

Preparation of Poly(1-vinylimidazole)-Grafted Magnetic Nanoparticles and Their Application for Removal of Metal Ions

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Received April 21, 2003. Revised Manuscript Received December 9, 2003

Poly(1-vinylimidazole) with a trimethoxysilyl terminal group (Im_n) was synthesized by telomerization of 1-vinylimidazole. The degree of polymerization (n) was determined by ^1H NMR to be 18. The Im_{18} with reactive silane terminal group was grafted directly onto nanosize magnetic particles (maghemite, $\gamma\text{-Fe}_2\text{O}_3$) through siloxane bonds to produce polymer-grafted magnetic nanocomposite particles (Mag-Im_{18}). The amount of polymer anchored on the particle was estimated by elemental analysis to be 5 wt %. The surface coverage of imidazolyl groups was estimated to be 0.44 mmol g^{-1} . A stable Mag-Im_{18} suspension was prepared, and the polymer coatings were chemically stable over a pH range of 3.5–10.0. The Mag-Im_{18} showed a selective binding of divalent metal ions with a binding strength in the order of $\text{Cu}^{2+} \gg \text{Ni}^{2+} > \text{Co}^{2+}$. At pH 5.3, the limiting adsorption capacity for Cu^{2+} ion was 0.11 mmol g^{-1} . Selective separation/recovery of Cu^{2+} ions from a $\text{Cu}^{2+}/\text{Co}^{2+}$ aqueous solution was demonstrated over a pH range of 3–7.

Introduction

Nanosize magnetic iron oxide particles have been studied extensively due to their wide range of applications in ferrofluids,¹ high-density information storage,^{2,3} magnetic resonance imaging (MRI),⁴ biological cell labeling and sorting,⁵ separation of biochemicals, targeting, and drug delivery.⁶ For many of these applications, surface modification of nanosize magnetic particles is a key challenge. In general, surface modification can be accomplished by physical/chemical adsorption or surface coating of desired molecules, depending on the specific applications. A silica coating⁷ on the surface of nanosize iron oxide particles, for example, could help

prevent their aggregation in liquids and improve their chemical stability. Surface modification of magnetic particles by organic compounds can be achieved via four major avenues: organic vapor condensation, polymer coating, surfactant adsorption, and direct silanation of silane-coupling agents. A number of synthetic polymers such as poly(ethylene glycol),^{8,9} poly(acrylamide),¹⁰ and poly(*N*-isopropylacrylamide),¹¹ as well as naturally occurring polymers such as dextran^{12, 13} and chitosan,¹⁴ were used for modifying the surface properties of magnetic particles to achieve desirable surface functionalities. These polymers physisorbed by electrostatic attraction, osmotic depletion, or hydrogen-bonding forces on particles showed limited stability, since they were not covalently bonded with particle surfaces. Direct silanation of magnetic particles using a silane-coupling agent is attractive for improving stability and control of surface properties. Use of 3-aminopropyltriethoxysilane (APTES) is a typical example of obtaining cationic amine groups on nanosize magnetic particles.¹⁵ The

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graft of APTES on the magnetic particles caused a drastic change in the electrokinetics of the particles in an aqueous solution. The isoelectric point (IEP) of maghemite particles shifted from pH 4.5 to 9.0 by silanation of APTES. The drastic shift in IEP suggests that the amine groups of APTES on the magnetite particles are mostly exposed to the aqueous environment with the silane groups anchored on the particle surfaces.

