

Factors Influencing Magnetic Polymer Microspheres Prepared by Dispersion Polymerization

Hongmei Zeng,¹ Qiongyu Lai,¹ Xueqi Liu,¹ De Wen,¹ Xiaoyang Ji²

¹College of Chemistry, Sichuan University, Chengdu 610064, China

²Analytical and Testing Center, Sichuan University, Chengdu 610064, China

Received 12 November 2006; accepted 3 June 2007

DOI 10.1002/app.26999

Published online 22 August 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Magnetic iron oxide (Fe_3O_4) was prepared by a coprecipitation method. Core-shell composite magnetic polymer microspheres with carboxyl groups were synthesized by the dispersion polymerization of styrene and acrylic acid in the presence of magnetic oxide, and dibenzoyl peroxide was used as an initiator. The synthesized magnetic polymer microspheres were characterized with X-ray diffraction, transmission electron microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, and so forth. The results indicated that the product was single-phase Fe_3O_4 , and its average size was about 10 nm. The configuration of the microspheres, which contained carboxyl groups, was spherical, and the average

size was about 2 μm . The results of vibrating sample magnetometry tests showed that the magnetic powders produced by different surfactants had different saturation magnetizations. When poly(ethylene glycol) with a weight-average molecular weight of 4000 was used as a surfactant, the saturation magnetization of the samples reached 69.2 emu/g. The factors that affected the shape, magnetism, size, and distribution of the microspheres were also studied. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3474–3480, 2007

Key words: coatings; core-shell polymers; dispersions; magnetic polymers

INTRODUCTION

Magnetic polymer microspheres have attracted a lot of interest because they can separate viruses quickly from normal human cells in external magnetic fields. Magnetic polymer microspheres are composed of a polymer and inorganic magnetic materials. They are endowed with functional groups on the surface by polymerization or surface modification. The surfaces of microspheres have carboxyl groups that can combine with the amino groups of the proteins of viruses and thus can be used in cell separation. In particular, when used as tumor-resisting supporters, they can control drug carriers by virtue of external magnetic fields. Because of the block effects of the macromolecular shell, magnetic polymer microspheres used as supporters can release drugs slowly and have very practical applications in disease therapy, especially as drug-targeting supporters.^{1–11} At present, the main methods used to prepare magnetic polymer microspheres are coblanding and monomer polymerization.^{12–18} They both use magnetic powders as initiation centers to be coated with polymer materials. Normally, the average size of magnetic

microspheres prepared by these methods is much bigger. In this work, iron oxide (Fe_3O_4) nanoparticles with an average size of 10 nm were prepared by a modified coprecipitation method. The magnetic particles were coated with a polymer and modified with carboxyl groups by dispersion polymerization. The characterization results of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet–visible (UV–vis), and IR spectroscopy for magnetic powders and microspheres were analyzed. Furthermore, factors, including the surfactant, dispersant, initiator, and amount of magnetic powder, influencing the formation, size, morphology, and magnetism of the magnetic polymer microspheres were also examined.

EXPERIMENTAL

Materials and reagents

All chemicals and solvents were analytical-grade and were used without any further purification, including ammonium ferrous sulfate, ammonium ferric sulfate, aqueous ammonia, dibenzoyl peroxide (BPO), sodium oleate, and poly(ethylene glycol) with a weight-average molecular weight of 4000 (PEG4000). Styrene (St) and acrylic acid (AA) were treated to remove the inhibitor before use. Double-distilled water was used throughout the study.

Correspondence to: Q. Lai (laiqy6@hotmail.com).

Preparation of the magnetic powders and polymer microspheres

Preparation of the magnetic powders

Magnetic particles were prepared by the coprecipitation method as follows.^{19,20} A mixture of poly(ethylene glycol) (PEG), ammonium ferrous sulfate, and ammonium ferric sulfate (molar ratio = 1 : 1.3) in a three-necked flask was heated to 60°C. Then, a mixture of concentrated ammonia and PEG was added and stirred quickly. After 10 min, the solution was heated to 85°C for 1 h. All synthetic procedures were performed under an inert (N₂) atmosphere. The magnetic precipitates were isolated from the solvent by magnetic decantation and washed with distilled water and ethanol several times to remove SO₄²⁻ and Cl⁻ ions. The solid product was dried *in vacuo* at 70°C for 24 h.

