Controllable preparation of high-yield magnetic polymer latex

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A R T I C L E   I N F O

Article history:
Received 10 February 2011
Accepted 26 April 2011
Available online 11 May 2011

Keywords:
Miniemulsion polymerization
Magnetic polymers
Morphology
Polymerization procedure

A B S T R A C T

In order to overcome the low conversion and complex post-treatment, four different polymerization procedures were adopted to prepare the magnetic polymer latexes. The results clearly show that the strategy using magnetic emulsion template-dosage is the most effective and feasible. Based on the optimized procedure, various factors including the type of initiators such as oil soluble initiator, water soluble initiator, redox initiator system, crosslinking agent, functional monomers etc. were systematically studied. Magnetic polymer latex with high monomer conversion of 85% and high magnet content of 31.8% was successfully obtained. Besides, core–shell structured magnetic polymer latex with good film forming property was also prepared, which is promising for potential applications such as magnetic coatings and modification of cementitious materials with controlled polymer location.

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1. Introduction

In recent years, magnetic polymer latex have attracted growing interests due to their extensively potential applications in the field of biomedicine, molecular biology, bioengineering like cell separation [1], magnetic storage media [2], drug delivery [3–8], immobilized enzymes [9,10], and magnetic resonance imaging [11,12]. All these practical applications desire the polymer latex to fulfill certain requirements including a uniform particle size distribution, high and homogeneous superparamagnetic content, good stability, and functionalized particle surface which is usually carboxyl-functionalized for the use of providing immobilization site for foreign molecules [9,13,14].

To date, many researchers have developed the methodology for synthesizing magnetic polymer latex by means of dispersion polymerization [15–17], conventional emulsion polymerization [18–21], precipitation polymerization [22], seeded [23–25]/soap-free [26,27]/inverse [28]/radiation induced emulsion polymerization [29], miniemulsion polymerization [30–33], pickering emulsion polymerization [34,35] and so on. In the case of conventional polymerization, the locus of polymerization is basically surfactant micelles. However, it’s very difficult for magnet particles to migrate or grow onto the micelles and polymer particles likewise. By contrast, the locus of miniemulsion polymerization is monomer droplet, which could be charged with the magnet particles beforehand following with further polymerization. Characteristic features of the miniemulsion polymerization technique may take the advantageous to become an efficient encapsulation method. Thus, miniemulsion polymerization is often selected as the common way to produce such kind latex.

The most challenging work in preparing magnetic polymer latex is how to obtain a high yield of polymerized monomer in a limited time period and simultaneously minimize or even eliminate the formation of pure polymer particles or free magnet particles without polymer covered. To our knowledge, such work is far from satisfactory. Cui et al. [31] put forward a hybrid emulsion polymerization system to synthesize magnetic polymer latex and got polymer latex with high magnetic content and few free magnetic particles, but the conversion of monomer is quite low, only about 20%. Ramirez and Landfester [36] originated a three-step method based on miniemulsion technology to produce magnetic particles with long polymerization time between 18 h and 24 h at 80 °C to achieve full conversion of styrene monomer. Up to 40% magnetite was encapsulated by polystyrene. In some cases, the existence of vacant polymer particle might require post-treatment like magnetic field separation to obtain magnetic polymer latexes with high magnetic response effect [37].

In this paper, a novel method for directly preparing uniform magnetic latex is introduced, characterized by controllable morphology and particle size distribution. A series of parameters are found to affect the final properties of the obtained latexes like conversion of monomer, particle size and distribution, morphology of particles and their response to magnetic field etc., which include the type of initiator, surfactant content, crosslinking agent, osmotic agent, functional monomer, main monomer, and the core–shell structure. The detail discussion on each parameter is also given for accomplishing the systematic work.

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2. Results and discussion

2.1. Polymerization procedure for preparing magnetic polymer latex

As introduced before, high conversion of monomers and high magnet content in the final dispersion are two main desired goals in the preparation of magnetic polymer latex. In this study, four polymerization procedures were adopted aiming at high monomer conversion and high magnet content. Comparing the characterization results of Latex 1–4 in Table 2, Procedure A gave the lowest conversion (10%) and magnet content (7%), while much higher conversion (71%) and magnet content (30.1%) are achieved through Procedure D. This can be explained by the different amount of polymerization locus and interaction between magnet nuclei and monomers, which differed in those polymerization procedures. In Fig. 1, schematic drawing of formation mechanism of magnet containing polymer particles in Procedure A–D are illustrated.

