

Preparation of Magnetic Ion-Exchange Resins by the Suspension Polymerization of Styrene with Magnetite

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ABSTRACT: Magnetic polymer microspheres composed of magnetite, styrene, and divinylbenzene were prepared by suspension polymerization to produce magnetic ion-exchange resins (MIEXs). The magnetite was grafted with oleic acid to improve the magnetic properties of the MIEXs and to prevent the magnetite from flushing out of the MIEXs. The shape and magnetic properties of the magnetic microspheres were investigated with scanning electron microscopy and vibrating-sample magnetometry. The average diameter of the prepared magnetic polymer microspheres was about 219 μm . The two types of MIEXs were prepared, magnetic cation-exchange resins (MCEXs) and magnetic anion-exchange resins (MAEXs). MCEX was prepared by sul-

fonation of magnetic polymer microspheres, and MAEX was made by a quaternization reaction with triethylamine of chloromethylated magnetic polymer microspheres. With diffuse-reflectance Fourier transform infrared spectroscopy, elemental analysis, and acid–base titration, the degree of substitution and ion-exchange capacity of the MIEXs were assessed. The efficiency of each MCEX and MAEX for the purification of contaminated water was examined with Co^{2+} and NO_3^- solutions, respectively. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2058–2067, 2003

Key words: magnetic polymers; polystyrene; ion exchangers; resins; microencapsulation

INTRODUCTION

Magnetic polymer microspheres are micrometer-size particles composed of a polymer and inorganic magnet materials such as Fe_3O_4 , Fe_2O_3 , nickel, and cobalt so that they exhibit the characteristics of both the polymer and the magnet.^{1–4} Magnetic polymer microspheres have been widely applied to biotechnology and medical science. Since the introduction of magnetic separation in the 1970s, much scientific and technical progress has been made in the methods of preparation and in practical applications. The usefulness and effectiveness of magnetic polymer microspheres have recently been extended to environmental technology to purify contaminated water, due to its relatively fast and easy separation and collection by magnetic control.^{5,6}

Magnetic polymer microspheres have generally been prepared by one-step processes, such as suspension and emulsion polymerization,^{7,8} or by two-step processes, such as electrostatic interaction⁹ and the chemical metal deposition of prepared polymer micro-

spheres.^{10–14} Because it is well known, suspension polymerization has been more suitable for massive production because of the smaller amounts of surfactants used.¹⁵

Recently, one of the most important applications of magnetic polymer microspheres in environmental technology has been for magnetic ion-exchange resins (MIEXs).⁶ The geometry of MIEXs depends on the method of preparation. Various studies have been performed to prepare MIEXs from magnetic polymer microspheres composed of a polymer core and a magnet shell.³ Also, a differently shaped MIEX can be prepared just after the random mixture and polymerization between a magnetic material and a monomer so that the polymer and magnet should randomly exist in both the inner and outer places.¹⁶

MIEXs with polymer shells and magnet cores are suitable structures for the removal of contaminants in the aqueous phases because the corrosion of magnets occurs when they are exposed to aqueous phases, which might continuously deteriorate the magnetic properties of the MIEX or cause secondary contamination during the process of water purification. Therefore, it is very important to incorporate the magnets into the resin without flushing them out and to preserve a sufficient thickness to attach chemical functional groups for the removal of ionic contaminants in aqueous solution.

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However, the problem of flushing out is inevitable as long as suspension polymerization is used, but it can be overcome through posttreatment. Some efforts have been made to remove the nonencapsulated and flushed out magnetites by methods such as the immersion of magnetic polymer microspheres into excess 1M HCl solution.¹⁷ This method, however, is time-consuming and is quite complicated for massive production. In addition, during the process, the magnetic polymer microspheres are able to induce the deterioration of the incorporated magnetite. Otherwise, pretreatment of the magnet is needed. One method that is used is to modify the surface of the magnetic materials with organic materials, resulting a well-dispersed ferrofluid in organic media. This produces a suitable morphology of magnetic polymer microspheres as analogous to the magnet core and polymer shell as possible.

To prepare magnetic latex particles, Yanase et al.¹ and Horton¹⁸ used ferrofluid colloids coated with a monolayer of oleic acid by strong chemisorption; it was then expected that the hydrophobic surface of the magnetite grafted by oleic acid would give rise to a decreasing flushing out of magnetite from the magnetic polymer microspheres during the suspension polymerization.

In this study, to prevent the magnetic particles from effectively incorporating into the MIEs and to safely improve their magnetic properties, oleic-acid-grafted magnetite was chosen because the effect of the grafting of oleic acid onto the surface could more favorably move the magnetite to the organic phase of styrene during suspension polymerization.¹⁹

The base material of the MIEs was polystyrene, which was crosslinked by divinylbenzene (DVB). In accordance with the type of chemical reaction on the polymer shell, the MIEs were classified into magnetic cation-exchange resins (MCEs) and magnetic anion-exchange resins (MAEs). With the advantages of oleic-acid-grafted magnetite over bare magnetite particles, MCEs and MAEs for the purification of contaminated water, which could be also utilized for some other activities, such as catalyst and enzyme activities, were prepared by conventional sulfonation and quaternization of amine reaction to magnetic polymer microspheres.^{20,21} MCEs and MAEs were characterized by diffuse-reflectance Fourier transform infrared (FTIR) spectroscopy and elemental analysis (EA). The ion-exchange capacity (IEC) was evaluated with acid-base titration, and the target removal capacity (TRC) was evaluated with Co^{2+} and NO_3^- to investigate the ion-exchange efficiency and contaminant-removal efficiency of the MCEs and MAEs.