Preparation of the polymer microspheres

The magnetic powders were dispersed in 30 mL of a 10% PEG4000 solution. After ultrasonic dispersion for 10 min, they were added to a mixed solution of 36 mL of alcohol and 6 mL of water (volume ratio = 6 : 1) and then transferred to a three-necked flask with a stirrer, two entries to pass nitrogen gas, and a condensation tube. With the protection of nitrogen gas, the solution was heated to 60°C at 300 rpm and reacted for 30 min at a constant temperature. Then, 2 g of BPO, 5 mL of St, and 1 mL of AA were added to it in turn. The reaction continued for 8 h. The microspheres were magnetically separated and then washed repeatedly with distilled water.

The microspheres were dipped into hydrochloric acid (pH = 2) for 24 h and then dipped into distilled water for 24 h to eliminate magnetic powders that were not coated by the polymer. The brown microspheres were prepared after being dried *in vacuo* at 70°C for 24 h.

Characterization and tests of magnetism

The magnetic powders and magnetic polymer microspheres were characterized with XRD patterns obtained on a Rigaku (Japan) D/Max-γA diffractometer with Cu Kα as incident radiation ($\lambda = 0.15418$ nm, 40 mA, 80 kV). The XRD intensity data were collected over the range of $10^\circ < 2\theta < 70^\circ$ at room temperature. The morphology and size of both the Fe₃O₄ and polymer particles were observed with TEM (JEM-100CX, Japan) and SEM (JSM-5900LV, Japan), respectively. Fourier transform infrared (FTIR) spectra of the powders and microspheres were recorded on an FTIR spectrophotometer (Nexus 670, United States). The UV-vis spectra of the samples dissolved in *N,N*-dimethylformamide were recorded

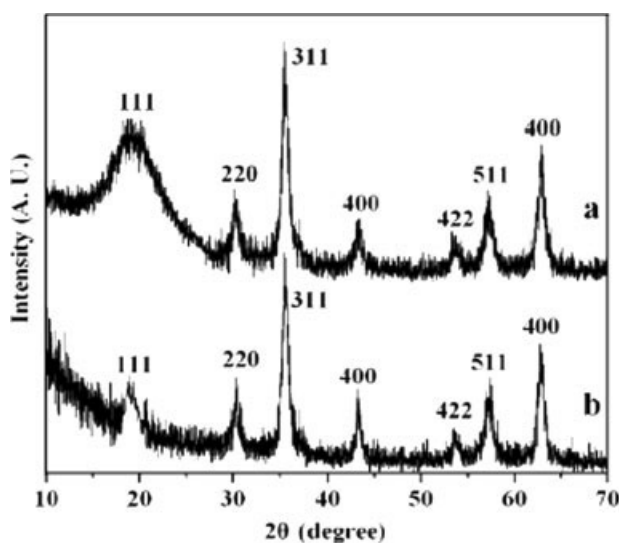


Figure 1 XRD patterns of the samples: (a) the magnetic microspheres and (b) the magnetic powder.

on a TU-1901 spectrophotometer (China). The magnetization of the samples was measured with a vibrating sample magnetometer (155-VSM, United States).

RESULTS AND DISCUSSION

XRD analysis

Figure 1(a,b) shows the XRD patterns of magnetic polymer microspheres and magnetic Fe₃O₄, respectively. As shown in Figure 1(b), the XRD data of the synthesized powders with chemical coprecipitation shows all the peaks of Fe₃O₄. The data are consistent with the standard spectrum of Fe₃O₄ (power diffraction file (PDF) 19-629). Therefore, XRD confirms the formation of pure Fe₃O₄. The peak widening in Figure 1(b) is caused by the nanometer magnitude. Compared with Figure 1(b), the (111) crystal face diffraction peak in Figure 1(a) strengthens obviously, but the intensities of the other do not change. The diffraction peak appearing around $2\theta = 19^\circ$ can be attributed to the St polymer, as reported.²¹⁻²³ The diffraction peak on the (111) crystal face of Fe₃O₄ in the polymer microsphere is strengthened because of the overlapping by the aforementioned peak with the diffraction peak on the (111) crystal face of Fe₃O₄.

SEM and TEM analysis

Figure 2 shows a TEM micrograph of the magnetic powders. The magnetic particles synthesized by chemical coprecipitation are almost spherical, with a narrow granularity distribution and a size of 10 nm. Figure 3 shows an SEM micrograph of the magnetic microspheres. The magnetic microspheres are spherical, with an average size of 2 μ m.