In commonly used one-step miniemulsion polymerization Procedure A, the monomers and ferrofluid were initially mixed together by ultrasonication. Ideally, all monomers are emulsified into monomer droplets with relatively the same droplet size. One should notice that despite ultrasonication employed, the exclusion between the monomer droplets and the ferrofluid is still unavoidable. During ultrasonication, it could not be ensured that every monomer droplet contains magnet nuclei, which leads to the low magnet content in the final dispersion. In the ideal case of miniemulsion polymerization, all monomer droplets will start polymerization to form primary particles and grow simultaneously with appropriate initiator amount and emulsifier amount. The droplets number at stage 2 should be equivalent to the number of final polymer particles at stage 4 in ideal case.

In Procedure B, ferrofluid, HD and emulsifier solution were ultrasonically mixed before monomer was allowed to swell those micelles. When radical enters into the monomer swollen micelles including containing with or without magnet nuclei, polymerization starts to form primary particles. It is believed that the number of monomer swollen micelles at stage 2 of Procedure B is much larger than the number of monomer droplets at stage 2 of Procedure A, which results in the much larger number of polymerization locus, primary particles, and consequently higher conversion at the end. Besides, unlike the Procedure A, the even distribution of magnet nuclei in micelles at stage 1 of Procedure B reduces the probability that many magnet nuclei are concentrated in one polymer particles. At the stage 2 of Procedure A, it is unavoidable that one...
monomer droplet contains many magnet nuclei while others may contain no or few magnet nuclei. Therefore, an obvious increase in magnet content in the final latex was also achieved in Procedure B, from 7% by Procedure A to 10% by Procedure B.

Due to the simultaneous initiation of monomer swollen micelles and growth of primary particles, the instability of growing primary particle may cause severe magnet leakage from the magnet containing micelles probably because of the migration of monomer from monomer swollen micelles to primary particles. Large amounts of initial monomer also caused decreased nucleation efficiency. Consequently the magnet content and conversion of Procedure B is still unsatisfactory. In virtue of the theory of seeded polymerization, Procedure C was designed to pay more attention on the percentage of the swelling monomer and fabricating primary polymer particles serving as seeds for succedent growth of particles in the system. At first step, only 20% monomer was used to swell micelles, after nucleation, the reduced amount of monomer existing in the system significantly improves the stability of the growing particles at stage 2 and therefore alleviates the leakage of magnet nuclei from the growing particles. The rest amount of monomer was then added after the stable magnet containing dispersion obtained at the end of stage 2, which could be regarded as seeds for the following stage 3. By doing so, compared with Procedure B, a noticeable increase in magnet content and slight increased conversion by Procedure C was realized.

In Procedure D, only 50% surfactants were utilized at the beginning, which elevate the proportion of produced MCM in the whole amount of micelles at stage 1. This helps to increase the magnet content in the final dispersion. Semi-batch dropwise addition of the rest monomer, initiator and surfactant was performed during stage 3. By this means, the nucleation efficiency and stability of primary latex particles were further improved. There are four advantages in Procedure D. (1) Monomer was pre-emulsified before dosed during stage 3, meaning that the fed monomer will not capture other surfactants from the reaction system. (2) Surfactants supplementation during particle growing helps to improve particle stability and reduce coagulum. (3) Monomer was fed in starved status, ensuring higher conversion. (4) Easier to control the distribution of functional monomer. Compared to other three procedures, Procedure D brings the best results in terms of monomer conversion, magnet content and uniformity of particle size. Consequently, Procedure D was chosen as the basic process to further investigate other influential factors such as initiator system, surfactant, functional monomers etc. for the preparation of magnetic polymer latex.