EXPERIMENTAL

Materials

Magnetite (Fe_3O_4 , Aldrich, Milwaukee, WI), the size of which was less than 5 μm and the saturated magne-

tization of which was 82 emu/g, was used as the magnetic material.²² The surface of as-received magnetite was modified to be hydrophobic by oleic acid (Aldrich). Styrene (Aldrich) was used as the basic monomer after it was purified of inhibitor by filtration through an inhibitor remover (Aldrich). Inhibitor-removed DVB (Aldrich), a well-known crosslinking agent, was used to improve the physical and chemical properties of the polymer microspheres. Azobisisobutyronitrile (AIBN; Aldrich) was used as a radical initiator for the suspension polymerization. Deionized (DI) water, in which poly(vinyl alcohol) (PVA; Aldrich) was dissolved, was the continuous media for the suspension polymerization.

Acetyl sulfate, which was prepared in our lab, and triethylamine, purchased from Aldrich, were used for the cation-exchange and anion-exchange reactions, respectively.

Preparation of the magnetic polymer microspheres

Grafting of oleic acid onto the surface of magnetite

Magnetite (20 g) was soaked with oleic acid (260 mL) in distilled (DI) water (500 mL), and the solution was shaken until all of the magnetite transferred to the oleic-acid phase. The oleic-acid-grafted magnetite aggregated and separated in the DI water after 10 min in the grafting reaction. The two-phase solutions composed of DI water and oleic acid, including the oleic-acid-grafted magnetite, were repeatedly washed with ethanol to remove the nonreacted oleic acid and were then vacuumed at 80°C.

Suspension polymerization

Styrene (4.26 wt %), DVB (0.54 wt %), and AIBN (0.09 wt %) were mixed and decanted into a three-necked flask, in which the as-received magnetite or the oleic-acid-grafted magnetite (0.48 wt %) was contained. The mixture was stirred for 1 h at room temperature under a N_2 atmosphere. DI water (94.54 wt %), in which PVA (0.09 wt %) was dissolved, was carefully added into the reactor with continuous stirring. The suspension polymerization for the magnetic polymer microspheres was performed for 16 h at 70°C under a N_2 atmosphere. After the suspension polymerization was complete, the product was washed with excess DI water and sieved with a 60 μm strainer to remove the remaining PVA and nonencapsulated magnetite. Pure product was obtained by drying under a vacuum at 60°C.

Preparation of the MIEs

Sulfonation for the MCEs. The dried magnetic polymer microspheres (20 g) were swollen with dichloro-

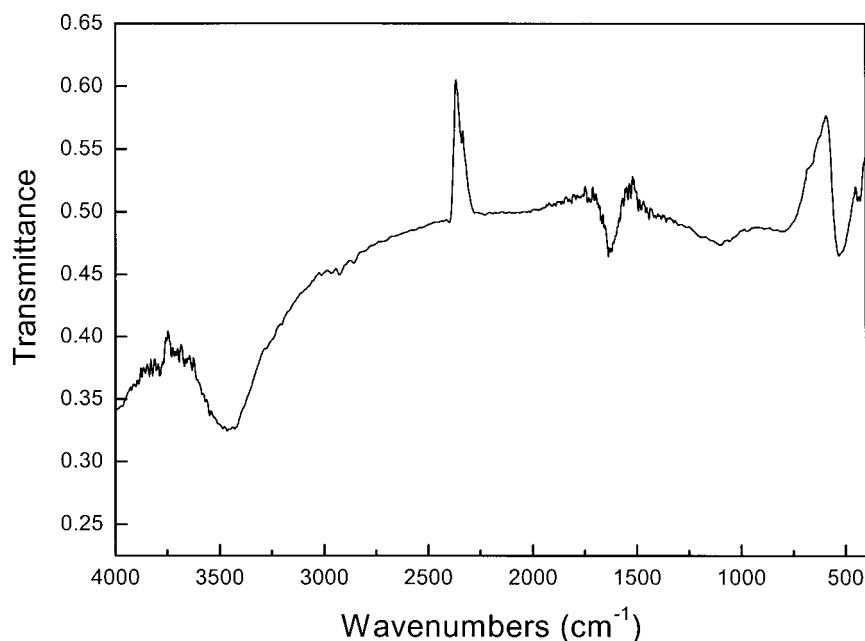


Figure 1 Diffuse IR spectrum of the oleic-acid-grafted magnetite.

ethane (150 mL) for 2 h at room temperature under a N_2 atmosphere. The reaction for attaching sulfonyl groups to the magnetic polymer microspheres was run for 2 h at $30^\circ C$ by the addition of acetyl sulfate (36 g) synthesized with acetic anhydride and sulfonic acid at $-10^\circ C$. The sulfonation reaction was terminated with 2-propanol (10 mL).

Quaternization with trimethylamine for the MAEXs. The magnetic polymer microspheres were chloromethylated to introduce a quaternary ammonium moiety into the benzene ring of polystyrene. The dried magnetic polymer microspheres (20 g) were swollen in *n*-hexane (200 mL) for 2 h at room temperature. The reaction for attaching chloromethyl moieties to the magnetic polymer microspheres was carried out for 16 h at room temperature with chloromethylethylether and boron trifluoride diethyl etherate as a substitute and a catalyst, respectively. The chloromethylated magnetic polymer microspheres were collected by washing with anhydrous acetone and dried under a vacuum at $60^\circ C$.

The quaternization reaction of the magnetic polymer microspheres was a typical nucleophilic substitution reaction between benzyl chloride and the triethylamine moieties. The chloromethylated magnetic polymer microspheres (20 g) were swollen in dimethylformamide (200 mL) for 2 h at room temperature under a N_2 atmosphere. Triethylamine (41.8 mL) and hydroquinone (0.1 g) were added to the reaction mixture, and then, the quaternization reaction proceeded for 16 h at room temperature under a N_2 atmosphere. The final product was consecutively washed with DI water, methanol, and a 1M NaCl solution and was consequently purified from the uninvolved materials.

