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迷你乳化聚合製備次微米高分子功能性複合乳膠顆粒
Synthesis of Submicron Polymer Functional Complex Latex via 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 the stabilizer 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 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 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.

Keywords: thermoresponsive; superparamagnetic;
N-isopropylacrylamide; inverse miniemulsion

1. INTRODUCTION

More and more attentions have been drawn to the preparation of different kinds of magnetic polymeric particles in the past decades due to the applications of magnetism to various fields, such as cell separation, protein purification, targeting drug delivery, environment and food analyses, organic and biochemical syntheses, and industrial water treatment. Several methodologies on the preparation of magnetic polymeric latexes have been investigated as reported. 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. 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.

Considering the mechanism of different emulsion polymerizations, the miniemulsion polymerization potentially assures the uniform loading of magnetic particles into latex particles. In miniemulsion polymerization, the magnetic particles are directly dispersed into the monomers of interest. The monomer droplets with magnetic nanoparticles act as ‘‘nanoreactors’’, and the magnetic polymeric particles can be prepared in situ. However, the magnetic separation becomes much more difficult when these magnetic polymeric particles are applied. To circumvent this problem, thermoresponsive and superparamagnetic hydrogel microspheres based on poly(N-isopropylacrylamide) (PNIPAAm) containing magnetite nanoparticles were synthesized in this study. Methacrylic acid (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. In this study, a two-step inverse miniemulsion polymerization was adopted to synthesize the Fe_3O_4/poly(NIPAAm-co-MAA) composite particles using Span 80 as the emulsifier. The superparamagnetic and thermoresponsive characteristics of this functional composite latex were investigated.

2. EXPERIMENTAL

Reagents Iron(II) chloride tetrahydrate (99%), Iron(III) chloride hexahydrate (97%), ammonium hydroxide (28% NH_3 in water, w/w), N-isopropylacrylamide (NIPAAm), methacrylic acid (MAA), N,N’-methylenebisacrylamide (MBA), ammonium persulfate (APS), sodium metabisulfite (SMBS) were purchased from ACROS and used as supplied. Poly(acrylic acid) (PAA oligomer: Mw~2000) was purchased from ALDRICH.

Synthesis of Ferrofluid 1g of PAA oligomer, 4.75 g of $FeCl_3 \cdot 6H_2O$ 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 7.5mL of 28% (w/w) NH_4OH was added and the stirring was continued at 400rpm for 30 min. Once the ammonium solution was added into the reactor, the color of the mixture turned from orange to black immediately.

Synthesis of Magnetic Polymeric Particles A suitable amount of NIPAAm, MAA, MBA, NH_4OH and ferrofluid were dissolved in deionized water homogenously at first, and then into the solution was added a Span 80 cyclohexane solution under ultrasonification. After the stable ultrafine monomer miniemulsion was formed, another ultrafine initiator miniemulsion was prepared by adding the solution of APS and SMBS into another Span 80 cyclohexane solution under ultrasonification. The reaction started immediately when these two miniemulsions were mixed homogeneously under ultrasonification, in which the system was kept at 25°C for 1 hour. The sample code, for example 2/8-3%-F1.8, of the composite copolymer latex represents the composition of feed mixture, where 2/8 is the molar ratio of MAA/NIPAAm (total amount of monomers is 0.023 mole), 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.

Characterization After the copolymerization, the latex solution was taken out of the reactor and a quantitative amount of inhibitor was added. It was then washed by 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℃ until the weight was no longer changed. The conversion of the monomers was calculated as follows.

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

where P is the weight of the dry copolymer obtained from the latex sample, F is the theoretical weight of the magnetite incorporated into the composite latex, and M_0 is the weight of monomers in feed.

To observe the morphology of the copolymer composite latex, the latex cyclohexane solution was diluted with cyclohexane and observed by using TEOL JSM-1200 EX II Transmission Electron Microscope (TEM).

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

The zeta potential and the size of the copolymer composite particles were measured by using a laser light scattering instrument (Malvern Zeta Sizer 3000H). In the zeta potential analysis, the dry sample was dissolved and diluted in pH=4, 7, 9 aqueous buffer solutions. In the measurement of particle size, the dry sample was dissolved and diluted with an excess distilled and deionized water at different temperatures to investigate its 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 distilled and deionized water. Then the absorbance or transmittance of the solution at a wave length of 450nm was measured at different temperatures by using a UV-Vis spectrometer (Thermo Spectronic gamma series).