Grafting of silane-terminated polymers on silica via chemical siloxane bonds has been reported in a number of studies.^{16,17,18–23} In our group, a number of polymers with trimethoxysilyl terminal groups were synthesized using the telomerization method. The synthesized polymers such as poly(octadecylacrylate),¹⁸ poly(styrene),¹⁹ poly(acrylonitrile),²⁰ and poly(methylacrylate)²¹ were used in developing polymer–silica hybrid materials. These polymers were immobilized on porous silica particles through siloxane covalent bonds. The polymer-grafted silica particles exhibited a satisfactory affinity for specific separation in high-performance liquid chromatography (HPLC). Poly(octadecylacrylate)-grafted silica (Sil-ODA_n), for example, showed a much better selectivity for structural isomers of polycyclic aromatic hydrocarbons through a highly ordered structure of side chains.²² The selectivity for polycyclic aromatic hydrocarbons was found to be enhanced by increasing the degree of polymerization of polymers on silica surface (polymer effect).²³

It is known that the polymer with terminal reactive groups can be grafted onto a surface of inorganic materials, and this grafting technique allows applications of the hybrid materials to many important fields. As aforementioned, the nanosize magnetic particles have been attracting attention in separation science and technology because they could be readily collected/moved from a complex multiphase system by an external magnetic field. Magnetic property of carriers has been exploited in the fields of drug delivery, labeling of cells, and separation of biomolecules. As the size of magnetic particles decreases to the nanometer scale, they become superparamagnetic, with a negligible residual magnetization in the absence of an external magnetic field. For this reason, the use of nanosize magnetic particles not only provides sufficient surface area desirable for end users but also maximizes dispersion of the particles due to minimized magnetic flocculation in the absence of an external magnetic field. Grafting the desired polymers on nanosize magnetic particles would result in new applications of magnetic

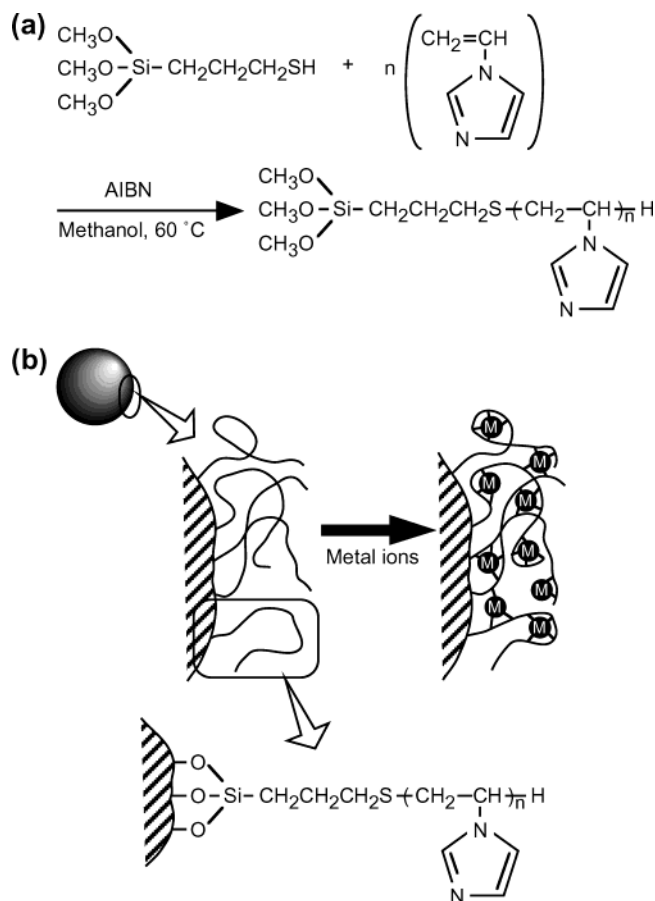


Figure 1. Synthesis of poly(1-vinylimidazole) (a) and schematic illustration of polymer-grafted magnetic particles (b).

carriers in a wide range of disciplines. In this paper, we report on the preparation and characterization of polymer-grafted nanosize magnetic particles as an organic–inorganic hybrid material.