Characterization

The grafting of oleic acid onto magnetite was confirmed through diffuse-reflectance FTIR spectroscopy (FTIR-8300, Shimadzu Co., Tokyo, Japan). The *specific retention mass* (SRM) of styrene, defined as the ratio of the remaining styrene in magnetite to 1 g of magnetite, was evaluated. The SRM of styrene of the as-received and oleic-acid-grafted magnetite were determined by the measurement of the amount of unadsorbed styrene after styrene was adsorbed into each magnetite, instead of quantifying the adsorbed styrene: 50 g of styrene was mixed with each 2 g of as-received or oleic-acid-grafted magnetite in a separation funnel for 1 h. Each magnetite was separated with a strong magnet from the mixture by the release of unadsorbed styrene. By weighing the released styrene, we indirectly determined the SRM. We assumed here that the mass of oleic acid grafted onto the surface of the magnetite was low enough to be negligible when the magnetite was weighed.

The shape and size of the MIEXs were observed with scanning electron microscopy (SEM; S-2500C, Noran Instruments, Inc., Madison, WI) and a particle size analyzer (Mastersizer, Malvern Instruments, Ltd., Worcestershire, United Kingdom). The magnetic properties of the MIEXs were determined with vibrating-sample magnetometry (VSM; VSM-5-15, Toei Kogyo Co., Ltd., Tokyo, Japan). Whether or not the functional group for ion exchange was successfully incorporated onto the magnetic polymer microspheres was confirmed with EA and diffuse IR spectrometry.

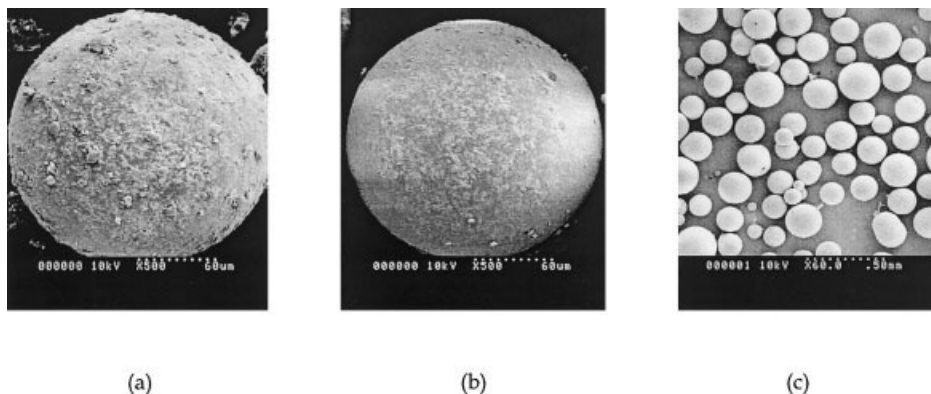


Figure 2 SEM micrographs of magnetic polymer microspheres prepared with (a) as-received and (b,c) oleic-acid-grafted magnetite.

IEC was evaluated through acid–base titration with 0.1N NaOH and 0.1N HCl solutions. MIEX (2 g as dry weight) was added into 50 mL of 0.1N NaOH solution, and then, the mixture was stirred for 2 h at room temperature. After separating the MIEX from the solution under a strong magnetic force, the amount of OH⁻ not exchanged but remaining in the solution was titrated with a 0.1N HCl solution.

The TRC for the metal cations and nitrate anions was evaluated by detection of the ion concentration with ultraviolet–visible (UV–vis) light spectrometry (UV–vis spectrometer 8453, Agilent/HP Foster City, CA). A cobalt (II) chloride hydrate (CoCl₂ · 6H₂O; 0.1M) solution and 1 or 2 g of MCEX were mixed for 30 min at pH 7. The amount of the nonexchanged Co²⁺ in the filtered-out solution was determined after calibration of the concentration, depending on the intensity of UV–vis absorbance. Ten milliliters of a 0.1M

KNO₃ solution was mixed with 1 or 2 g of MAEX for 30 min at pH 7. The TRC of MAEX for NO₃⁻ was obtained by analysis of the amount of remaining NO₃⁻.

RESULTS AND DISCUSSION

The diffuse-reflectance FTIR spectrum of oleic-acid-grafted magnetite after the removal of unreacted oleic acid is shown in Figure 1. It is well known that the free carboxylic acid group of oleic acid shows a stretching IR band at 1710 cm⁻¹, whereas the IR band of the bound carboxyl group on the magnetite appears at a lower frequency and broadens. Thus, the IR band of the chemisorbed carboxylate group appeared at 1630 cm⁻¹, due to antisymmetric stretching of the grafted oleic acid, and the broad stretching near 3500–3300 cm⁻¹ was mainly due to absorbed water and hydroxyl groups on the magnetite.^{23–25} The as-received magnetite did not disperse but aggregated and precipitated in