### 2.2. Initiator system

It is known that initiator system is also one of the key parameters in emulsion polymerization. Emulsion polymerization using water soluble initiator involves steps of decomposition of initiator in aqueous phase and entrance of radical into particles, while in oil soluble case: polymerization is directly initiated within the particle. It is believed that this two different initiation mechanism will lead to different results in the preparation of magnetic latexes. Batches initiated with SPS, AIBN, CHPO/FeSO₄ redox initiator system were investigated as Latex 4, Latex 6 and Latex 9 respectively, while all the other factors were kept constant. It can be seen from Table 2, magnetic polymer latex with relatively high conversion and magnet content were successfully produced by using different initiators based on Procedure D.

Fig. 2 shows the TEM images of the magnetic polymer particles in the above three latexes. It is clearly observed that spherical particles with Fe₃O₄ nano-nuclei encapsulated in the polymer matrix are obtained. However, the Fe₃O₄ nanoparticles of Latex 6 and Latex 9 are not uniformly dispersed in the interior of the particles. They congregate mainly in one side in the particles, while Latex 4 shows more uniformly dispersed magnet nuclei morphology. Such different morphologies indicate that micro phase separation occurred during polymerization. This is in accordance with what reported by other researchers [31,39]. It is supposed that using interfacial redox initiator system Latex 9 can get a better uniform magnet polymer composite particle by restricting the production location of radicals at the interface between aqueous phase and oil phase. Unfortunately, the result is dissatisfaction. The distribution of Fe₃O₄ in polymer particles of Latex 9 is even more crescent like. Moreover, large quantities of free magnetic particles without polymer covering are produced.

Recall that when using AIBN or redox system as initiator, the decomposition of initiators mainly takes place inside the MCMSM and the produced radicals are oil soluble. Therefore, all steps of the initiation of monomer and the following polymer chain growth occur inside the particle. Owing to the incompatibility between Fe₃O₄ nano nuclei and growing polymer chains, magnet nuclei are expelled to one side during particle growth. In addition, lots of free magnetic particles without polymer coating are produced in Latex 9. This probably ascribes to the lower nucleation efficiency at polymerization stage 2 by using redox initiator system, which should be also responsible for the lower conversion efficiency compared to the other two. Relatively speaking, in SPS initiated system, the distribution of polymer growth is random in the sphere bulk, moreover, the initiation starts from the outside to inside, keeping most of the Fe₃O₄ nano nuclei from moving outwards. However, a few of vacant polymer particles are also found, which may be due to the secondary nucleation initiated by radicals in aqueous phase [23].

It is also noticeable that using AIBN as initiator, the latex has higher conversion, smaller particle size, and narrower size distribution (see Table 2, Latex 6). In the case of AIBN, it is solubilized in the MCMSM and then decomposed. This leads to an extremely little opportunity for radicals present in aqueous solution. Each MCMSM is an independent reactor where initiation and polymerization are taking place. The initiation locus and high initiation efficiency leads to a much larger number of primary particles and tremendous decrease on the possibility of secondary nucleation. Increase in polymerization locus results in smaller particle size after polymerization. Almost all the MCMSM are homogeneous and uniform, hence when the particle growth period ends, they have a similar particle size and narrower size distribution.

### 2.3. Surfactants

The amount of surfactants plays a crucial role in emulsion polymerization. Polymer particle size and stability could be perfectly controlled by changing the amount of surfactants used. In this study, combination of anionic and non-ionic surfactants is used to provide a better colloidal stability for the latex through the electrostatic and electrosteric effects. As explained for the Procedure D in Fig. 1, the amount of surfactant will influence the amount of micelles at stage 1, the number of monomer swollen micelles at stage 2, and hence the number of primary particles at stage 3. Consequently, the surfactant amount must be an important parameter influencing the conversion and particle size for the final latexes. It could be seen that the average particle size drops down from 194 nm to 144 nm along with increasing the surfactant amount in Latex 5–8. Latex 5 represents a low conversion, which probably results from the less polymerization locus and deteriorated stability of the growing particles, signified by the high PDI index up to 0.205. It should be pointed out that the magnet content of Latex 5 is 41.5%, even higher than the theoretical magnet content 33% according to the recipe. It must be resulted from the lower monomer conversion.
2.4. Crosslinking agent (DVB)

