monomer, should

be added into the monomer solution to ensure the pH value of the solution and to be able to keep the stability of the ferrofluid. After that, the ferrofluid was added. Finally, the aqueous monomer solution containing magnetic nanoparticles (dispersing phase) was dispersed in Span80 cyclohexane solution (continuous phase) under ultrasonification (Dr. Hielscher UP-50H, 100% amplitude output for 5 min). On the other hand, in the preparation of initiator miniemulsion, the aqueous solution of APS and SMBS was dispersed into another Span80 cyclohexane solution under ultrasonification (Dr. Hielscher UP-50H, 100% amplitude output for 1 min).

The reaction started immediately when these two miniemulsions were mixed homogeneously under ultrasonification (Dr. Hielscher UP-50H, 80% amplitude output), in which the system was kept at 25°C. This reaction was completed rapidly within several minutes. To ensure full conversion of the monomer, the reaction was prolonged for 1 h. After polymerization, the magnetic polymeric particles were washed by ethanol and water repeatedly several times with the aid of centrifugation.

Conversion

After the copolymerization, the latex solution was taken out of the reactor. A quantitative amount of inhibitor was introduced into the latex and, immediately, the sample was quenched to an ice bath. For the removal of the remaining monomers and initiator, it was washed using ethanol and water under the help of centrifugation many times, to obtain the precipitates of the copolymers. Then, the sample was dried in a vacuum oven at 70°C, until the weight was no longer changed. The conversion of the monomers was calculated as follows:

$$\text{Conversion} = (P - F)/M_0 \times 100\% \qquad (1)$$

where P is the weight of the dry copolymer obtained from the latex sample, F is the theoretical weight of the

TABLE I
Ingredients and Conditions for the Preparation of Monomer Miniemulsion

Monomer solution (dispersing phase)	
NIPAAm + MAA (mole)	0.023
MBA (crosslinking agent) (mole)	6.98×10^{-4} to 1.163×10^{-3}
Ammonium solution (mL)	The same volume as MAA
Ferrofluid (g)	2
Deionic acid water (g)	6.98
Continuous phase	
Cyclohexane (g)	50
Span80 (g)	2

At 25°C; under ultrasonification for 5 min.

TABLE II
Ingredients and Conditions for the Preparation of Initiator Miniemulsion

Initiator solution (dispersing phase)	
Initiator (APS) (g)	0.36
Accelerator (SMBS) (g)	0.36
Deionic acid water (g)	2
Continuous phase	
Cyclohexane (g)	10
Span80 (g)	0.4

At 25°C; under ultrasonification for 5 min.

magnetite incorporated into the composite latex, and M_0 is the weight of the monomers used in the feed.

Morphology of composite particles

To observe the morphology of the copolymer composite latex, the latex cyclohexane solution was diluted with cyclohexane and observed using JEOL JSM-1200 EX II transmission electron microscope (TEM).

Analysis of thermoproperties (TGA and DSC)

The dry copolymers were subjected to TGA (Perkin–Elmer TGA-7). The temperature was kept at 100°C for 10 min, and was then raised to 700°C, at a heating rate of 10°C/min. For DSC analysis, the dry copolymers were subjected to DSC (TA instruments), with a heating rate of 10°C/min.

Measurement of particle size and ζ potential

The ζ potential and the size of the copolymer composite particles were measured by using a laser light scattering instrument (Malvern Zeta Sizer 3000H). In the ζ potential analysis, the dry sample was dissolved and diluted in aqueous buffer solutions (of pH 4, 7, and 9). For the measurement of particle size, the dry sample was dissolved and diluted with an excess of distilled and deionized water at different temperatures, to investigate its thermoresponsive properties.

Thermoresponsive properties

Beside the particle size measurement at different temperatures, the cloud point observation was also used to study the thermoresponsive properties of the composite latex. The dry sample was dissolved and diluted with an excess of distilled and deionized water. Then, the absorbance or transmittance of the solution, at a wave length of 450 nm, was measured at different temperatures by using a UV–vis spectrometer (Thermo Spectronic gamma series).

Measurement of magnetization of composite latex

The magnetizations of composite particles were measured by Squid magnetometer (Quantum Design MPMS5) at the condition of 298 K and ±10,000 G applied magnetic field. The measurement was repeated five times to examine the magnetic property of the magnetic nanoparticles, which was incorporated into the copolymer latex. In addition, the saturation magnetization, remanence, and coercivity were also measured.