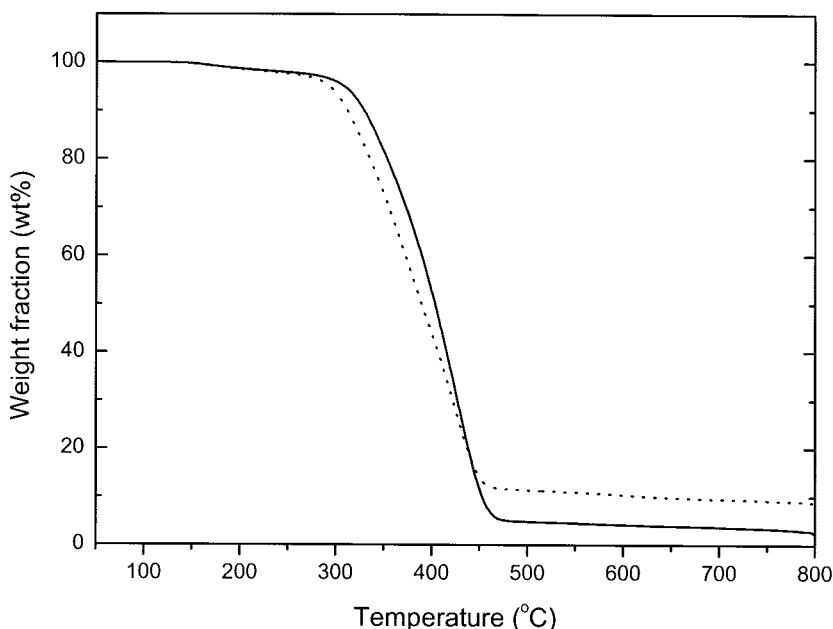


Figure 3 TGA of magnetic polymer microspheres prepared with (—) as-received and (- - -) oleic-acid grafted magnetite.

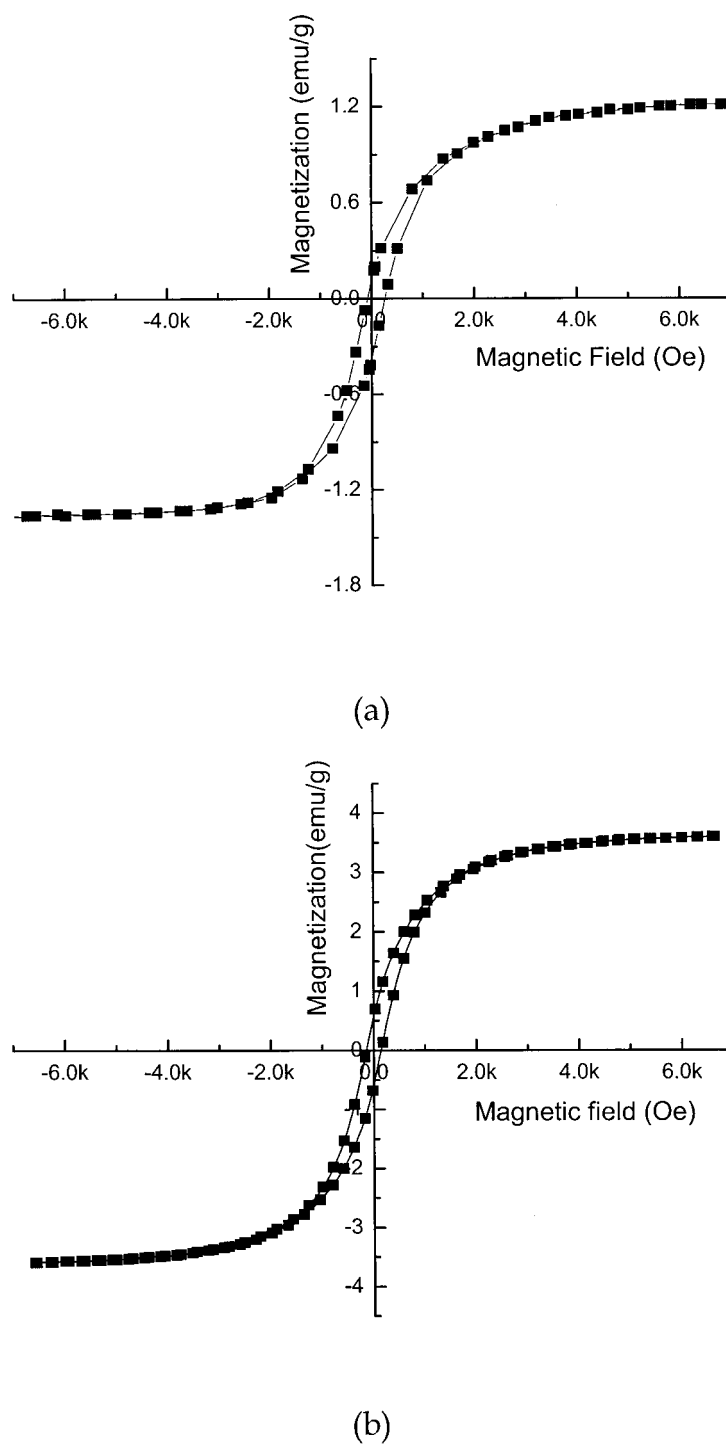
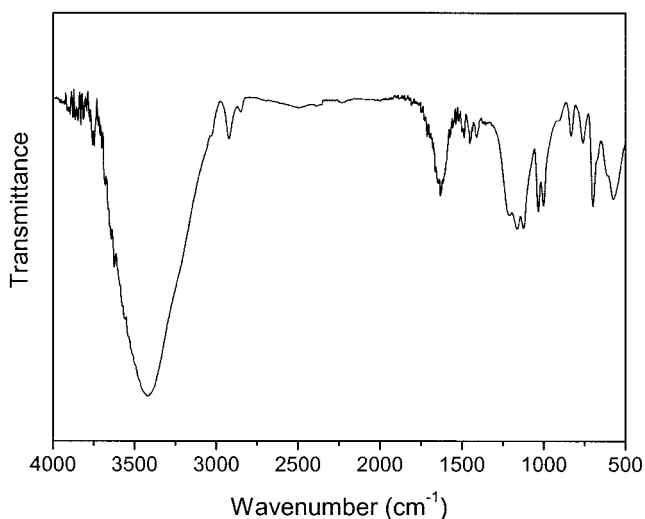