Phase separation of polymerizing polymer chain and magnet nuclei is the main reason causing uneven distribution of magnet nuclei in spherical polymer particles. In order to achieve uniform distribution of magnet particles in polymer particles, crosslinking agent was employed to reduce the mobility of growing polymer chain and to increase the viscosity of the polymerizing polymer phase in the growing particles in order to avoid phase separation at utmost. During preparation of Latex 11, 2% crosslinking agent DVB was added into the pre-charge at stage 1 to allow it migrating into those monomer swollen micelles. Accordingly, with the added DVB, the internal viscosity of the growing primary particles should increase, which is beneficial to reduce the monomer chain mobility so as to prevent phase separation. TEM image in Fig. 3 shows that the effect is somehow helpful. Fig. 4 is the particle size distribution result of Latex 7 and 11. Latex 7 has 14.2% small particles with particle size around 46.9 nm by volume, while Latex 11 exhibits a clear single model particle size distribution. It’s confirmed that the addition of DVB promotes the elimination of minor tiny particles to some extent, which is believed to be generated from the secondary nucleation. Besides, the magnet content of Latex 11 is 33%, almost equal to the theoretical value. The increased magnet content is also probably due to the increasing internal viscosity and less tendency of magnet particles to be separated out.

2.5. Osmotic agent (HD)

Osmotic agent, usually HD utilized, is very important in mini-emulsion polymerization to prevent particles from coalescence caused by Ostwald ripening [31]. Compared with Latex 12, Latex 7 with HD shows much narrower particle size distribution, with PDI index of 0.107, suggesting that HD can effectively improve the uniformity of the produced latex. On the other hand, one should note that the integration of HD in Latex 7 leads to relatively bigger particle size and lower conversion than Latex 12, implying that the existence of HD in the primary particles could reduce the osmotic pressure of monomer which is the main driving force of monomer migrating from monomer droplets to the growing particles. Due to the reduced osmotic pressure, the diffusion rate of monomer from the droplets to particles is depressed, so that the conversion is lower. Fig. 3 shows the TEM images of Latex 7 and Latex 12.

2.6. Functional monomers

In most cases of emulsion polymerization, minor functional monomers including AA, MAA, AAm etc., were often used to provide better stability of latex or to meet requirements of applications. In our study, we compared latexes with (Latex 10) and without AA (Latex 7) as functional monomer. It could be found that

![Fig. 2. TEM images of: (A) Latex 4 using SPS, (B) Latex 6 using AIBN, (C) Latex 9 using redox initiator, and (D) ferrofluid.](image-url)
Fig. 3. TEM images of: (A) Latex 7 without DVB added; (B) Latex 10 with AA added; (C) Latex 11 with DVB added; and (D) Latex 12 without HD added.

Fig. 4. Particle size distributions by volume of Latex 7 and Latex 11.
the particle size distribution is getting broader when AA was incor-
porated, which originates from the self-nucleation of those water
soluble oligomers in aqueous phase, although oil soluble initiator
was used.

TEM images in Fig. 3 shows that the latex with AA has a much
clearer interface between magnet nuclei and polymer. The reason
is probably that firstly, the polymerization locus is more likely re-
stricted to the interface region, and secondly, the more hydrophilic
polymerizing polymer chains are mainly propagating in the surface
of particles due to the hydrophilic character of co-monomer AA.

The zeta potentials and mobility of Latex 7 and 10 versus pH are
shown in Fig. 5. The isoelectric point of Latex without carboxyl
group is approximately 5.5, where the zeta potential is zero. As
for the latex with carboxyl group on particle surface, the isoelectric
point could not be found in the pH range from 2 to 10. The surface
shows negative charge potential and its value drops down with the
increase of PH. Therefore, it’s deduced that the latex displays better
electrostatic stability in basic environment due to the ionization of
carboxyl group. The distribution of –COOH in the latex was deter-
mined by conductometric titration. The amount of surface carboxyl
groups on the nanospheres is 0.17 mmol/g, suggesting about three
carboxyl groups present on each particle.