RESULTS AND DISCUSSION

Synthesis and stability of ferrofluid

The traditional method to prepare Fe_3O_4 nanoparticles was using the chemical coprecipitation of ferric and ferrous salts in alkaline medium.[20] However, the Fe_3O_4 nanoparticles synthesized by this method would aggregate easily. So, a new process in which PAA oligomer was introduced into the recipe was used in the traditional coprecipitation method, and was used to synthesize the stable water-base ferrofluid. The preparation and characterization of this new ferrofluid had been presented and discussed in our previous work.[21] The Fe^{2+} and Fe^{3+} ions would a form complex with the carboxylic acid groups in PAA oligomer. As the ammonium solution was added, Fe_3O_4 nanoparticles could be synthesized in situ. Because the PAA oligomer not only acted as the template for Fe_3O_4 nucleation and also hindered the growth of particles, the size of the particles was confirmed to be about 5–10 nm in diameter using TEM observation[21] or about 8.3 nm by the Debye–Scherrer equation, with the aid of XRD diffraction pattern,[21] which was smaller than the traditional product.[18–19]

Because the ferrofluid was stabilized by PAA oligomer, the ionized degree of PAA oligomer and the stability of ferrofluid could be controlled by adjusting the pH value of the solution. It was found from Figure 2 that the ferrofluid became unstable, and that the particle coagulation was observed visually when the pH value was less than 5. This was because the ionized degree of acid groups was less than 90% when the pH value was less than 5, which was not sufficient to keep the stability of Fe_3O_4 nanoparticles suspended in ferrofluid.[21] Therefore, ammonium solution, whose volume was equal to the volume of MAA, should be added in the monomer solution before the addition of ferrofluid to suspend the magnetic nanoparticles into the MAA monomer solution homogeneously and stably.

XRD was also used to investigate the effect of PAA oligomers on the preparation of magnetic nanoparticles in our previous work.[21] The results show that the nanoparticles prepared in the presence of PAA oligomers not only had the characteristic peaks of
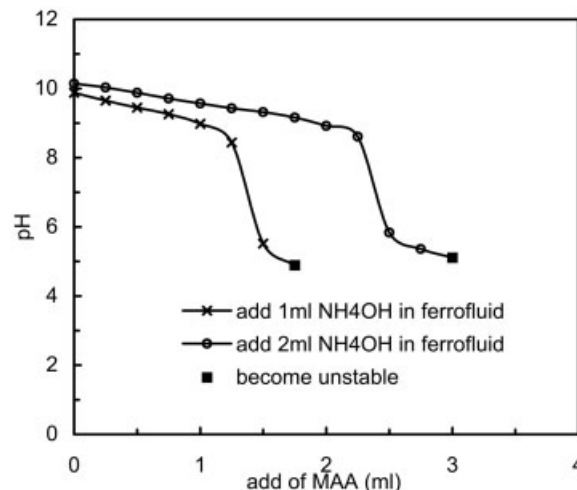

Figure 2 Stability of ferrofluid in MAA monomer solution with various pH values. (The stability was observed visually.)

standard Fe_3O_4 crystal but also had a diffraction peak at ~$2\theta = 32.8°$, which was the characteristic peak of the Fe_2O_3 crystal. These results indicated that a small amount of Fe_2O_3 particles consisted of the ferrofluid, since the particles were synthesized in the initial condition with low pH value (in PAA oligomer solution of pH 2.43), although the pH value of the final ferrofluid was 8.8 after the addition of ammonium solution. In the beginning of the precipitation reaction, the acidic condition would oxidize the Fe^{2+} to form Fe^{3+} that would produce Fe_2O_3 or oxidize the Fe_3O_4 to become Fe_2O_3.

Synthesis of magnetic polymeric particles

After the addition of the ammonium solution into monomer solution, the water-based stable ferrofluid, stabilized by PAA oligomers, could disperse in the monomer (NIPAAm and MAA) solution homogeneously. In this step, the carboxylic acid groups of MAA were ionized to $COO^-NH_4^+$, and the magnetic nanoparticles could be suspended into the MAA monomer solution stably. Then, the monomer solution containing magnetic nanoparticles, which served as the dispersing phase, was mixed with the cyclohexane solution containing Span80, the continuous phase, and thus formed the monomer miniemulsion. The polymerization occurred when the monomer miniemulsion was mixed with the initiator miniemulsion. Such type of inverse miniemulsion was called "two-step miniemulsion polymerization." In this method, two kinds of miniemulsions containing different solutes (monomers and initiators in our system) should be prepared first. Then, these two miniemulsions were mixed well to homogenize the concentrations of these two miniemulsions in the continuous phase (cyclohex-

ane). The mechanism of the solute exchange between these two miniemulsions consisted of five steps: (1) micellar diffusion, (2) surfactant layer opening, (3) molecular diffusion, (4) indicator reaction, and (5) de-coalescence.[22]

In miniemulsion polymerization, as is well known, Ostwald ripening, which disrupts emulsions, depends upon the solubility of the dispersed phase molecules in the continuous phase.[23] Because the surface energy and the chemical potential of the monomers in small droplets are higher than those in large droplets, monomers diffuse from small to large droplets, which then lead to emulsion destabilization. Davies and Smith[24] suggested the addition of small amounts of costabi-lizer, insoluble in continuous phase, which acted as an osmotic agent, would stabilize the system against Ostwald ripening (molecular diffusion). This approach was first presented by Higuchi and Misra,[25] who concluded that the addition of a small amount of costabilizer would retard the emulsion degradation by molecular diffusion, because the slow rate of diffusion of the costabilizer would permit the monomers to remain essentially equilibrated among the droplets.