The magnetizations of composite particles were measured by SQUID magnetometer (Quantum Design MPMS5) at the condition of 298K and ±10000 gauss 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.

3. RESULTS AND DISUSSION

Preparation of Ferrofluid A new process, in which PAA oligomer was introduced into the recipe used in the traditional co-precipitation method, was used to synthesize the ferrofluid. The Fe^{2+} and Fe^{3+} ions formed complex with the carboxylic acid groups in PAA oligomer and then Fe_3O_4 nanoparticles could be synthesized in-situ after the ammonium solution was added. The size of the particles was about 5~10 nm as shown in Figure 1. The stability of ferrofluid could be controlled by adjusting the pH value of the solution as shown in Figure 2. The ferrofluid became unstable and 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. Therefore, the ammonium solution, whose volume was equal to the volume of MAA, should be added in the monomer solution before the addition of ferrofluid in order to suspend the magnetic nanoparticles into the MAA monomer solution homogeneously and stably.

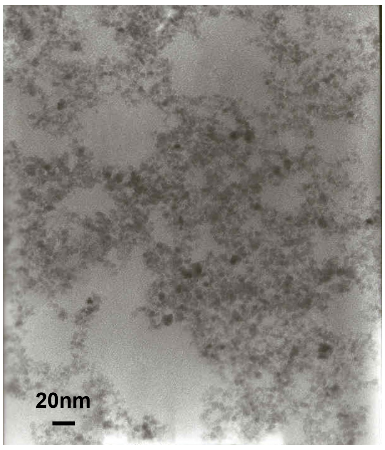

Figure 1. TEM photograph of ferrofluid prepared by the method of co-precipitation in the presence of PAA oligomers.

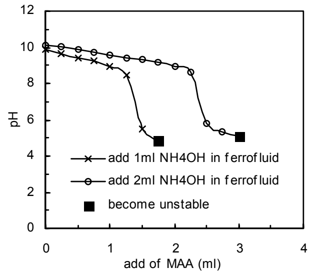

Figure 2. Stability of ferrofluid in MAA monomer solution with various pH values.

Figure 3 shows the FTIR spectra of the Fe_3O_4 nanoparticles, the pure PAA oligomers and the ferrofluid. The strong band at ca. 1710 cm^{-1} as shown in the FTIR spectrum of PAA oligomer is attributed to the carbonyl group stretch of the PAA oligomer, and the bands at ca. 1400-1450 cm^{-1} are attributed to the stretch of C-O and the deformation vibration of OH. In addition, the bands at ca. 1150-1280 cm^{-1} are attributed to the aliphatic acid. The FTIR spectrum of the ferrofluid shows that the peak of 1710 cm^{-1} shrank and two new peaks at ca. 1540 and 1405 cm^{-1} appeared due to the binding of the carboxylic acid groups to the surface of the nanoparticles to form the carboxylate groups. The new peaks correspond to the COO^- anti-symmetric vibration and the COO^- symmetric vibration, which mean the bidentate bonding of the carbonyl groups to the surface Fe atoms. The remaining but shrank peak at 1710 cm^{-1} is due to C=O stretch and indicates that some fraction of the PAA oligomers were bonded to nanoparticles either in monodentate form or as an acid. Consequently, the interaction between PAA oligomers and Fe_3O_4 nanoparticles was through chemical bonding.

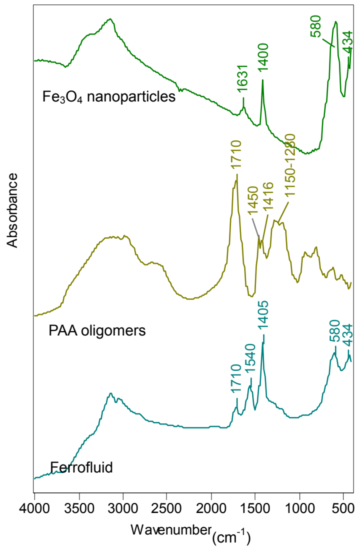

Figure 3. FTIR analysis of Fe_3O_4 nanoparticles, PAA oligomers, and the ferrofluid.