In the following experiments Latex 13–16, no matter what kind
of initiator used, using AM as functional monomer brings a wider
particle size distribution and smaller particles due to the similar
reasons in case of AA. TEM images as Fig. 6 shows that latexes with
AM as functional monomer have much more free magnet nuclei
lack of polymer-encapsulation. It seems that AA can contribute a
better colloid stability than AM due to ionization of carboxyl
groups, while AM improves colloid stability usually by electrosteric
function.

To conclude, an optimized procedure and formulation to pre-
pare magnetic polymer latex with high monomer conversion of
83% and high magnet content of 31.8% was obtained in Latex 13.

2.7. Main monomers

St and MMA are often chosen as the main monomers for latex
preparation. However they often lead to different results due to
their different intrinsic features such as water solubility, surfactant

![Fig. 5. Zeta potential, mobility vs PH value of Latex 7, Latex 10.](image)

![Fig. 6. TEM images of: (A) Latex 13 with AA and (B) Latex 15 with AM.](image)
adsorption, radical penetration, and diffusion, etc. [40]. In our study, we have also paid a few attentions to compared behaviors of St and acrylate monomers such as MMA. St and MMA were used as main monomer for the preparation of Latex 10 and Latex 17 respectively. It was found that Latex 17 has bigger particle size, broader particle size distribution and lower conversion than Latex 10. After stage 2 monomer swelling, quite a number of smaller particles were observed as shown in Fig. 7, which could be assigned as the non-swelled micelles due to the much higher intrinsic hydrophilic feature of MMA. The existence of non-swelled micelles may cause secondary nucleation during stage 3, which is known as one of the main reasons for instability during emulsion polymerization. All these reasons lead to bigger particle size, broader particles size distribution and lower conversion in case of MMA as main monomer.

2.8. Core shell structure

Film forming property is desired for latexes in many applications such as coatings and paints. It is known that neither latexes with St nor with MMA as main monomer has good film forming property due to the high glass transition temperature 105 °C for both PS and PMMA. In order to prepare magnetic latex with good film forming property at room temperature, core–shell structured magnetic latex was designed by incorporating a ‘soft monomer’ butyl acrylate (BA) into the shell composition. The recipe of Latex 18 was designed based on Latex 17, using MMA as the particle hard core and MMA–BA as soft shell. The $T_g$ of shell polymer was designed to be approximately $-4 \, ^\circ C$. From the TEM observations shown in Fig. 8, it could be clearly seen that compared with Latex 17, Latex 18 shows morphology of continuous polymer matrix with relatively uniformly dispersed magnet nuclei, implying good film forming property.

3. Magnetic properties

Magnetization curves of the dried magnetic fluid and dried synthesized latex are shown in Fig. 9. Neither remanence nor coercivility is observed in all the samples, indicating superparamagnetic
property. The saturation magnetization of ferrofluid, Latex 7, Latex 10 and Latex 13 are 51.829 emu/g, 14.103 emu/g, 15.385 emu/g and 17.061 emu/g, respectively. The magnet contents of Latex 7, Latex 10 and Latex 13 calculated from the ratio of the original saturation magnetization results are 27.2%, 29.7%, and 32.9%, which are in agreement with the TGA test results in Table 2. In all these experiments, the mass ratio of magnet nuclei and monomers was fixed at 1:3. Higher saturation magnetization of latexes could be achieved by increasing the proportions of ferrofluids during preparation.

4. Experimental

4.1. Materials

Styrene (St), Methyl methacrylate (MMA), Butyl acrylate (BA), Divinylbenzene (DVB), Azodisobutyronitrile (AIBN), Sodium persulphate (SPS), Cumene hydroperoxide (CHPO), Acrylic acid (AA), Acrylamide (AM), Ferrous sulfate heptahydrate (FeSO$_4$·7H$_2$O), Iron (III) chloride hexahydrate (FeCl$_3$·6H$_2$O), Octane, Oleic acid (OA), Hexadecane (HD), a 25% ammonium hydroxide solution (NH$_3$·H$_2$O), 1 mol/l hydrochloric acid (HCl) were used without further purification. Redox initiator system was composed of CHPO and FeSO$_4$·7H$_2$O. Anionic surfactants, sodium dodecyl benzene sulfonate (SDBS) and sodium lauryl ether sulfate, and nonionic surfactant, ethoxylated fattyalcohols with 30 EO repeating units were used in combination with proportion of 3:3:2 in mass. Double-deionized water (DDI) was used throughout the work.