On the basis of the ideas from Wormuth[13] and Landfester et al.,[26] the cyclohexane-insoluble ferrofluid consisting of PAA oligomer stabilized the magnetic particles, and NH_4Cl salt was used as the costabilizer to prevent the Ostwald ripening in our inverse miniemulsion. In addition, keeping the temperature of the system as low as 25°C during the polymerization also prevented the monomers, NIPAAm and MAA, from being soluble in cyclohexane. Consequently, the homogeneous magnetic composite particles were prepared.

In this polymerization, because the concentration of Span80 was not higher than its critical micelle concentration (CMC ~ 4 g Span80/100 g cyclohexane), the reaction would be initiated in the monomer droplets and not in the micelles. Consequently, when the magnetic colloids can disperse in monomer droplets homogeneously, the composite latex particles would maintain its homogeneous morphology during polymerization. TEM images showed the homogeneous morphology of the latex particles in Figure 3(a).

An additional experiment, in which the concentration of Span80 in cyclohexane was higher than its CMC, was conducted for comparison. From Figure 3(b), it was found that a significant amount of magnetic nanoparticles were not encapsulated by latex particles. It was suggested that the magnetic nanoparticles coated by hydrophilic polymers more likely could not diffuse through the hydrophobic oil continuum and travel to the micelles in the emulsion when compared to the monomers. Therefore, some latex particles without magnetic nanoparticles could be observed, as shown in Figure 3(b).
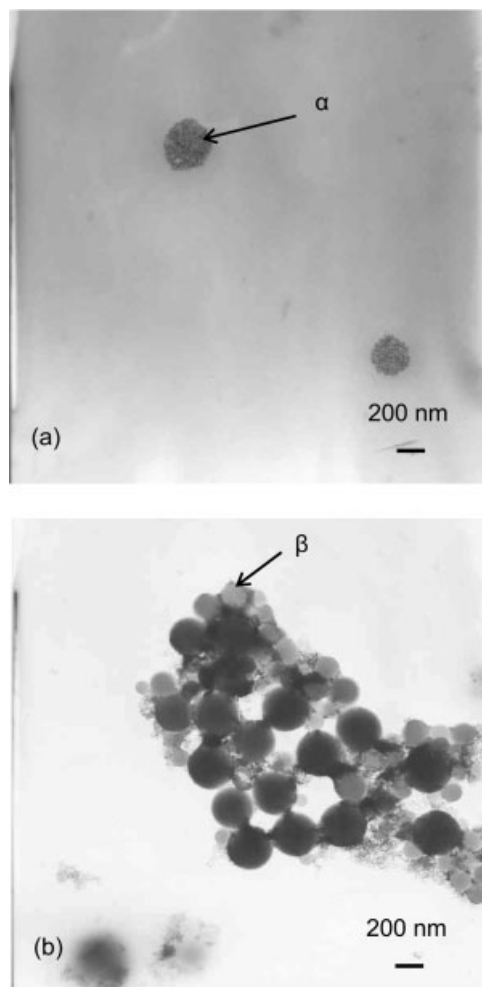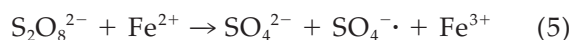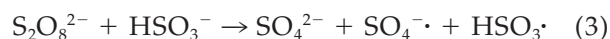

Figure 3 TEM of composite latex. (a) Concentration of Span80 < CMC and (b) concentration of Span80 > CMC, where α and β indicate the latex particle containing magnetic nanoparticles and the latex particle without magnetic nanoparticles, respectively.