XRD was also used to investigate the effect of PAA oligomers on the preparation of magnetic nanoparticles as shown in Figure 4. The results show that the nanoparticles prepared in the presence of PAA oligomers not only had the characteristic peaks of standard Fe_3O_4 crystal but also had an diffraction peak at ca. 2θ=32.8°, which was the characteristic peak of Fe_2O_3 crystal. These results indicate that a small amount of Fe_2O_3 particles consisted in the ferrofluid because the particles were synthesized in the initial condition with low pH value (in PAA oligomer solution 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.

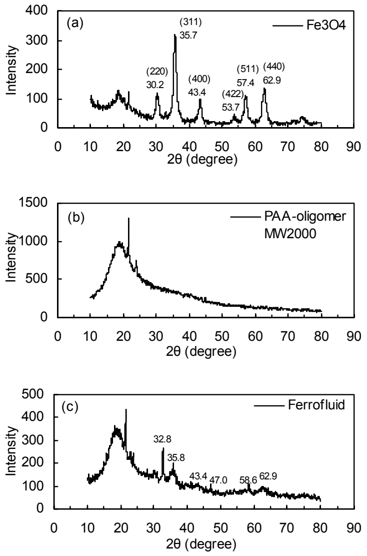

Figure 4. XRD pattern of the pure Fe_3O_4 nanoparticles (a), PAA oligomers (b), and ferrofluid particles (c).

Preparation of Magnetic Polymeric Particles After the addition of the ammonium solution into monomer solution, the water-base stable ferrofluid could disperse in the monomer (NIPAAm and MAA) solution homogeneously. Then the monomer solution containing magnetic nanoparticles, served as the dispersing phase, was mixed with the cyclohexane solution containing Span80, the continuous phase, 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 concentration of these two miniemulsions in the continuous phase (cyclohexane). 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, (5) decoalescence.

The cyclohexane-insoluble ferrofluid consisting of PAA oligomer stabilized magnetic particles and NH_4Cl salts was used as the co-stabilizer to prevent the Ostwald ripening in our inverse miniemulsion. In addition, keeping the temperature of the system as low as 25℃ during the polymerization also prevented the monomers, NIPAAm and MAA, from being soluble in cyclohexane. Consequently, the homogeneous magnetic composite particles were prepared.

The reaction would be initiated in the monomer droplet not in micelle. So the composite latex particles would maintain its homogeneous morphology as shown in Figure 5(a). If the micelle existed, significant amount of latex particles without containing magnetic Fe_3O_4 produced (Figure 5(b)).

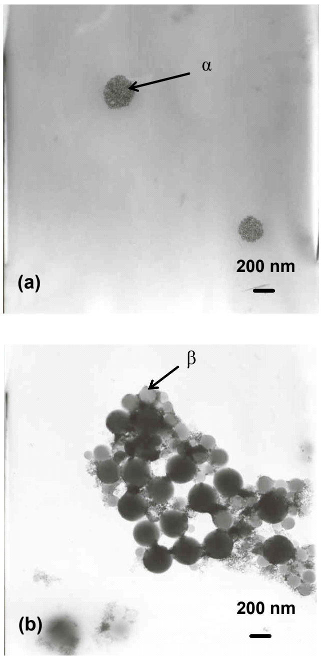

Figure 5. TEM of composite latex (a) concentration of span 80 < CMC and (b) concentration of span 80 > CMC, where α and β indicate the latex particle containing Fe_3O_4 nanoparticles and the latex particle without containing Fe_3O_4 nanoparticles, respectively.

The polymerization took place rapidly at 25℃ because three possible redox initiator reactions coexisted in our system: (a) reaction between APS and SMBS (b) reaction between APS and Fe^{2+}, and (c) reaction between SMBS and Fe^{3+}. Since the polymerization was catalyzed by the magnetic particles, this would be one reason that led into the well incorporation of magnetic particles inside the polymer latex particles. In addition, the acid groups containing monomer, MAA, was also likely to adsorb on the magnetic particles and could copolymerize with other monomers. This also increased the compatibility between the magnetic particles and polymer matrix.