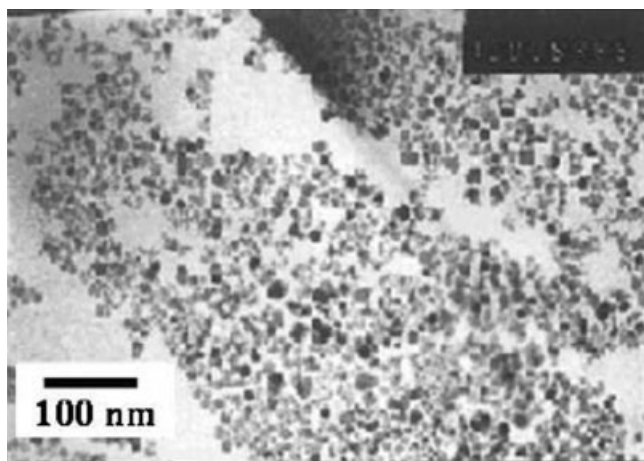


Figure 2 TEM micrograph of the Fe_3O_4 particles.

IR and UV-vis analysis

Figure 4 shows the IR spectra of the magnetic powders and microspheres. A strong absorption peak can be observed at 565 cm^{-1} in Figure 4(a), which can be ascribed to the vibration peak of the Fe—O bond. Similarly, a strong peak at 531 cm^{-1} in Figure 4(b) is the characteristic stretching vibration peak of the Fe—O bond. A series of absorption peaks in the region of $2000\text{--}1600\text{ cm}^{-1}$ and the peaks at 3025 , 756 , and 697 cm^{-1} can be attributed to the typical absorption of polystyrene.²⁴ The absorption peak near 1150 cm^{-1} corresponds to the C—O bond of $-\text{CH}_2-\text{O}-\text{CH}_2-$ or COO^- groups.²⁵ The absorption peaks at 3350 cm^{-1} and $1450\text{--}1500\text{ cm}^{-1}$ correspond to the OH^- group and COO^- group, respectively.^{26,27} Such a series of absorption peaks appearing at 1720 (C—O), 1270 (C=O), and 906 cm^{-1} (OH) implies the existence of AA in the magnetic microspheres. The results confirm that St undergoes copolymerization with AA and that the microspheres contain carboxyl groups.

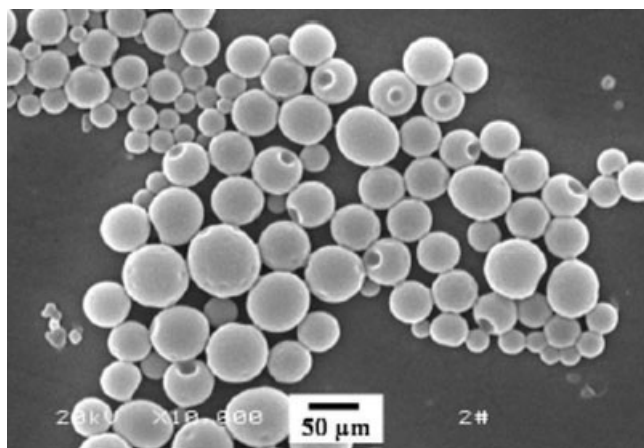


Figure 3 SEM photograph of the magnetic microspheres.

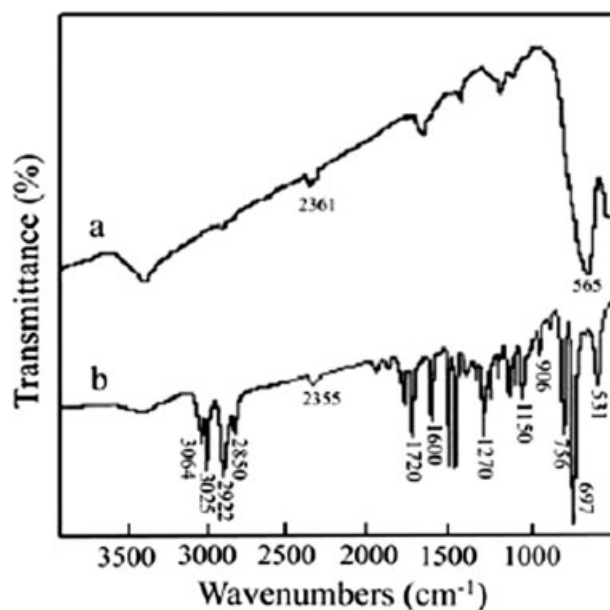


Figure 4 FTIR spectra of the samples: (a) the magnetic powder and (b) the magnetic microspheres.