The polymerization took place rapidly at 25°C, because three possible redox initiator reactions coexisted in our system: (a) reaction between APS and SMBS [eqs. (2)–(4)],[27] (b) reaction between APS and Fe^{2+} [eq. (5)], and (c) reaction between SMBS and Fe^{3+} [eq. (6)].

$$S_2O_5^{2-} + H_2O \rightarrow 2HSO_3^- \qquad (2)$$

$$S_2O_8^{2-} + HSO_3^- \rightarrow SO_4^{2-} + SO_4^- \cdot + HSO_3 \cdot \quad (3)$$

$$SO_4^- \cdot + H_2O \rightarrow HSO_4^- + OH^- \cdot \qquad (4)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + SO_4^- \cdot + Fe^{3+} \qquad (5)$$

$$Fe^{3+} + HSO_3^- \rightarrow HSO_3 \cdot + Fe^{2+} \qquad (6)$$

Since the polymerization was catalyzed by the magnetic particles, this would be one of the reasons that led to the incorporation of magnetic particles inside

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TABLE III
The Conversion of Reaction

Sample type	Conversion (%)
1/9–3%-F1.8	88.73
2/8–3%-F1.8	86.20
3/7–3%-F1.8	86.16
2/8–3%-F1.8	86.20
2/8–4%-F1.8	94.29
2/8–5%-F1.8	95.67
2/8–3%-F1.8	86.20
2/8–3%-F2.5	85.15
2/8–3%-F4.1	74.86
2/8–3%-F5.8	49.27
2/8–3%-F8.3	44.90

Reaction time, 1 h.

TABLE IV
The Glass Transition Temperature (T_g) of the Composite Particles from DSC Measurements

Sample type	T_g (°C)
1/9–3%-F1.8	112.91
2/8–3%-F1.8	123.05
3/7–3%-F1.8	147.10
2/8–4%-F1.8	123.06
2/8–5%-F1.8	133.49

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the polymer latex particles. In addition, the acid groups containing monomer, MAA, was also quite likely to adsorb on the magnetic particles and could copolymerize with other monomers. This also increased the compatibility between the magnetic particles and the polymer matrix.

Conversion of polymerization

Table III shows the conversion of monomers after polymerization for 1 h. The results indicate that when the mole ratio of NIPAAm to MAA or when the concentration of the crosslinking agent was higher, the reaction conversion (at time = 1 h) increased. The increased proportion of MAA would cause two effects on the reaction. One is the decrease of the decomposition of initiators in more acidic medium.[28] The other is the increase of Fe^{2+} ions from Fe_3O_4, which would act as a free radical quencher [eqs. (7)–(10)],[29] although the iron ions also act as accelerator [eqs. (5) and (6)]. Both effects caused the decrease in conversion. The increased concentration of crosslinking agent would increase the conversion, because the crosslinking agent, MBA, acts as a comonomer that provides two vinyl groups and increases the rate of polymerization.

$$Fe^{2+} + R_n\cdot + H_2O \rightarrow R_nOH + Fe^+ + H^+ \quad (7)$$

$$Fe^+ + S_2O_8{}^{2-} \rightarrow FeSO_4{}^+ + SO_4{}^{2-} \quad (8)$$

$$Fe^{2+} + SO_4{}^-\cdot \rightarrow FeSO_4{}^+ \quad (9)$$

$$FeSO_4{}^+ + R_n\cdot \rightarrow R_nSO_4{}^- + Fe^{2+} \quad (10)$$

The effect of magnetic particles on the conversion of polymerization is also shown in Table III. The larger amount of magnetic particles that participated in the reaction reduced the reaction conversion. This was because a small amount of Fe_2O_3 consisted of the

ferrofluid,[21] which would act as a radical quencher.[13] In addition, the larger amount of Fe^{2+} irons would quench radicals as discussed earlier in eqs. (7)–(10).

Thermoproperties

From the DSC measurements, the glass transition temperature (T_g) of these composite latex particles could be found, as shown in Table IV. It shows that increasing the concentration of MAA or crosslinking agent would increase the T_g of the composite latex. This was because the T_g of PMAA was higher than that of PNIPAAm, and the higher amount of crosslinking agent would hinder the segmental motion of polymer chains.

Figure 4 shows the TGA analysis of homopolymers and magnetic composite latex particles. The pure PNIPAAm had a significant weight loss at 400°C. But there were two stages of degradation shown in the TGA curve of PMAA. The initial stage of degradation (250–300°C) was due to the dehydration and decarboxylation of the carboxylic acid groups of the PMAA[30–32] while the main degradation temperature was near 400°C. The TGA curve of PMAAN, produced by the polymerization of MAA in the presence of
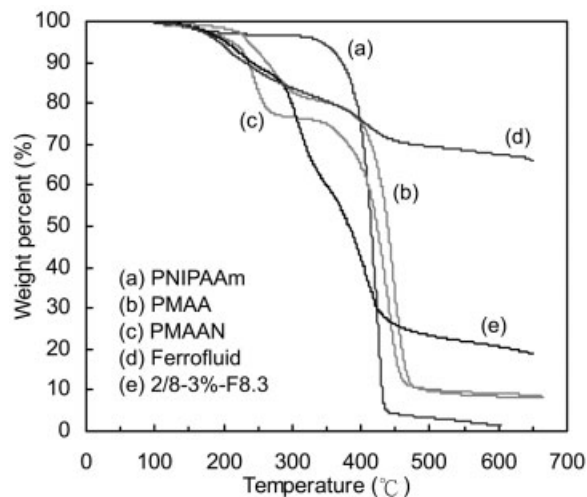