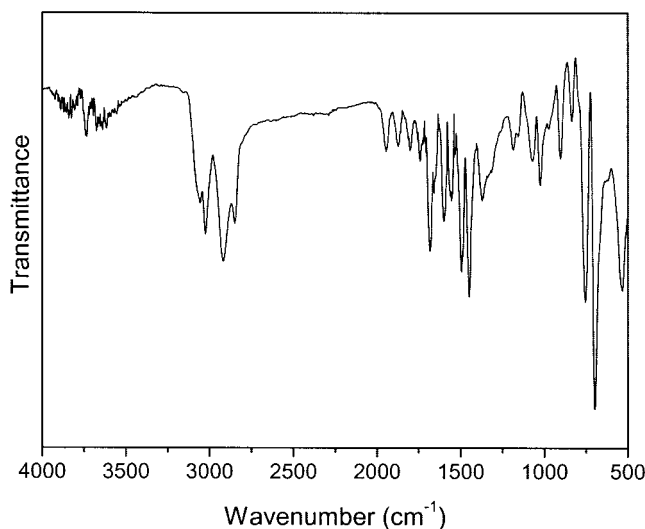
Figure 4 Magnetic hysteresis loops of magnetic polymer microspheres prepared with (a) as-received and (b) oleic-acid-grafted magnetite.

homogeneous organic or inorganic solvent, whereas oleic-acid-grafted magnetite dispersed well in toluene and styrene. To compare how those magnetites accommodated organic monomers such as styrene, the SRM was measured. The SRM of styrene by oleic-acid-grafted magnetite (20 g of styrene/1 g of magnetite) was approximately two times as large as that of as-received magnetite (9.9 g of

styrene/1 g of magnetite). Although the measurement of SRM gave more or less inaccurate results, the oleic acid acted as an interfacial adhesive between magnetite and styrene because the chemisorption between oleic acid and magnetite and the physisorption between oleic acid and styrene were expected, as in hexadecane and cyclohexane.¹⁹



(a)



(b)

Figure 5 Diffuse IR spectra of MIEXs: (a) MCEX and (b) MAEX.

The prepared magnetic polymer microspheres, including as-received magnetite and oleic-acid-grafted magnetite, are shown in Figure 2. The latter [Fig. 2(b)]

had a lower amount of magnetite flushed out from the surface of the polymer than the former [Fig. 2(a)]. This result indicated that the grafting of oleic acid onto the surface of magnetite played an effective role in preventing the oleic-acid-grafted magnetite from flushing out from the organic monomers, styrene and DVB, during the suspension polymerization under severe agitation conditions. Figure 2(c) illustrates the diameter of bead-like microspheres ranging between 100 and 300 μm . The average diameter of the magnetic polymer microspheres was 219 μm , and the average specific surface area was 0.0285 m^2/g .

The amount of magnetite contained in the magnetic polymer microspheres was evaluated by thermogravimetric analysis (TGA). As shown in Figure 3, the magnetic microspheres made by as-received magnetite were completely decomposed at over 450°C and left about 3.0 wt % magnetite. The microspheres made by the oleic-acid-grafted magnetite had a similar decomposition temperature, and the residual weight loss over 600°C was about 9.0 wt %. Thus, the amount of magnetite contained in the magnetic polymer microspheres for the oleic-acid-grafted magnetite was about three times higher than that for as-received magnetite.

To compare two types of microspheres made with as-received magnetite and with oleic-acid-grafted magnetite, the magnetic properties were measured. As shown in Figure 4, the average magnetization of the magnetic polymer microspheres made with the oleic-acid-grafted magnetite (3.6 emu/g) was approximately three times as large as that of the magnetic polymer microspheres made with the untreated magnetite (1.21 emu/g), although the preparation compositions of compounds were identical in the suspension polymerization. The oleic-acid-grafted magnetite was more likely to be surrounded by organic monomers than the as-received magnetite and to be located further inside the styrene droplet during the polymerization. This result was also proven by TGA analysis and SEM photography.

The average density of the magnetic microspheres prepared with the oleic-acid-grafted magnetite with VSM results was calculated as follows. The average saturated magnetization was 82 emu/g, and the average magnetization of the magnetic polymer micro-

TABLE I
Elemental Analysis of MCEX and MAEX

Sample	Atomic classification (wt %) ^a					Composition in segment units	
	C	H	N	Cl	S	<i>x</i>	<i>y</i>
MCEX	63.7	6.5	—	—	8.5	3.98	—
MAEX	90.1	7.7	0.4	1.8	—	0.244	0.353

^a We calculated organic elements only in MIEXs, and the weight of magnetite was subtracted from the total weight of the resin.

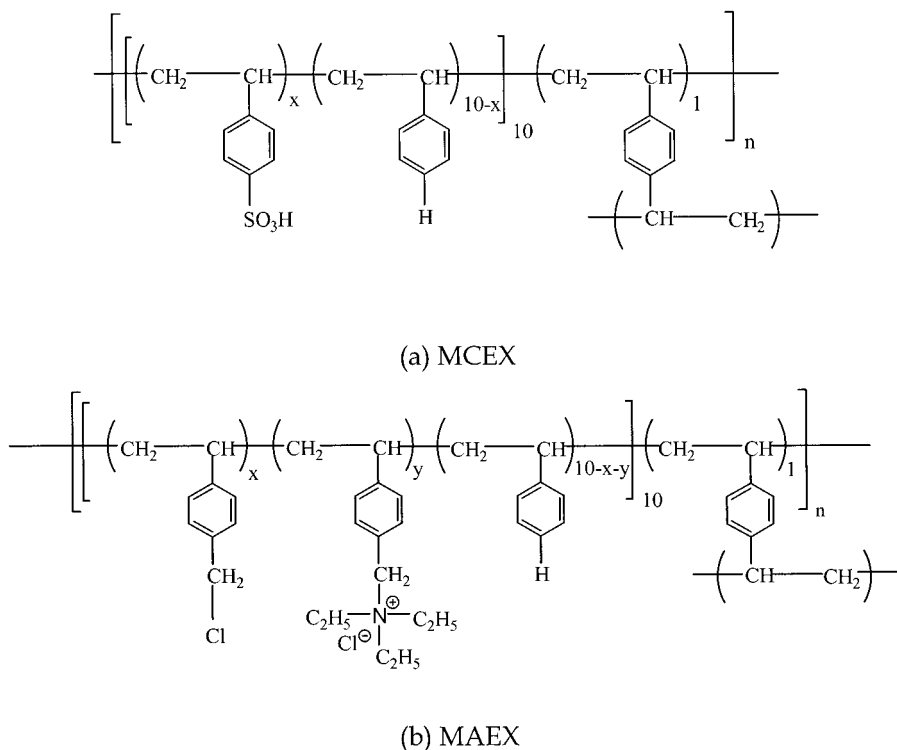


Figure 6 Segment unit models of (a) MCEX and (b) MAEX.