Poly(1-vinylimidazole) is chosen to graft on nanosize magnetic particles, as the resultant organic–inorganic hybrid magnetic materials are anticipated to expand the sorbent-based separation technology to a multiphase complex system, ranging from biological cell sorting to industrial effluent detoxification and recovery of valuables. We are interested in poly(1-vinylimidazole), as it is known to form complexes with such metal ions as Cu(II),²⁴ Zn(II),²⁵ Cd(II),²⁶ Ag(I),²⁷ and Hg(II).²⁸ The preferred coordination number (N) has been found to be 2 for Ag(I), 4 for Cu(II) and Zn(II), and 6 for Cd(II). In this study, a newly synthesized poly(1-vinylimidazole) with trimethoxysilyl terminal groups is chemically anchored (grafted) on nanosize maghemite particles that are to be used for the removal and recovery of heavy metals from industrial effluents. Figure 1 shows schematically the preparation procedure and the resulting configuration of grafted polymers (thick lines) with bond metals (M). Compared with the polymer-coating method, the polymer-grafting (direct silanation) method offers a number of distinct advantages. First, particle size

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shows little effect on polymer immobilization. Polymer chains immobilized on magnetic particles would remain flexible. Polymer-grafted magnetic particles can be used in good solvents of the polymer. Finally, the method is applicable to many kinds of polymers.

Experimental Section

Materials. Commercial 1-vinylimidazole (Tokyo Kasei, Japan) was distilled and the fraction boiling at 83 °C (7 mmHg) was used as starting material for polymerization. Used as a telogen, 3-mercaptopropyltrimethoxysilane (MPS) was purchased from Azmax Co. Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol and was used as an initiator. Nanosize maghemite (γ -Fe₂O₃) particles having an average diameter of 28 nm were purchased from Alfa Aesar. The surface area of the particles was determined by the BET method to be 40 m² g⁻¹.

Preparation of Poly(1-vinylimidazole). Telomerization of poly(1-vinylimidazole), Im_{*n*}, where *n* is the average degree of polymerization, was accomplished by dissolving 1-vinylimidazole (2.72 mL, 30 mmol) and MPS (0.3 mL, 1.5 mmol) in distilled methanol (30 mL), followed by the addition of 2 wt % AIBN (56.4 mg, 0.33 mmol). The solution was stirred at the reflux temperature for 48 h in an N₂ gas atmosphere. After completion of reaction, the solution was concentrated in vacuo. White precipitates were formed upon the addition of diethyl ether to the residue solution at -20 °C. The precipitates were filtrated and washed thoroughly with diethyl ether and dried in vacuo. The average degree of polymerization (*n*) was determined by ¹H NMR spectroscopy. In methanol-*d*₄, the integral values of peaks around δ = 6.78–7.46 ppm (three protons of imidazolyl ring) and δ = 0.60 ppm (two protons of SiCH₃) were used to calculate the degree of polymerization.

Silanation. The synthesized Im_{*n*} was silanized onto nanosize magnetic particles in toluene/methanol (80:20 volume ratio) solution at the reflux temperature for 2 days. The silanized particles were washed repeatedly with organic solvents and collected by centrifugation (Allegra 64R Centrifuge, Beckman Coulter). After washing, the particles were dried in vacuo.

Characterization. The immobilization of poly(1-vinylimidazole) on the magnetic particles was characterized by surface sensitive diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) methods. Infrared spectra in the wave-number range of 4000–600 cm⁻¹ were obtained with an FTS 6000 spectrometer (Bio-Rad Laboratories). A sample of finely crushed KBr was used as the background. All spectra were obtained using 128 scans at a nominal resolution of 4.0 cm⁻¹ and presented without background correction. The binding stability of polymer on nanosize magnetic particles in acidic or basic solutions was evaluated by measuring the amount of immobilized polymer on the magnetic particles before and after their immersion in aqueous solutions for 1 h over a wide pH range. For this purpose, semiquantitative DRIFTS was used. Polymer detachment was evaluated by the absorbance ratio (*R*) of DRIFTS stretching vibrations bands of C=N from imidazolyl rings at 1496 cm⁻¹ and Fe–O–H from magnetic particles at 694 cm⁻¹. The *R* is defined as

$$R = (\text{Abs}_{1496}/\text{Abs}_{694})/(\text{Abs}(0)_{1496}/\text{Abs}(0)_{694}) \quad (1)$$

A absorbance ratio (*R*) of 1 indicates a robust binding of the polymer on the magnetic particles with negligible polymer desorption. A small *R* value is indicative of substantial detachment of the grafted polymer from the magnetic particles. The quantity of Im_{*n*} on the magnetic particles was determined by elemental analysis using a CHN CORDER MT-6 analyzer (Yanaco Analytical Instruments Co.).