Figure 4 TGA analysis of homopolymers and composite particles.

ammonium solution, also shows a two-stage degradation. The first-stage degradation which occurred near 250°C was due to the dehydration from the destruction of polyelectrolyte complex between COO^- and NH_4^+ and, simultaneously, the formation of amide bonding. As the temperature was raised to 400°C, the main degradation of PMAAN occurred. As expected, the TGA curve of magnetic composite latex particles shows a multi-stage degradation, which is a combination of the degradation behaviors of PNIPAAm, PMAA, PMAAN, and ferrofluid.

Measurement of ζ potential

Figure 5 shows the ζ potential of the composite latices. The carboxylic acid groups partially remained in the unionized state in the pH = 4 buffer solution, and the ζ potentials of these latices thus were small negative values. When the pH value of the buffer solution was changed to 7 and 9, these acid groups were almost ionized, and the ζ potentials of these latices became more negative. These results indicate that, although some of the acid groups might be adsorbed on the magnetite surfaces and the continuous phase in the inverse miniemulsion polymerization (cyclohexane) was very hydrophobic, a significant amount of acid groups still appeared on the surface of the composite latex. These acid groups on the surface of latex particles actually are very useful to the conjugation of enzyme and protein, adsorption of metal ions, or other applications. As expected, it is found from Figure 5 that the ζ potential became more negative when the proportion of MAA increased. However, the ζ potential became less negative when the concentration of crosslinking agent increased. It is suggested that the higher crosslinking degree fixed the acid groups in-
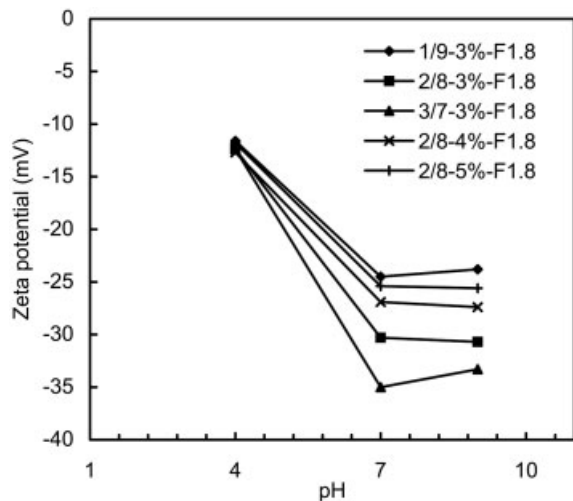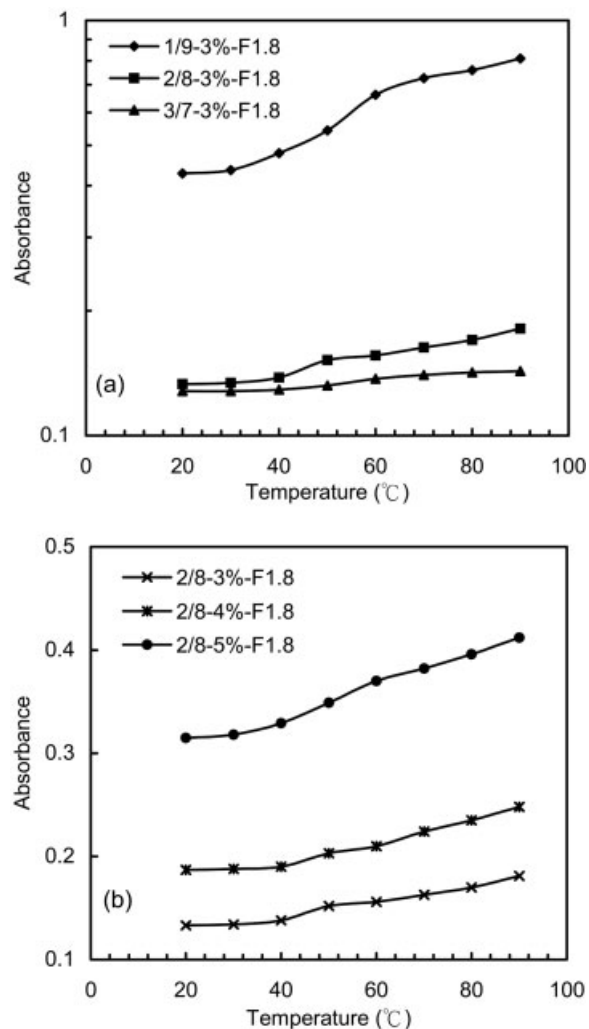