With the formation of magnetic microspheres, the Fe—O absorption peak shifts from 565 to 531 cm^{-1} , and its intensity weakens gradually. Figure 5 shows the UV-vis absorption spectra of samples. Pure polystyrene samples [shown in Fig. 5(a)] absorb below 300 nm ; hence, the absorption between 300 and 700 nm can be attributed to the embedded Fe_3O_4 nanoparticles [shown in Fig. 5(b)].²⁷ However, the absorption is not very obvious, and this can be related to the solubility of the sample in the solvent. These results reveal that there may be some interaction between the Fe_3O_4 nanoparticles and polymer backbone, and this is similar to the reported results.^{23,28,29}

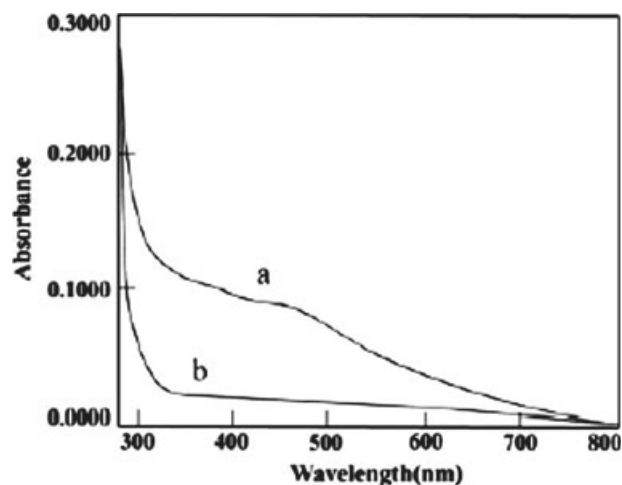


Figure 5 UV-vis spectra of the samples: (a) the magnetic microspheres and (b) the polymer.

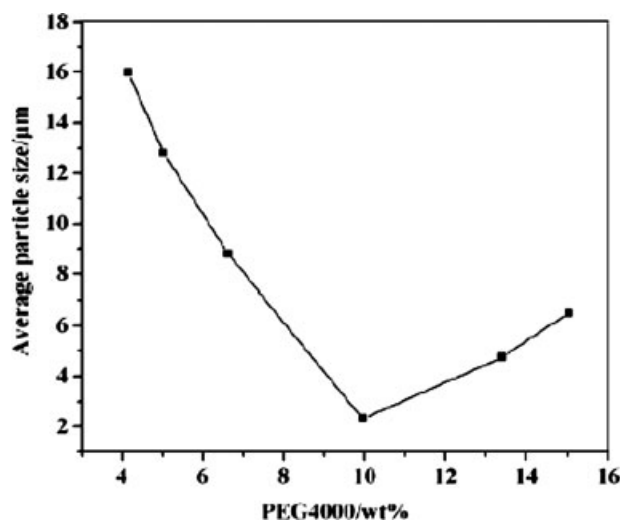


Figure 6 Effect of PEG on the average size of the microspheres.

Magnetic microsphere sizes

Effect of the PEG concentration

As shown in Figure 6, the primary particle size is significantly affected by the concentration of PEG. With an increase in the PEG concentration, the magnetic microsphere size decreases gradually. However, when the PEG concentration increases to a certain degree, the magnetic microsphere size starts to

increase. The reason is that with an increase in the PEG concentration, Fe_3O_4 magnetic powders can be dispersed into tinier particles that absorb the initiator, which leads to an increase in the activated centers and a decrease in the particle size. However, when the PEG concentration keeps increasing, some of the dissociative PEG is absorbed onto the surface of the magnetic microsphere and becomes new initiating centers. The new centers can initiate polymerization. The polymer wraps on the surface of the microsphere, and this leads to the average particle size of the microsphere increasing. The experimental results confirm that at a PEG4000 concentration of 10 wt %, the microsphere size is the minimum, with an average size of 2 μm .

Figure 7 shows SEM micrographs of magnetic microspheres prepared at different concentrations of PEG4000. As shown in Figure 7, at a PEG4000 concentration of 10 wt %, the microsphere average size is the minimum, and its shape is well regulated. The conclusion is the same as that drawn from Figure 6.

Effect of the composition of the dispersants

The dispersant is also one of the important factors determining the particle size. Figure 8(a) is an SEM micrograph of the magnetic microspheres produced in a dispersant of ethanol and water. Figure 8(b) is an SEM micrograph of the magnetic microspheres