Characterization of Magnetic Polymeric Particles Table 1 shows the conversion of monomers after polymerization for 1 hour. The results indicate that when the mole ratio of NIPAAm to MAA or the concentration of crosslinking agent was higher, the reaction conversion (at time= 1 hour) increased. The increased proportion of MAA would cause two effects on reaction. One is the decrease of the decomposition of initiators in more acidic medium. The other is the increase of Fe^{2+} ions from Fe_3O_4 which would act as a free radical quencher, although the iron ions also act as accelerator. Both effects caused the decreasing of conversion. The increased concentration of crosslinking agent would increase the conversion because the crosslinking agent, MBA, acts as a co-monomer which provides two vinyl groups and increases the rate of polymerization. The effect of magnetic particles on the conversion of polymerization is also shown in Table 1. The larger amount of magnetic particles participated in the reaction reduced the reaction conversion. This was because a small amount of Fe_2O_3 consisted in the ferrofluid, which would act as a radical quencher.

Table 1. The conversion of reaction. (reaction time: 1 hour)

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

From the DSC measurements as shown in Table 2, it shows that increasing the concentration of MAA or crosslinking agent would increase the Tg of the composite latex. This was because the Tg of PMAA was higher than that of PNIPAAm and the higher amount of crosslinking agent would hinder the segmental motion of polymer chains.

Figure 6 shows the TGA analysis of homopolymers and magnetic composite latex particles. The pure PNIPAAm had a significant weight loss at 400℃. But there were two stages of degradation shown in the TGA curve of PMAA. The initial stage of degradation (250~300℃) 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℃. The TGA curve of PMAAN, produced by the polymerization of MAA in the presence of ammonium solution, also shows a two-stage degradation. The first-stage degradation which occurred near 250℃ 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℃, 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.

Table 2. The glass transition temperature (Tg) of the composite particles from DSC measurements.

Sample type	Tg (℃)
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

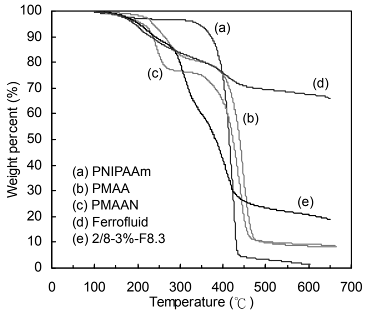

Figure 6. TGA analysis of homopolymers and composite particles.

The carboxylic acid groups partially remained unionized state in the pH=4 buffer solution and the zeta 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 zeta 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 were very useful for the conjugation of enzyme and protein, adsorption of metal ions, or other applications.

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 7. In addition, the average diameter of the latex at different temperatures was also measured by the light scattering as shown in Figure 8. These results proved that the composite latex really has 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 due to 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℃), because the co-monomers, MAA and its ionized form, were very hydrophilic. For the same reason, the particles with higher amount of hydrophilic co-monomers, MAA and its ionized form, would have better swelling behavior that caused the larger particle size and lower absorbance as shown in Figure 7 and Figure 8. But the particles with higher crosslinking would hinder the swelling of latex particles that caused the smaller particle size and higher absorbance.

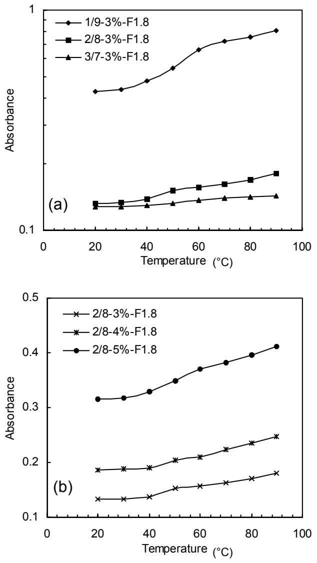

Figure 7. Cloud point analysis of composite latex, where the pH value of the solution was 7 during the measurements. (a) the effect of monomer ratio (b) the effect of crosslinking agent.

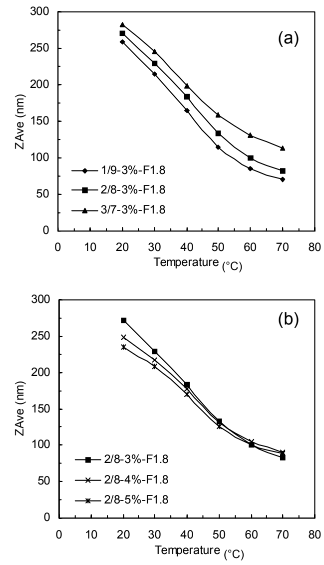

Figure 8. The average diameter of composite latex particles with various temperatures, where the pH value of the solution was 7 during the measurements. (a) the effect of monomer ratio (b) the effect of crosslinking agent.