Transmission electron microscopy (TEM) was used to confirm that the suspensions of polymer-grafted magnetic particles remained as nanosize dispersions. The TEM micrographs were recorded using a JEOL 2000FX transmission electron microscope. A drop of the prepared nanosize magnetic particle

suspensions (1000 ppm) was placed on carbon-coated copper grids and dried under ambient conditions.

Surface-sensitive electrokinetics, or more specifically the ζ -potential of particles, has been used as a powerful signature to characterize the degree of immobilizing ionic molecules on a particulate surface.¹⁵ The ζ -potential of nanosize magnetic particles with Im_{*n*} (Mag-Im_{*n*}) and without polymer (Mag) was measured in 1 mmol NaCl background electrolyte solutions using a Zetasizer 3000HSA (MALVERN Instruments Ltd.) Dilute suspensions of magnetic particles were prepared at a particular pH, which was adjusted by the addition of NaOH or HCl stock solutions. The ζ -potential of the suspension was measured. The results presented in this paper are the average of two independent measurements.

Magnetic properties of the maghemite particles before and after treatment were measured with a Quantum Design (San Diego, CA) 9T-PPMS dc magnetometer/ac susceptometer. The measurement was conducted at room temperature with a magnetization field strength from 9 to -9 T (the magnetic induction *B*) and frequency between 1000 and 5000 Hz.

The adsorption of selective ions on the prepared magnetic hybrid particles in an aqueous solution was measured to determine the loading capacity of heavy metals on the polymer-grafted magnetic particles. Copper, nickel, and cobalt ion solutions were prepared by dissolving CuSO₄·5H₂O, NiCl₂·6H₂O, and CoCl₂·6H₂O, respectively, in deionized water to a desired concentration. The prepared magnetic particles were dispersed in 10 mL of the prepared metal ion-containing aqueous solutions by ultrasonication. A contact time of 1 h was allowed at room temperature. The suspension was then centrifuged at 25 000 rpm (30 000*g*) for 30 min. The supernatant was collected and analyzed for metal ion concentration by atomic absorption spectroscopy (SpectraAA-110, Varian Inc.). The amount of metal ions loaded on magnetic particles was determined from the difference of the initial and equilibrium metal ion concentrations in solutions. The solution pH was adjusted by HCl and NaOH stock solutions. As a check of metal ion balance, a few measurements were performed to determine the amount of metal ions loaded on the particles. In this case, the metal-loaded particles were washed with a strong acid, and the metal ions washed off the particles were measured. The strong acid was used to ensure a complete detachment of the loaded metal ions into washing solutions. Within the experimental error, these two methods led to the same result, as anticipated. We chose the first method as it is simpler and less prone to errors incurred by incomplete washing.

Results and Discussion

Preparation of Polymer–Magnetic Nanoparticle Hybrids. Poly(1-vinylimidazole) with a terminal trimethoxysilyl group (Im_{*n*}) was prepared by telomerization of 1-vinylimidazole with 3-mercaptopropyltrimethoxysilane. The average degree of polymerization, *n*, is 18, as determined by ¹H NMR. The synthesized Im₁₈ was immobilized onto nanosize maghemite particles (γ -Fe₂O₃). Immobilization was accomplished through the reaction between the terminal trimethoxysilyl groups of Im₁₈ and the Fe–OH groups on the magnetic particles. The resulting magnetic particles were successively washed with alcohol and dried in vacuo. Figure 2 shows the DRIFTS spectra of maghemite particles before and after the immobilization of the Im₁₈. As shown in this figure, the spectral features of poly(1-vinylimidazole) (spectrum c) are observed on Im₁₈-immobilized maghemite particles (spectrum b) by the presence of vibration bands at 1496, 1416, and 1227 cm⁻¹, respectively. These bands are absent on the spectrum of untreated maghemite particles shown by spectrum a. These spectral features confirm the pres-