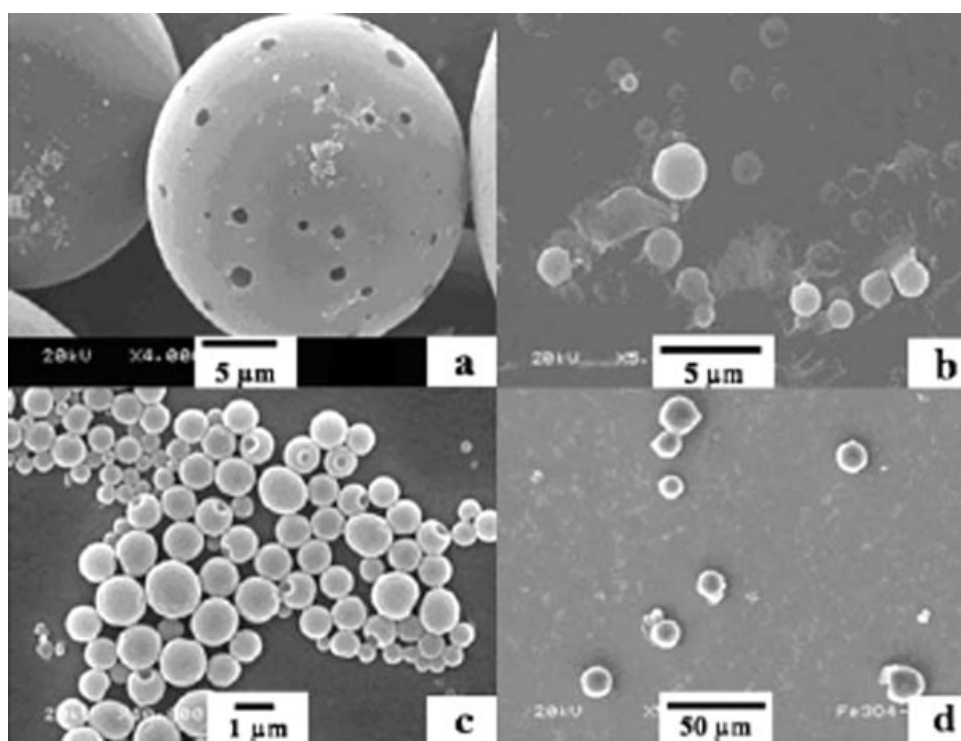


Figure 7 SEM photographs of the samples: (a) 4 wt % PEG4000, (b) 6 wt % PEG4000, (c) 10 wt % PEG4000, and (d) 12 wt % PEG4000.

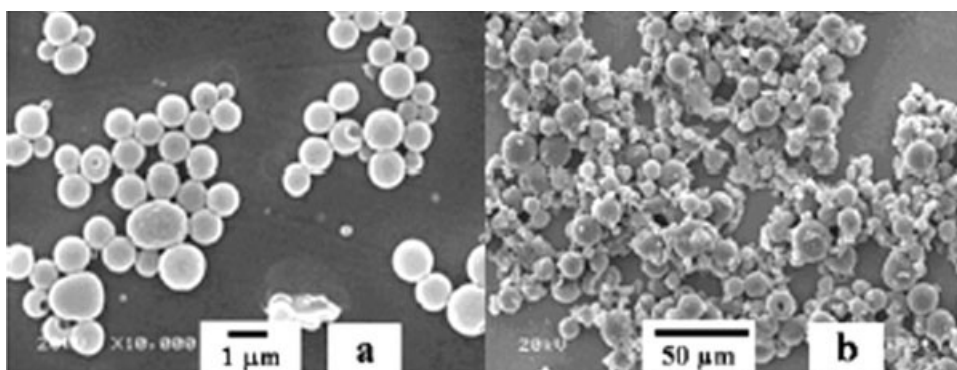


Figure 8 SEM photographs of the magnetic polymer microspheres prepared with different dispersants: (a) ethanol/water and (b) acetone/water.

produced in a dispersant of acetone and water. In comparison with Figure 8(a), the average size of the magnetic microspheres in Figure 8(b) is bigger, and the shape is irregular. The reason is that the dispersants of ethanol and water are on intimate terms with the magnetic particles, initiator, and monomer. However, acetone is a nonprotic solvent, and the polarity of the dispersant composed of acetone and water is relatively small, so the particle size of the microspheres should diminish. However, as the solubility of the monomers and polymers increase relatively, redundant monomers and dissolved polymers are absorbed around the surface of the microspheres simultaneously, and this increases the average size of the microspheres and widens the distribution.

Effect of the weight ratio of the magnetic powder to the polymer

Table I shows the effects of various amounts of the magnetic powders on the magnetic microsphere size. As the amount of the magnetic powders increases, the particle size of the microspheres decreases gradually. This phenomenon results from the fact that the monomers are distributed mostly on the interface of the magnetic latex in the dispersant, which is in equilibrium between the dispersant and magnetic particles. The surface of the magnetic latex is the major region of polymerization. As the amount of the magnetic powders increases, the region of poly-

TABLE I
Effect of the Amount of Fe_3O_4 on the Average Size and Configuration of the Magnetic Microspheres