The experimental work was carried out with the following steps: preparation of the oil-based Fe$_3$O$_4$ particles, synthesis of the magnetic polymer latex according to the specific polymerization procedure, and latex characterization.

4.2. Preparation of oil-based Fe$_3$O$_4$ ferrofluid

The magnetic polymer latex is prepared via four different polymerization procedures. Procedure A is based on the common one-step miniemulsion polymerization cited by majority of the researchers [10,23,32,38]. Details as followed, 10 g St, 8 g Fe$_3$O$_4$ ferrofluid and 0.4 g Hexadecane as osmotic agent were mixed as oil phase. The total amount of surfactant (2.5% mass percentage of oil phase) was dissolved in 60 ml water to constitute the aqueous phase. Then the oil phase was added to the aqueous phase and ultrasonicated (300 w, 0.5 h, Bilon, Shanghai) together in an ice bath. The use of ice bath was to prevent the polymerization occurring during ultrasonication. Finally the homogenized miniemulsion was poured into 250 ml four necked glass reactor and initiated by SPS (1% of monomer by mass) in air for 4 h at 85 °C.

Procedure B is based on emulsion-template method [9,14], in a typical run, Fe$_3$O$_4$ ferrofluid and HD was ultrasonicated with surfactant containing water phase in an ice-cooled bath, the magnetic-template miniemulsion was obtained and then the monomer was added into the aqueous phase and ultrasonicated (300 w, 0.5 h, Bilon, Shanghai) together in an ice bath. The use of ice bath was to prevent the polymerization occurring during ultrasonication. Finally the homogenized miniemulsion was poured into 250 ml four necked glass reactor and initiated by SPS (1% of monomer by mass) in air for 4 h at 85 °C.

Procedure C is a modified template method. After ultrasonication of ferrofluid and all surfactant containing water phase, only distilled water (50 ml) in air with vigorous stirring. As the solution was heated to 80 °C, NH$_3$·H$_2$O (28 wt.%, 50 ml) was added, quickly followed by addition of oleic acid (5.0 g). The reaction was allowed to proceed for 2 h at 80 °C, and then the temperature was increased to 90 °C to vapor NH$_3$ assisted with vacuum, for 30 min. The produced Fe$_3$O$_4$ particles were neutralized by 1 N HCl, washing five times with distilled water to discard OA by the magnetic separation procedure. Then, by dispersed with 30 ml ethanol and introducing octane (10 g) in the medium, the magnetite particles modified by oleic acid were extracted in situ into the octane and stable colloid organic ferrofluid with a magnet weight content of 65% was obtained by sonicating 20 min to disperse (that is, no sediment). The resultant magnet particles were about 10 nm observed by TEM.

4.3. Emulsion polymerization of Magnetic polymer latex

The magnetic polymer latex is prepared via four different polymerization procedures.

Fig. 9. Room-temperature magnetization curves of dried magnetic fluid and latex.
eral amounts of latex were dried in a vacuum oven at 80°C. The dried latex was then characterized with respect to its magnetic properties under dry conditions.

BHV-50HTI, Riken, Japan) was used to analyze the magnetic properties of the particles. Vibrating sample magnetometry (VSM; Oxford Instruments, UK) was employed to measure the magnetic properties. The experimental temperature was in the range of room temperature to 550°C.

Conversion was determined by measuring the weight percentage of the sample latex, and magnet content (S) by testing the latex. It’s shown that emulsion polymerization is an effective method for encapsulating Fe₃O₄ with polymer. A reproducible method, characterizing by uniform magnetic latexes, was introduced in this paper. It’s shown that emulsion polymerization is an effective method for encapsulating Fe₃O₄ with polymer.