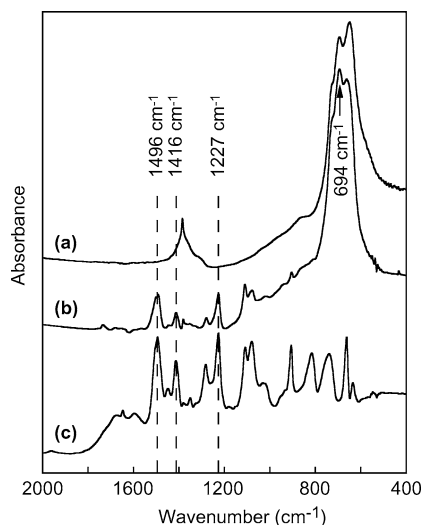


Figure 2. FT-IR spectra (DRIFTS) of (a) magnetic particles (Mag, γ -Fe₂O₃), (b) poly(1-vinylimidazole)-grafted magnetic particles (Mag-Im₁₈), and (c) poly(1-vinylimidazole).

Table 1. Elemental Analysis of Magnetic Particles with (Mag-Im₁₈) and without (Mag) Poly(1-vinylimidazole) Immobilization

	C%	H%	N%	C/N
Mag	0.00	0.22	0.00	
Im ₁₈ (calcd) ^a	52.1	7.30	22.8	2.29
Im ₁₈	54.9	7.11	22.7	2.42
Mag-Im ₁₈	3.03	0.48	1.22	2.48

^a Calculated for Im₁₈·18H₂O.

ence of poly(1-vinylimidazole). The IR peak around 1385 cm⁻¹ on spectrum a is assigned to residual NO₃⁻ ions from synthesis of the magnetic nanoparticles. Table 1 shows the elemental analysis of magnetic particles before and after the graft of the polymers. For the particles without polymer coatings, a small quantity of hydrogen (0.22 wt %) was determined. The presence of such a low level of hydrogen is anticipated for γ -Fe₂O₃ particles that contain surface hydroxyl (Fe-OH) groups. The elemental analysis showed about 5 wt % of Im₁₈ being bound to magnetic nanoparticles. From the determined nitrogen content (N%), the amount of imidazolyl groups on the polymer bound to the maghemite particles is estimated to be 0.44 mmol g⁻¹. It is evident that the carbon to nitrogen mass ratio (C/N value) remained the same, even after Mag is converted to Mag-Im₁₈. This finding suggests that the poly(1-vinylimidazole) is not damaged during the immobilization reaction and Im₁₈ was grafted onto magnetic particles. The results of thermal gravimetric analysis showed a drastic change in thermal responses of the maghemite particles without and with polymer grafting.

Although the DRIFTS and elemental analysis presented here does not provide any direct indication of a poly(1-vinylimidazole) binding mechanism with the maghemite surface, it is known that silane coupling agents with alkoxy-silyl or chlorosilyl groups react with a surface of metal oxide such as silica, titan oxide, and iron oxide. It is therefore reasonable to infer that the silane groups of poly(1-vinylimidazole) are being immobilized/anchored on magnetic particles via coupling reactions with hydroxyl groups on the surface of maghemite (γ -Fe₂O₃). Once all the available surface sites are occupied by the silane coupling groups, such

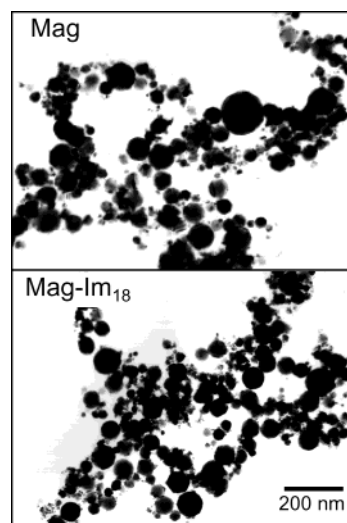


Figure 3. Transmission electron micrographs of Mag and Mag-Im₁₈.

anchoring is saturated. The association among poly(1-vinylimidazole) in a good solvent can be considered minimal, resulting in a grafting of one-molecule thickness.