spheres made with the oleic-acid-grafted magnetite was 3.6 emu/g. Thus, the weight fraction of magnetite in a microsphere on average was 4.4 wt %. With these results, the density of the microspheres was derived from the following equation:

$$\frac{1}{\rho} = \frac{0.956}{\rho_S} + \frac{0.044}{\rho_M} \quad (1)$$

where ρ is the density of the magnetic polymer microsphere, ρ_S (1.05 g/cm³) is the density of styrene (density of DVB \approx density of styrene), and ρ_M (5.2 g/cm³) is the density of magnetite.²²

According to the equation, the density of the magnetic polymer microspheres was 1.088 g/cm³. Therefore, the prepared MIEXs made with oleic-acid-grafted magnetite preserved better magnetic properties and simultaneously flushed out less magnetite than those made with as-received magnetite. In other words, the process of preparing MIEXs would be massively more economical and environmentally friendly in the industrial fields if oleic-acid-grafted magnetite is applied instead of unmodified magnetite. As a microsphere accommodates a much higher quantity of magnetite, the magnetic separation process also becomes economical because a lower magnetic force is needed for collection.

Diffuse-reflectance FTIR spectroscopy and EA were performed to measure the degree of the sulfonation, chloromethylation, or quaternization of the magnetic

microspheres. The attached sulfonyl groups of the MCEX were identified with the strong stretching band of S=O in the range 1300–1000 cm⁻¹, whereas the broad stretching band near 3500–3300 cm⁻¹ resulted from the O—H of absorbed water into the MCEX. The chloromethylation reaction of magnetic polymer microspheres was proven by the strong absorption band of C—Cl groups at 750 cm⁻¹, and the quaternization of chloromethylated magnetic polymer microspheres was confirmed by the medium stretching band at 1080 and 1020 cm⁻¹ derived from the absorption of C—N in the quaternary ammonium moieties of MAEXs, as shown in Figure 5(b).

The EA of MCEXs and MAEXs and the number of substituted sulfonyl groups and quaternary ammonium groups theoretically calculated with the following segment unit model are summarized in Table I. As shown in Figure 6, it was assumed that every 11th monomer unit was a crosslinking point, and all 10 of the segment units were, on average, regarded as a new repeating unit because 9 mol % of DVB in total monomers (styrene and DVB) were assumed to be fully reacted in the suspension polymerization. In addition, the segment unit models for the MCEXs and MAEXs were postulated to have neither substitution reaction in DVB nor substitution gradient from outer shell to inside in MIEX.

Thus, the repeating units of the polystyrene backbone for MCEX were composed of 1 mol unit of crosslinker (DVB), x mol of sulfonyl group, and $10 - x$

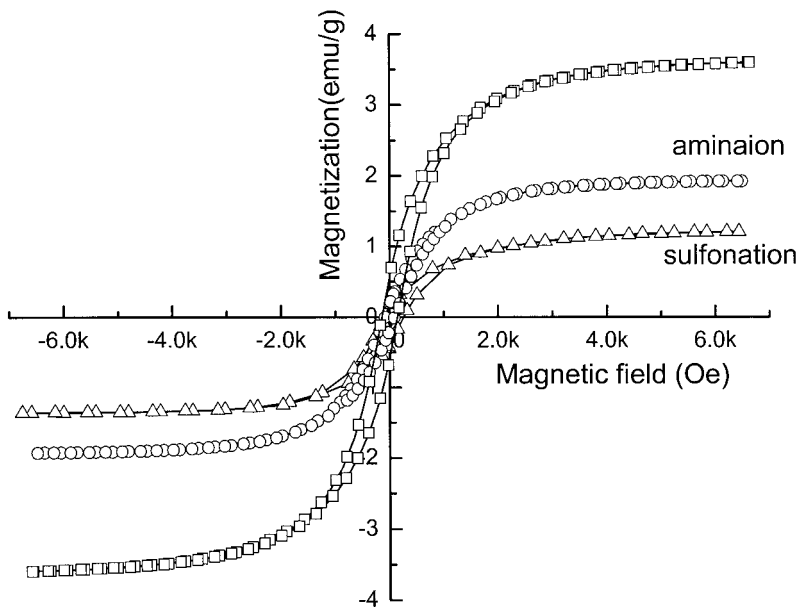


Figure 7 Magnetic hysteresis loops of (□) magnetic polymer microspheres, (Δ) MCEX, and (○) MAEX.

mol of unreacted styrene for MCEX among 10 benzene rings. On the basis of EA, eq. (2) was set as follows. The total weight of a segment unit is given by

$$[(12 \times 8) \times 10]_C + [9 \times 10]_H + [32.07 \times x]_S + [(16.0 \times 3) \times x]_O + [(12 \times 10)_C + 10_{H}]_{DVB} \quad (2)$$

where the subscripts C, H, S, O, and DVB stand for constitutional components, that is, carbon, hydrogen, sulfur, oxygen, and DVB, respectively.