Magnetic powder (wt %)	Average size ($\pm 0.1 \mu\text{m}$)	Microsphere configuration
1.0	15.0	Similar sphericity
2.0	10.0	Elliptical sphericity
3.5	5.0	Sphericity
7.0	2.0	Sphericity
14.0	—	—

merization also increases. Thus, the particle size of the microspheres decreases. However, the particle size will not decrease infinitely. When the amount of the magnetic powder is exorbitant, the content of magnetic Fe_3O_4 in the microspheres increases rapidly, so the magnetic interaction among the particles strengthens, and particles aggregate together. The result is that no steady microspheres can form. As shown in Figure 9, at an Fe_3O_4 concentration of 14 wt %, Fe_3O_4 is not encapsulated in the particles but scatters on the surface of the macromolecular polymer. This result is in agreement with what has been reported.³⁰

Effect of the initiator and its concentration

As shown in Table II, with an increase in the initiator concentration, the size of the particles increases. There are two direct results from the increase in the initiator concentration. First, the increase in the radical concentration leads to an increase in the oligomer

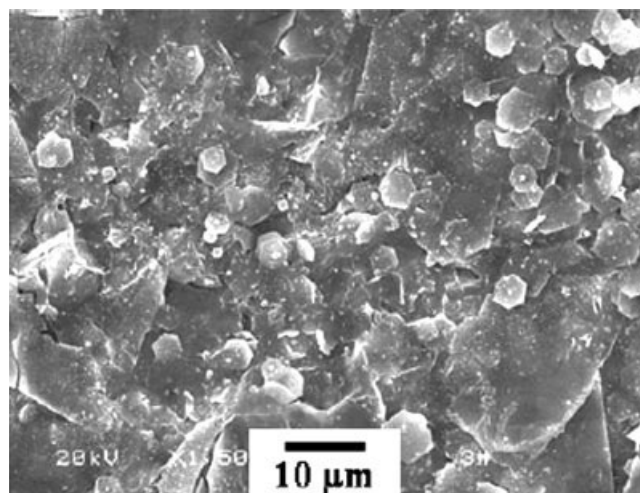


Figure 9 SEM photograph of the microspheres synthesized with a magnetic powder concentration of 14 wt %.

TABLE II
Effect of the Initiator Concentration on the Average Size of the Magnetic Microspheres

Initiator concentration (wt %)	Average size ($\pm 0.1 \mu\text{m}$)
2.8	2.0
5.6	4.0
8.4	10.0
10.0	15.0

concentration. Second, during the course of the graft reaction, the chain of St shortens, and its solubility in the dispersants increases; this leads to a decrease in the stability and strengthening of the polymerization. Therefore, bigger particles are produced. In the course of dispersion polymerization, nucleation starts from an oligomer chain and separates out from a continuous medium because of indissolubility for the dispersant as the molecular weight reaches a critical point. Thus, with a higher initiator concentration, there are fewer nuclei produced in the polymerization, and this leads to fewer and bigger final polymer particles. That is because the concentration of the oligomer chain, which reaches a critical molecular weight, is lower.

As shown in Figure 10, although the shape of the microspheres changes little, the particle size changes from 5 to 15 μm , and the particle size distribution is wider. The impact of the initiator concentration on the average particle size of the magnetic microspheres is shown in Table II. According to Table II, with a gradual increase in the initiator content, the average particle size of the produced microspheres increases too. If the initiator concentration is smaller, the integral sphere cannot be obtained because the surface of the magnetic particle cannot be encapsulated completely. The result shows that when the initiator concentration is 2.8 wt %, the production size

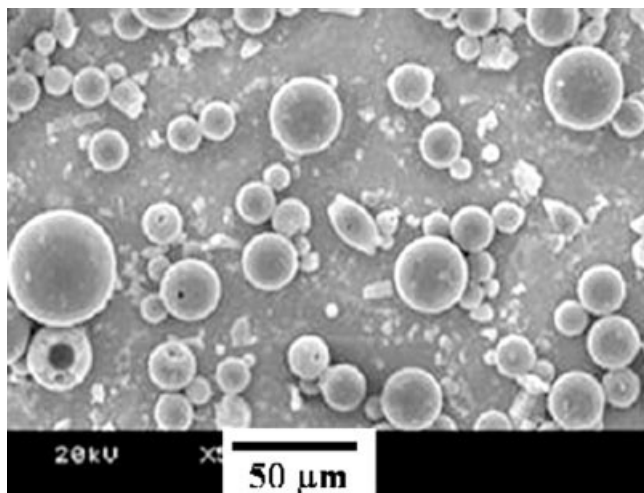


Figure 10 SEM photograph of the microspheres synthesized at an initiator concentration of 10 wt %.