Characterization of Polymer-Magnetic Nanoparticle Hybrids. Magnetic nanoparticles without polymer grafting were highly dispersive in water by ultrasonication due to hydroxyl groups on the surface of particles. Mag-Im₁₈ was also readily dispersed in water. The dispersion state of the particles was confirmed visually by the observed brown color of the suspension. The aqueous dispersions of ungrafted and polymer-grafted particles were stable for several hours. Figure 3 shows transmission electron micrographs without (Figure 3a) and with (Figure 3b) polymer coatings. Comparison of the transmission electron microscope (TEM) micrographs confirms that the original size and shape of the particles were retained after Im₁₈-grafting. Both the DRIFTS spectra and elemental analysis indicated that the polymer-grafted particles were covered by poly(1-vinylimidazole). Since the particles were washed several times with methanol, which is a good solvent for poly(1-vinylimidazole), it was considered that the polymer that remained was anchored chemically on the surface of particles, mostly likely through siloxane bonds. The polymer layer on the magnetic particles was sufficiently thin as such that the TEM was unable to detect its presence around the core of maghemite particles. The area occupied by one polymer molecule can be estimated to be 2.75 nm² from the known surface area of magnetic particles (40 m² g⁻¹) and the amount of polymer grafted (0.0242 mmol g⁻¹). This area is equivalent to a molecular diameter of 0.94 nm, which is a reasonable value for a flexible polymer molecule in a good solvent.

The results from ζ -potential measurement of magnetic nanoparticles confirm the immobilization of Im₁₈ on magnetic particles. Figure 4 shows that the particles are positively charged at lower pH and negatively charged at higher pH. However, the isoelectric point (IEP) of the maghemite increased from pH 6.9 to 7.4 with Im₁₈ immobilization. In a previous paper,¹⁵ we reported a significant change in the ζ -potential of

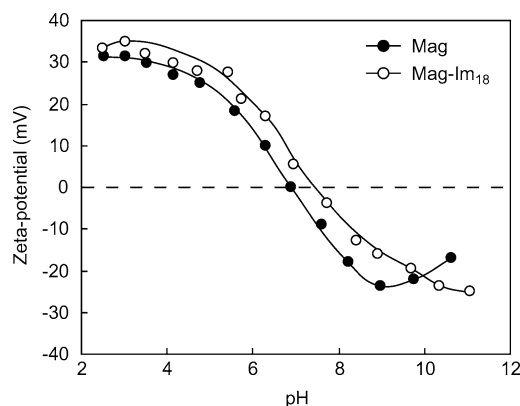


Figure 4. ζ -Potentials of magnetic particles with (Mag-Im₁₈) and without (Mag) poly(1-vinylimidazole) immobilization.

Table 2. Stabilities of Mag-Im₁₈ in Acidic and Basic Solutions^a

pH	R	pH	R
2.7	0.76	8.0	> 1
3.0	0.82	9.1	0.94
3.5	0.92	10.0	> 1

^a The samples were immersed in aqueous solutions for 1 h at ambient temperature. $R = (\text{Abs}_{1496}/\text{Abs}_{694})/(\text{Abs}(0)_{1496}/\text{Abs}(0)_{694})$.