Table 1

<table>
<thead>
<tr>
<th>Latex No.</th>
<th>Procedure</th>
<th>Main monomer (g)</th>
<th>Ferrofluid (60%) (g)</th>
<th>Functional monomer (g)</th>
<th>DVB (g)</th>
<th>HD (g)</th>
<th>Surfactant (%/oil)</th>
<th>Initiator (g)</th>
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</table>

5. Latex characterizations

The particle size distribution was measured by laser dynamic light scattering (DLS) instrument (Malvern Zeta Sizer 3000H). Transmission electron microscopy (TEM; Hitachi H-7650B) was used to observe the microscopic morphology of the magnetic polymer particles. Thermogravimetric analysis (TGA) was performed with a DSC/TGA thermal analysis system (DTG-60H, Shimadzu, Japan). The experimental temperature was in the range of room temperature to 550°C, heating at a ramp rate of 10°C/min under nitrogen atmosphere. Vibrating sample magnetometry (VSM; BHV-50HTI, Riken, Japan) was used to analyze the magnetic properties of the particles under dry conditions.

Conversion of the synthesized latex was tested as followed: several amounts of latex were dried in a vacuum oven at 80°C under constant weight. Using the followed formula to calculate:

\[ \text{Conversion} = \frac{W_f}{W_i} (1 - S) / W_i A \]

Here, \( W_f \) is the weight of the sample latex, \( W_i \) is the weight of dried latex, \( S \) is the magnet content of magnetic particles tested by TGA, and \( A \) is the weight percentage of total monomer in the reaction mixture.

The size distribution of the latexes was determined by measuring the electrophoretic mobilities (\( \mu_e \)) and Zeta potentials (\( \zeta \)) at 25°C under different pH conditions using a Zeta-Sizer (Model 3000, Malvern Instruments). The pH was controlled using different buffers (phthalic acid at pH 2 and 3, acetate at pH 4 and 5, phosphate at pH 6 and 7, borate at pH 8 and 9, and carbonate at pH 10).

The surface distribution of –COOH in the latex was determined by conductometric titration according to Hen’s method [41]. Four milliliters of original latex was diluted with 24 ml of water and its solids content was measured by gravimetry method. The pH value of the diluted latex was first adjusted to 11.5 ± 0.02 using 0.385 mol/l NaOH solutions, and then the latex was titrated with 0.01 M HCl solution under the monitor of a DDS-307 conductometer (Leici, Shanghai, China). Therefore, a back titration was carried out to obtain the curve. The amount of surface carboxyl groups on nanospheres is calculated according to the formula: –COOH (mmol/g nanospheres) = \( VW/N \), where \( N \) is the concentration of standard solution of HCl, \( V \) is the total volume of this solution consumed in the titration and \( W \) is the total nanospheres employed.

6. Conclusion

A reproducible method, characterizing by uniform magnetic latex with high conversion of monomers and high magnet content is introduced in this paper. It’s shown that emulsion polymerization is an effective method for encapsulating Fe₃O₄ with polymer. Polymerization procedure is testified vital to the outcome of the
experiments. Four different polymerization procedures are investigated. Among these, magnetic template-dosage procedure is found to be the most effective for synthesizing high yield magnetic polymer latex. The related factors were carefully discussed, and finally to obtain a controlled polymerization. It’s interesting to note that using AIBN, other than using water soluble initiators, can get smaller particle, a much narrower size distribution and higher conversion, but also leads to phase separation within particles. Crosslinking agent DVB can help to restrict such phenomena to some extent. With the absence of osmotic agent HD, latex achieves a broader size distribution. Latex using MMA as main monomer has a broader particle size distribution, bigger particle and lower conversion than using St. A core shell structured magnetic polymer latex with good film forming property was also successfully prepared. Electrokinetic characterization shows that the functional latex after surface modification had good colloid stability in water and basic conditions. The latexes are superparamagnetic which is favorable for many applications. The potential applications for this magnetic latex could be targeted drug delivery, magnetic coating, anti-corrosion coating for steel, modification of cementitious materials with controlled polymer location.

Acknowledgments

The supports from the National Natural Science Foundation of China (Grant No. 50802050) and the 11th Five-Year National Key Technologies R&D Program of China (Grant No. 2006BAG05B03) are appreciated.

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