Figure 9 shows the particle volume ratios and surface area ratios of composite particles at 20℃ to 70℃, which indicate the thermo-responsiveness of these composite particles. The results show that the volume and the surface area of these particles were larger at 20℃ than those at 70℃ due to their thermoresponsive properties. The ratio was reduced as the proportion of the MAA or crosslinking agent increased, which meant 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. While in higher crosslinked sample, the crosslinking structure hindered the swelling and shrinking of latex particles, so the thermoresponsive ability was reduced.

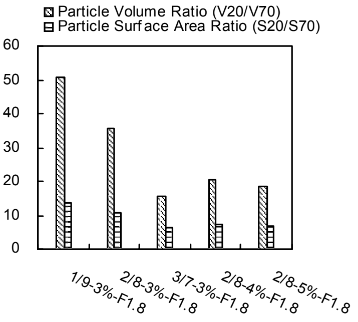

Figure 9. The particle volume ratios and surface area ratios of composite particles at 20°C to 70°C.

The reversibility of the thermoresponse property was also examined by the absorbance and the particle size measurement. From Figure 10, the composite latices showed an acceptable reversibility when the heating and cooling process were repeated several times. This result indicates that these product could be recycled many times.

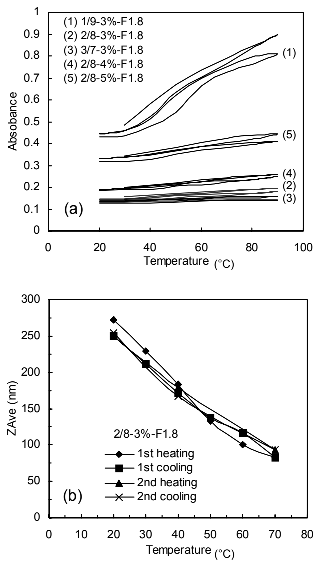

Figure 10. The reversible thermoresponsive properties of composite latices (a) form the cloud point analysis and (b) form the particle size analysis, where the pH value of the solution was 7 during the measurements.

It is well known that the Fe_3O_4 nanoparticles show a superparamagnetic property. But when there was a quantity of Fe_2O_3 in the ferrofluid and the magnetic nanoparticles were encapsulated by chemically polymerization, the magnetic property of the composite particles 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 11.

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 due to the following two reasons: (1) the saturation magnetization decreased when the particle size was smaller than 10 nm in diameter, and (2) 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 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.

The original data showed that the saturation magnetizations of these composite particles were all about 0.65 emu per gram of composite particles. Comparing to the saturation magnetization of ferrofluid (magnetic particles), it was found that the composite particles only contained 1.8 wt% iron oxide for each sample that was also confirmed by TGA measurement. This value is extremely low compared to the best encapsulation in previous reports (18~30 wt%) 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 hr was reduced to lower than 50% as shown in Table 1. 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.

In order to compare the magnetic property of the magnetic particles before and after polymerization, Figure 11 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 all about 35 emu/g, the remanence and coercivity were all zero, and there was no magnetic hyteresis loop for each sample. It could be concluded that the intrinsic properties of magnetic nanoparticles were not changed after the inverse miniemulsion polymerization.

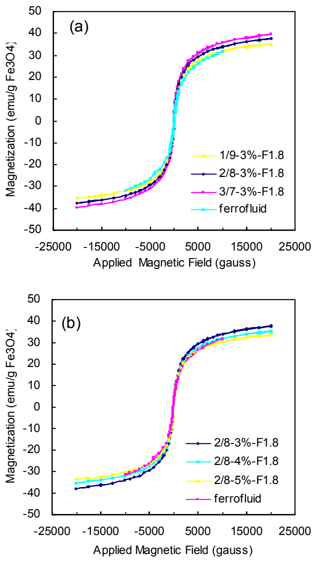

Figure 11. The squid analysis of the latex particles. (a) the effect of monomer ratio (b) the effect of crosslinking agent.

4. CONCLUSION

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 co-stabilizer. 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℃), but the thermo-responsiveness was reduced as the proportation of the 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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