Figure 6 Cloud point analysis of composite latex, where the pH value of the solution was 7 during the measurements. (a) The effect of monomer ratio and (b) the effect of crosslinking agent.

side the particles and reduced the ability of acid groups exposing on the surface. In addition, the sample, 3/7–3%-F1.8, showed a slightly less negative ζ potential in pH = 9 buffer solution compared with that in pH = 7 buffer solution. It is suggested that the particles, which were incorporated with a significant amount of MAA, would have a better swelling behavior and a larger swollen particle size in pH = 9 buffer solution, which reduced the charge density on the particle surface.

Thermoresponsive property

The thermoresponsive property of the composite latex was investigated by measuring the absorbance of the latex solution at the wave length of 450 nm at different temperatures, as shown in Figure 6. In addition, the average diameter of the latex at different temperatures
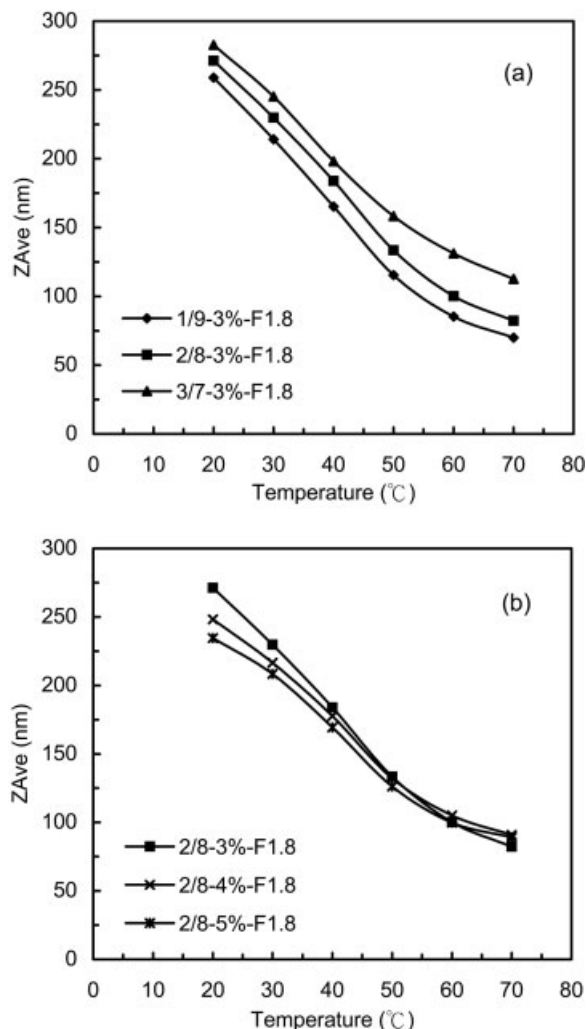

Figure 5 The ζ-potential of latex particles in various pH buffer solutions.

Figure 7 The average diameter of composite latex particles with various temperatures, where the pH value of the solution was 7 during the measurements. (a) The effect of monomer ratio and (b) the effect of crosslinking agent.

was also measured by light scattering, as shown in Figure 7. From these results, it proves that the composite latices, synthesized by the inverse miniemulsion, really have the thermoresponsive property as expected. When the temperature was higher than the lower critical solution temperature (LCST), the size of the composite latex became smaller, and the absorbance was increased due to the shrinking of latex. In contrast, the size of the composite latex became larger and the absorbance was decreased because of the swelling of latex when the temperature was lower than the LCST. The LCST value of composite latex seemed to be higher than the intrinsic LCST of PNIPAAm (32°C), because the comonomers, MAA and its ionized form, were very hydrophilic. For the same reason, the particles with higher amount of hydrophilic comonomers, MAA and its ionized form, would have better swelling behavior that caused the

larger particle size and lower absorbance, as shown in Figures 6 and 7. But the particles with higher crosslinking would hinder the swelling of latex particles that caused the smaller particle size and higher absorbance.

Figure 8 shows the particle volume ratios and surface area ratios of composite particles at 20–70°C, which indicate the thermoresponsiveness of these composite particles. The results show that the volume and the surface area of these particles were larger at 20°C than those at 70°C because of their thermoresponsive properties. The ratio was reduced as the proportion of the MAA or crosslinking agent increased, which meant that the strength of the thermoresponsive ability decreased as the proportion of the MAA or crosslinking agent increased. In MAA rich sample, the hydrophilic property of MAA reduced the thermoresponsive ability of the latex sample. In higher crosslinked samples, the crosslinking structure hindered the swelling and shrinking of latex particles, and so the thermoresponsive ability was reduced.