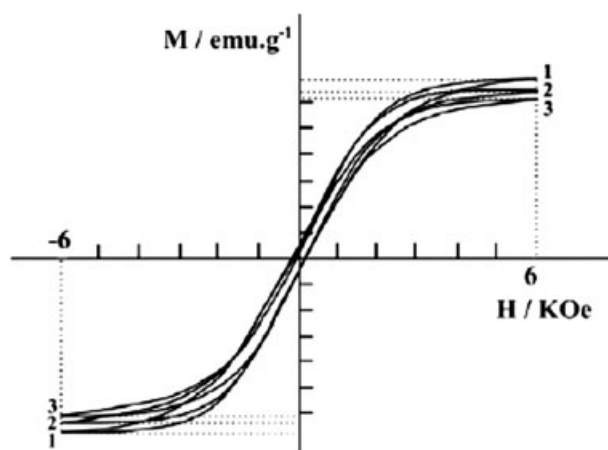


Figure 11 Magnetization curves of samples 1–3 in Table III.

is smaller and the magnetism is much stronger than those of the others.

Magnetic properties

The magnetic properties of the magnetic powders and magnetic microspheres have been analyzed with vibrating sample magnetometry results, as shown in Figure 11 and Tables III and IV.

The saturation magnetizations of the samples obtained with different surfactants are shown in Table III, and they vary from 60.6 to 69.2 emu/g. Table III shows that without the consideration of other factors, the magnetic powders produced by different surfactants have different saturation magnetizations. A sample's magnetization is strongest when PEG4000 is used as the surfactant. The particle size has been reported to influence the magnetic properties of materials. The bigger the particle size is, the larger the saturation magnetization is.³¹ However, the particle size is affected by surfactants. Therefore, the saturation magnetizations of the samples prepared in different surfactants are different.

Figure 11 shows the magnetization curves of samples 1–3 in Table III measured at room temperature. The nanometer Fe_3O_4 magnetic powders produced by coprecipitation have high saturated magnetization, low coercivity, and little hysteresis.

TABLE III
Magnetization of Fe_3O_4 Powders Obtained in Different Surfactants

Sample	Surfactant	Test temperature ($^{\circ}\text{C}$)	Saturation magnetization (emu/g)
1	PEG4000	13.5	69.2
2	Tween 80	13.5	63.8
3	Sodium oleate	13.5	60.6

TABLE IV
Magnetization of Magnetic Polymer Microspheres
Obtained at Different PEG Concentrations

Sample	PEG concentration (wt %)	Average size ($\pm 0.1 \mu\text{m}$)	Magnetic powder (wt %)	Saturation magnetization (emu/g)
1	5.0	12.0	3.0	2.1
2	8.0	6.0	5.5	3.8
3	10.0	2.0	14.2	9.8

Table IV shows the magnetizations of microspheres obtained from the same surfactant with different concentrations. After the magnetic powders are embedded, the saturation magnetization of the magnetic microspheres decreases drastically from 69.2 to 9.8 emu/g. One of the important reasons is that there is less magnetic powder per unit of weight of the microspheres than the pure magnetite particles. The other reason is that the nonmagnetic polymer coating layer influences the uniformity or magnitude of the magnetization because of the quenching of surface movements.^{32–34}

The relationship between the magnetic microspheres and the concentration of PEG has been discussed already. The reason for the increase in the saturation magnetization from sample 1 to sample 3 in Table IV is that with the microsphere size decreasing from sample 1 to sample 3, the mass proportion of the magnetic powders in the microspheres increases from 3.0 to 14.2%. It is obvious that the differences of the three samples with respect to the saturation magnetization are related to the weight percentages of the magnetic powders, and this is similar to the reported result.³⁵

CONCLUSIONS

The results indicate that the Fe_3O_4 particles prepared by the coprecipitation method are spherical, about 10 nm in size, and superparamagnetic. The results of vibrating sample magnetometry tests show that the magnetic powders produced by different surfactants have different saturation magnetizations. When PEG4000 is used as the surfactant, the saturation magnetization of a sample has been found to be 69.2 emu/g.

Composite magnetic polymer microspheres with a core-shell structure have been prepared by the dispersion polymerization method. The configuration of the microspheres, which have carboxyl groups, is spherical, and the average size is about 2 μm .

The shape, size, and distribution of the particles are affected by PEG, the dispersants, the initiator, and the weight ratio of the magnetic powders to the polymers. From 5 to 15 wt %, the size of the microspheres decreases with an increase in the PEG content. However, beyond that range, the size of the

microspheres increases. When ethanol and water are used as dispersants, the size of the microspheres is smaller than that of the others, and the particle size distribution is narrow. With an increase in the magnetic powder concentration, the size of the microspheres tends to decrease. When the initiator concentration is 2.8 wt %, the size of the magnetic microspheres is smaller, and the magnetism is much stronger.