The sulfonated segments are given by

8.5 (wt %)

$$= \frac{32.07x}{[(12 \times 8) \times 10]_C + [9 \times 10]_H + [32.07 \times x]_S + [(16.0 \times 3) \times x]_O + [130]_{DVB}} \quad (3)$$

By the evaluation of the x value from the segment unit model on the basis of the composition of MCEX, sulfonyl groups were attached at an average of about 4 per each 10-segment unit.

TABLE II
Comparison of IEC by EA, Titration, and TRC by UV-vis Spectroscopy

Sample	Capacity (mequi-mol/g)		
	IEC ^E	IEC ^T	TRC ^U
MCEX	2.66	2.25	0.49
MAEX	0.26	0.21	0.18

IEC^E = ion exchange capacity evaluated by EA based on segment unit model; IEC^T = ion exchange capacity evaluated by acid-base titration; TRC^U = target removal capacity evaluated by UV-vis spectroscopy.

The chloromethylation degree of the polystyrene microspheres was similarly evaluated from the amount of chloride and nitrogen in the EA results. If we assumed that only quaternized amines exist, the MAEX consisted of four kinds of repeating units, which were chloromethylated styrene (x), aminated benzyl (y), unreacted styrene ($10 - x - y$), and 1 mol unit of DVB. Thus, total weight fraction of a repeating unit in MAEX is given by

$$[x(12 \times 9) + y(12 \times 15) + (10 - x - y)12 \times 8]_C + [9x + 24y + (10 - x - y) \times 8]_H + [35.45x + 35.45y]_{Cl} + [14y]_N + [130]_{DVB} \approx 48x + 149y + 1170 \quad (4)$$

where the subscripts C, H, Cl, N, and DVB denote the constitution of carbon, hydrogen, chloride, nitrogen, and DVB, respectively.

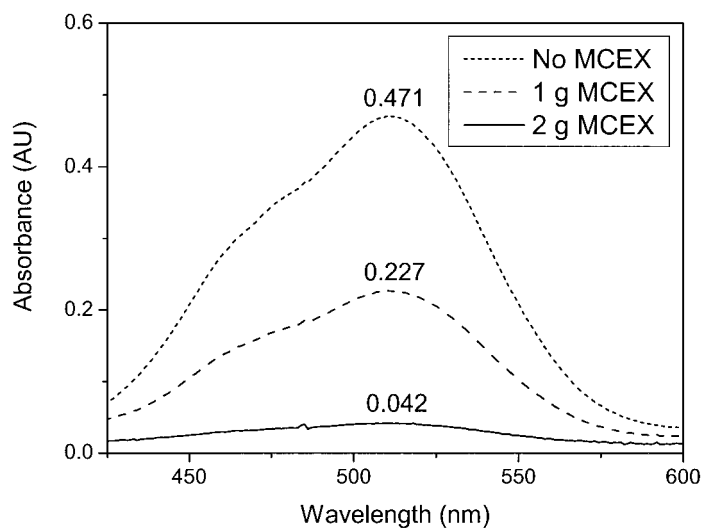
The weight fraction of chloride is given by

$$1.8 \text{ (wt \%)} = \frac{35.45x + 35.45y}{48x + 149y + 1170} \quad (5)$$

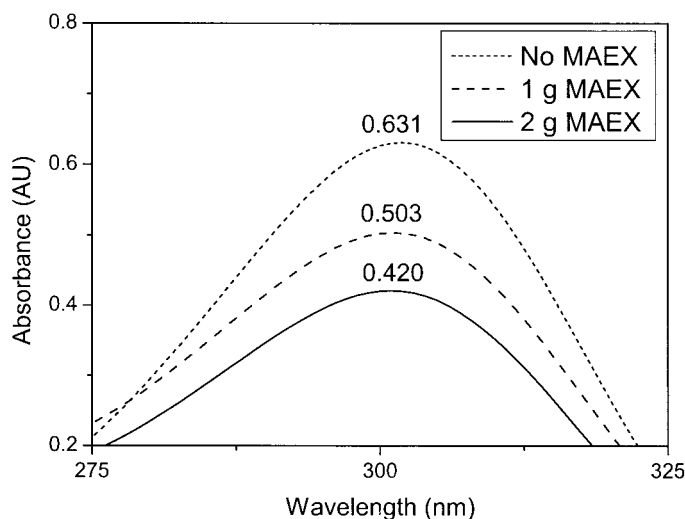
and weight fraction of nitrogen is also given by

$$0.4 \text{ (wt \%)} = \frac{14y}{48x + 149y + 1170} \quad (6)$$

From these two equations, the value of x and y were obtained as 0.244 and 0.353, respectively. Consequently, the summation of the x and y values was recognized the number of attached chloromethylene groups. The molar ratio of chloromethylated styrene to the initial styrene was 0.6, the value of which was



(a)



(b)

Figure 8 UV-vis spectra for the evaluation of the TRC of (a) MCEX and (b) MAEX.

lower than the reported one.²⁰ Hence, it was estimated that quaternary ammonium groups were incorporated into the magnetic polymer microspheres at 3 per each 10-segment unit.

The deviation is still under investigation; however, it seems that any side reaction was one between chloromethylethylether or boron trifluoride diethyletherate and magnetite rather than a reaction with the polymer resin during the chloromethylation reaction. In addition, during sulfonation for the preparation of MCEXs, the magnetite was deteriorated by strong sulfonic acid. As shown in Figure 7, the magnetizations of MCEX and MAEX were much lower than those of the unreacted magnetic microspheres. The saturated

magnetization of MCEX was three times lower, and that of MAEX was about two times lower than that of the unreacted magnetic microspheres after sulfonation and amination, respectively.