The reversibility of the thermoresponse property was also examined by the absorbance and particle size measurement. From Figure 9, the composite latices showed an acceptable reversibility when the heating and cooling process were repeated several times. This result indicates that these products could be recycled many times.

Magnetization of composite latex

It is well known that the Fe_3O_4 nanoparticles show a superparamagnetic property. But when the quantity of Fe_2O_3 in the ferrofluid and the magnetic nanoparticles were encapsulated by chemical polymerization, the magnetic property of the composite particles
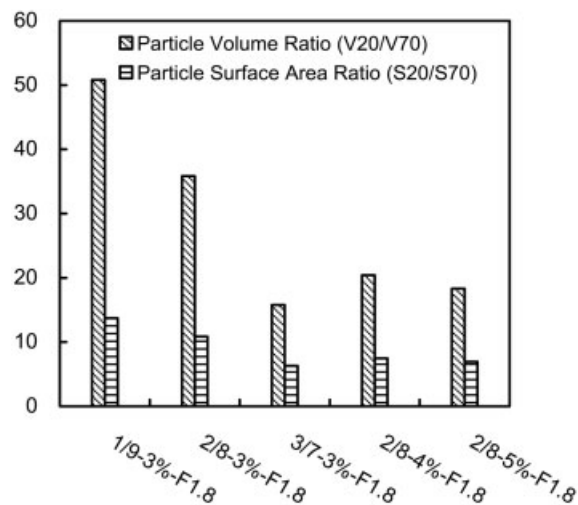

Figure 8 The particle volume ratios and surface area ratios of composite particles at 20–70°C.

should be examined. When a magnetic field was applied, the dipolar particles aligned themselves with the applied magnetic field, and resulted in a measurable magnetization. The result of the squid analysis is shown in Figure 10.

The saturation magnetization of the ferrofluid was about 35 emu/g (emu per gram of iron oxide in the ferrofluid). The amount of iron oxide was determined by using TGA analysis, which was close to the theoretical value calculated from the recipe of feed composition. The value of 35 emu/g was lower than the saturation magnetization of pure Fe_3O_4 nanoparticles reported previously (>50 emu/g). This was because both Fe_3O_4 and Fe_2O_3 consisted in our ferrofluid, and the saturation magnetization of Fe_2O_3 nanoparticles was lower than that of Fe_3O_4 nanoparticles. So the saturation magnetization of nanoparticles in the ferrofluid, which consisted of a small amount of Fe_2O_3

Figure 10 The squid analysis of the latex particles. (a) The effect of monomer ratio and (b) the effect of crosslinking agent.

nanoparticles, was lower than that of pure Fe_3O_4 nanoparticles. Furthermore, the remanence and coercivity were zero, and there was no magnetic hyteresis loop, as shown in Figure 10. These results indicate that the magnetic nanoparticles synthesized in the presence of PAA oligomers were superparamagnetic.[33]

The original data showed that the saturation magnetizations of these composite particles were all about 0.65 emu/g of composite particles. Compared to the saturation magnetization of ferrofluid (magnetic particles), it was found that the composite particles only contained 1.8 wt % of iron oxide for each sample, which was also confirmed by TGA measurement. This value is extremely low compared to the best encapsulation in previous reports (18–30 wt %),[13,34] because the monomer conversion and the encapsulation are the two major considerations in this work. If the content of iron oxide was increased up to 5 wt %, the conversion at $t = 1$ h was reduced to lower than 50%,
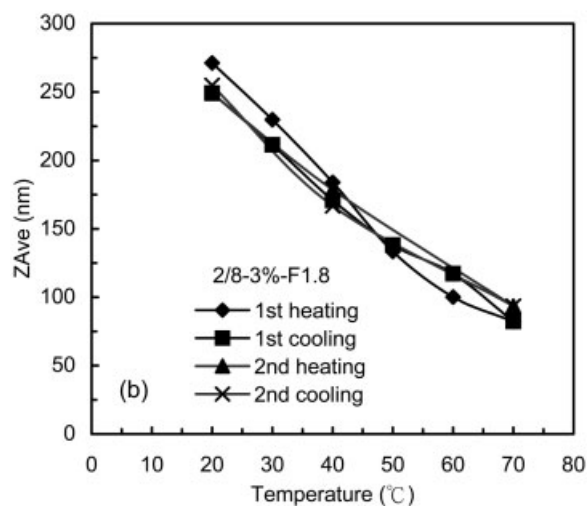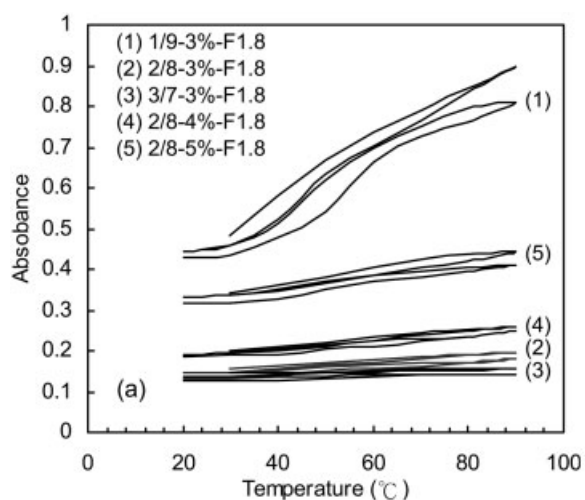