References

- Goetze, T.; Gansau, C.; Buske, N.; Roeder, M.; Ornert, P. G.; Bahr, M. *J Magn Magn Mater* 2002, 252, 399.
- Denga, Y.; Wanga, L.; Yanga, W.; Fua, S.; Ellassarib, A. *J Magn Magn Mater* 2003, 257, 69.
- Gubin, S. P. *Colloids Surf A* 2002, 202, 155.
- Horák, D.; Semenyuk, N.; Lednický, F. *J Polym Sci Part A: Polym Chem* 2003, 41, 1848.
- Liu, X. Y.; Ding, X. B.; Zheng, C. H. *Synth Chem* 2001, 9, 281.
- Qiu, G. M.; Zhu, B. K.; Xu, Y. Y. *J Appl Polym Sci* 2005, 91, 328.
- Deng, Y. H.; Yang, W. L.; Wang, C. C. *Adv Mater* 2003, 15, 1729.
- Xie, X.; Zhang, X.; Bu, Y. B.; Gao, H. F.; Zhang, H.; Fei, W. Y. *J Magn Magn Mater* 2004, 280, 164.
- Zhang, J. H.; Ding, X. B.; Peng, Y. X. *J Appl Polym Sci* 2002, 85, 2609.
- Ritter, J. A.; Ebne, A. D.; Daniel, K. D.; Stewart, K. L. *J Magn Magn Mater* 2004, 280, 184.
- Horak, D. *Macromol Mater Eng* 2004, 289, 341.
- Hoark, D.; Benedyk, N. *J Polym Sci Part A: Polym Chem* 2004, 42, 5827.
- Guan, Y. P.; Jiang, B.; Zhu, X. H.; Liu, H. Z. *J Chem Ind Eng* 2000, 51, 315.
- Li, X. H.; Ding, X. B.; Sun, Z. H. *J Funct Polym* 1995, 8, 73.
- Csetneki, I.; Faix, M. K.; Szilágyi, A.; Kovács, A. L.; Németh, Z.; Zrinyi, M. *J Polym Sci Part A: Polym Chem* 2004, 42, 4802.
- Yanase, N.; Noguchi, H.; Asakura, H.; Suzuta, T. *J Appl Polym Sci* 1993, 50, 765.
- Lee, Y.; Rho, J.; Jung, B. *J Appl Polym Sci* 2003, 89, 2058.
- Horák, D. *J Polym Sci Part A: Polym Chem* 2001, 39, 3707.
- Wei, Y. Q.; Lai, Q. Y.; Yu, D.; Ji, X. Y. *Chin J Inorg Chem* 2003, 19, 411.
- Chen, D. H.; Liao, M. H. *J Mol Catal B* 2002, 16, 283.
- Zhao, J.; Ming, W. H.; Lv, X. L. *Chem J Chin Univ* 1995, 6, 1960.
- Hong, R. Y.; Pan, T. T.; Li, H. Z. *J Magn Magn Mater* 2006, 303, 60.
- Antolini, F.; Pentimalli, M.; Luccio, T. D. *Mater Lett* 2005, 59, 3181.
- Liu, X. Y.; Ding, X. B.; Zheng, Z. H. *Polym Int* 2003, 52, 235.
- Maity, D.; Agrawal, D. C. *J Magn Magn Mater* 2007, 308, 46.
- Deya, S.; Royb, A.; Dasc, D. *J Magn Magn Mater* 2004, 270, 224.
- Liang, X.; Wang, X.; Zhuang, J. *Adv Funct Mater* 2006, 16, 1805.
- Jiang, L.; Sun, W.; Kim, J. *Mater Chem Phys* 2007, 101, 291.
- Sun, Y. B.; Ding, X. B.; Zheng, Z. H. *Eur Polym J* 2007, 43, 762.
- Qiu, G. L.; Qiu, G. M.; Hu, L. *Fine Chem* 2001, 18, 274.
- Hong, R. Y.; Pan, T. T.; Han, Y. P. *J Magn Magn Mater* 2007, 310, 37.
- Li, G. J.; Yan, S. F.; Zhou, E. *Colloids Surf A* 2006, 276, 40.
- Ma, M.; Zhang, Y. *Colloids Surf A* 2003, 224, 207.
- Li, L. C.; Jiang, J.; Xu, F. *Mater Lett* 2007, 61, 1091.
- Li, L. C.; Jiang, J.; Xu, F. *Eur Polym J* 2006, 42, 2221.