The IEC of MCEX obtained by acid-base titration was 2.25 mequiv mol/g, which was approximately 85% of the IEC calculated from the results of EA and the segment unit model, as shown in Table II. The pink color of the 0.1M Co^{2+} aqueous solution was visibly faded in 10 min by 1 g of MCEX and was diminished further by 2 g, as Co^{2+} ions were removed from aqueous solution through capture by the sulfonyl groups of the MCEX.

As shown in Figure 8, the intensity of UV-vis

absorbance at 510 nm proportionally decreased as the concentration of Co^{2+} was decreased after removal by MCEX. The average TRC for Co^{2+} ions was 0.49 mequiv mol/g, according to the calibration of the intensity of UV-vis absorbance at 510 nm. The difference between the TRC of MCEX for Co^{2+} ions determined by UV-vis spectroscopy and the IEC of MCEX determined by acid-base titration was due to the selectivity and the chelation efficiency, depending on the size of the ions, charge valence, and water conditions such as pH. The efficiency of the TRC for various hazard ions such as Mn^{2+} , Cd^{2+} , and Pb^{2+} and different charged metal ions such as Li^+ , Na^+ , Ca^{2+} , and Al^{3+} for different pH conditions will be published elsewhere.

The IEC of the MAEX, as obtained by acid-base titration, was 0.21 mequiv mol/g, which was approximately 96% of the IEC calculated from the results of EA and the segment unit model, as shown in Table II, whereas the average TRC of the MAEX for NO_2^- ions determined by UV-vis spectroscopy at 300 nm was 0.18 mequiv mol/g. The difference between the IEC of MAEX determined by acid-base titration and the TRC of MAEX may have been due to the differently sized ions and the pH.

CONCLUSIONS

MIEXS, divided into cation and anion categories, were prepared from magnetic polymer microspheres obtained by the incorporation of oleic-acid-grafted magnetite. The oleic acid was grafted onto the surface of commercial magnetite, which was confirmed by diffuse IR analysis. The magnetic polymer microspheres made with oleic-acid-grafted magnetite had clean surfaces without the flushing-out phenomenon of magnetite. The average magnetization of the magnetic polymer microspheres made with oleic-acid-grafted magnetite was three times as large as that of the magnetic polymer microspheres made with untreated magnetite.

On the basis of EA and the segment unit model, the sulfonyl moieties of MCEX were attached at approximately 4 per each segment, the quaternary ammonium moieties of MAEX were attached at 3 per each 10 segments, and the efficiencies of the IECs of MCEX

and MAEX were 85 and 96%, respectively. The TRC of MCEX for Co^{2+} was determined as one-fourth that of the ICE because of the influences of the size and valence of the target ion. MAEX, however, showed little difference between ICE and TRC, which was caused by the size of the target ion.

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References

1. Yanase, N.; Noguchi, H.; Asakura, H.; Suzuta, T. *J Appl Polym Sci* 1973, 50, 765.
2. Müller-Schulte, D.; Brunner, H. *J Chromatogr A* 1995, 711, 53.
3. Wang, Y.; Feng, L.; Pan, C. *J Appl Polym Sci* 1998, 70, 2307.
4. Lubbok, F. J.; Mok, C. C. K.; Eldridge, R. J. U.S. Pat. 4,447,475 (1984).
5. Bergemann, C.; Müller-Schulte, D.; Oster, J.; à Brassard, L.; Lübke, A. S. *J Magn Magn Mater* 1999, 194, 45.
6. Bursill, D. *Water Sci Technol Water Suppl* 2001, 1, 1.
7. Ballard, M. J.; Eldridge, R. J.; Bates, J. S. U.S. Pat. 5,900,146 (1999).
8. Bradbury, D.; Elder, G. R.; Hendawi, A. T. S. A. U.S. Pat. 5,855,790 (1999).
9. Sauzedde, F.; Elaïssari, A.; Pichot, C. *Colloid Polym Sci* 1999, 277, 846.
10. Tokuoka, K.; Senna, M.; Kuno, H. *J Mater Sci* 1986, 21, 493.
11. Mastro, T.; Senna, M. *Colloid Polym Sci* 1990, 25, 987.
12. Lee, J.; Senna, M. *Colloid Polym Sci* 1995, 273, 76.
13. Warshawsky, A.; Upson, D. A. *J Polym Sci Part A: Polym Chem* 1989, 27, 2995.
14. Warshawsky, A.; Upson, D. A.; Ferrar, W. T.; Monnier, J. R. *J Polym Sci Part A: Polym Chem* 1989, 27, 3015.
15. Kawaguchi, H. *Prog Polym Sci* 2000, 25, 1171.
16. Kim, Y. K.; Lee, K. J. *J Nucl Sci Technol* 2001, 38, 785.
17. Ding, X.; Li, W.; Zheng, Z.; Zhang, W.; Deng, J.; Peng, Y. *J Appl Polym Sci* 2001, 79, 1847.
18. Horton, R. L. U.S. Pat. 4,661,327 (1987).
19. Tadmor, R.; Rosensweig, R. E.; Frey, J.; Klein, J. *Langmuir* 2000, 16, 9117.
20. Sparrow, J. T. *Tetrahedron Lett* 1975, 52, 4637.
21. Kobayashi, T.; Nagai, T.; Ono, M.; Wang, H. Y.; Fujii, N. *Eur Polym J* 1997, 33, 1191.
22. Cornell, R. M.; Schwertmann, U. *The Ion Oxides*; VCH: New York, 1996.
23. Lensnikovich, A. E.; Shunkevich, T. M.; Naumenko, V. N.; Vorobyova, S. A.; Baykov, M. W. *J Magn Magn Mater* 1990, 85, 14.
24. van Ewijk, G. A.; Vroege, G. J.; Philipse, A. P. *J Magn Magn Mater* 1999, 201, 31.
25. Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Instruction to Spectroscopy*, 3rd ed.; Harcourt: Orlando, FL, 2001; Chapter 2.