Figure 9 The reversible thermoresponsive properties of composite latices from the (a) cloud point analysis and (b) particle size analysis, where the pH value of the solution was 7 during the measurements.
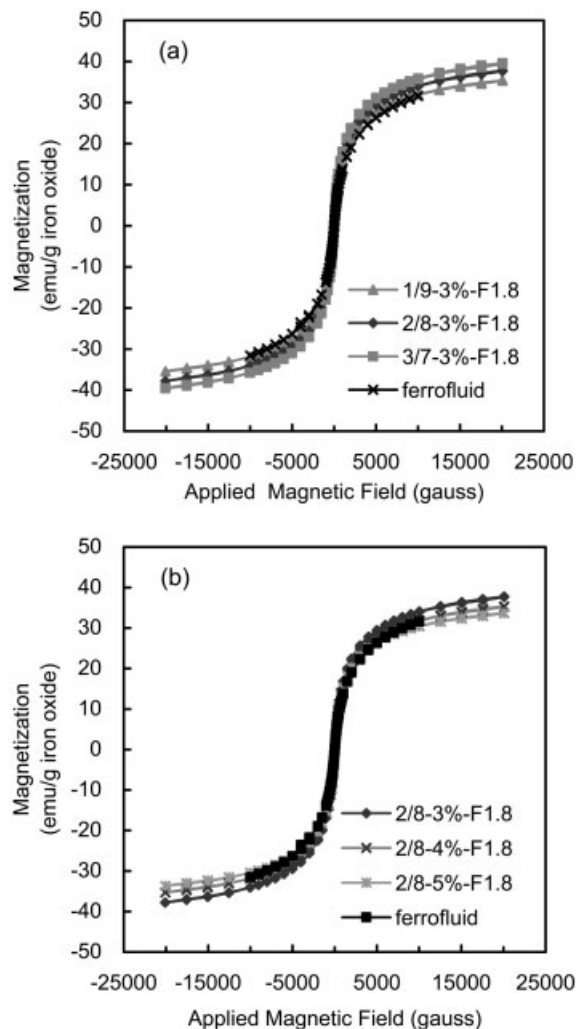
as shown in Table III. However, in our system, the thermoflocculation of composite particles, induced by their thermoresponsive property, could efficiently improve the magnetic separation even if the content of iron oxide is low.[17,18]

To compare the magnetic property of the magnetic particles before and after polymerization, Figure 10 shows the magnetization curve of composite particles with the unit of emu per gram of iron oxide nanoparticles, where the amount of nanoparticles was determined by using TGA analysis. It could be found that these curves are similar. The saturation magnetizations were ~35 emu/g, and the remanence and coercivity were zero, and there were no magnetic hyteresis loop for each of the samples. It could be concluded that the intrinsic properties of magnetic nanoparticles were not changed after the inverse miniemulsion polymerization.

CONCLUSIONS

In this work, PAA oligomers were used as the stabilizer to produce a stable water-based ferrofluid containing Fe_3O_4 nanoparticles. It was then suspended homogeneously and stably in monomer solution by adjusting the pH value of the solution. Subsequently, the Fe_3O_4/poly(NIPAAm-*co*-MAA) composite latex particles were prepared via W/O miniemulsion polymerization. This polymerization proceeded in cyclohexane at room temperature with Span80 as the emulsifier, while the added ferrofluid also played a role as a costabilizer. The distribution of magnetic nanoparticles inside the composite latex particles was found to be homogeneous. But the higher proportion of magnetic nanoparticles would reduce the reaction rate. The volume phase transition temperature (LCST) of the composite latex seemed to be higher than the intrinsic LCST of PNIPAAm (32°C), but the thermoresponsiveness was reduced, as the proportion of MAA or crosslinking agent was increased. The remanence and coercivity of the composite latices were zero, and the magnetic hysteresis loop was not observed. It could be concluded that the composite latices synthesized in this work were superparamagnetic and thermoresponsive.

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