magnetic particles by the modification of the particles with 3-aminopropyltrimethoxysilane (APTES). The IEP of the magnetic particles silanized with APTES are in a pH range of 8.5–9.2. The silanation of APTES on magnetic particles not only reduces the number of negative surface sites but also induces positive surface sites due to protonation of immobilized surface amine groups.¹⁵ In the current case, the surface of the particles was covered by immobilized Im₁₈. The tertiary amine in imidazolyl groups is much less amenable to protonation. As a result, the IEP was shifted only to a slightly higher pH by immobilizing poly(1-vinylimidazole). Nevertheless, Figure 4 shows that the ζ -potential of Mag-Im₁₈ particles is more positive below the IEP and less negative above the IEP than that of untreated maghemite particles. All of this experimental evidence points to the grafting of poly(1-vinylimidazole) on nanosize maghemite particles.

The Mag-Im₁₈ prepared in this study can form stable dispersions in water, methanol, ethanol, chloroform, and toluene without adding any other surfactants. In contrast, the untreated maghemite dispersions prepared by ultrasonication in methanol and ethanol are unstable and the particles settled down after several hours. It was extremely difficult to disperse the maghemite particles in chloroform and toluene. It is certain that the presence of electrostatic repulsion between the grafted Im₁₈ polymer chains facilitates stabilization of Im₁₈-grafted magnetic nanoparticles in various liquids. More importantly, the presence of anchored polymer on nanosize maghemite particles in good, nonaqueous solvent induces a steric repulsion, which contributes to steric stabilization. The observed stability of the grafted particles in methanol, ethanol, chloroform, and toluene suggests the flexible nature of the polymers anchored on the particle surfaces. In Table 2, the absorbance ratio (R) defined by eq 1 showed a negligible change after the synthesized Mag-Im₁₈ particles were immersed in aqueous solutions of pH 3.5–10.0 for 1 h. This finding suggests that the Im₁₈-immobilized magnetic nanopar-

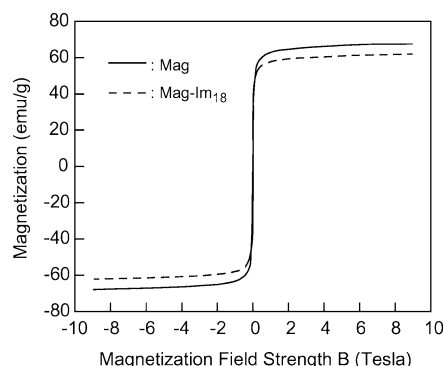


Figure 5. Room-temperature magnetization curves of nano-size maghemite particles without (Mag) and with poly(1-vinylimidazole) (Mag-Im₁₈).

ticles (Mag-Im₁₈) can be used in a wide range of aqueous environments.

With a single layer of poly(1-vinylimidazole) molecules anchored on nanosize maghemite particles, the reduction in magnetization by polymer coatings would be minimal. To confirm this hypothesis, the magnetization characteristics of maghemite particles before and after polymer grafting were determined. The magnetization curves in Figure 5 show that the reduction in saturation magnetization by polymer grafting is indeed minimal, by approximately 6%, indicating a 6 mass % surface coverage of polymer. This surface coverage value agrees well with the value of 5% derived from the elemental analysis. The polymer-grafted maghemite particles with such magnetization characteristics are suitable for industrial applications as magnetic carriers.

Application for Removal of Metal Ions. The coordination numbers and complex stability constants of various polymer ligands–metal ion complexes have been reported.²⁹ Recently, as a method of treating metal-polluted industrial effluent and municipal water, polymer–metal ion complexes were investigated for such polymer systems as cross-linked polymers^{30–32} and polymer hydrogels.^{33,34} Metal ion binding properties of imidazole and poly(1-vinylimidazole) have been reported by many researchers.^{24–28} Poly(1-vinylimidazole), for example, has shown several different coordination numbers with metal ions.

The removal of various metal ions from aqueous solutions is possible by using the Mag-Im₁₈ as a collector. Figure 6 shows the removal efficiency of Cu²⁺, Ni²⁺, and Co²⁺ from their bulk solutions. The order of removal efficiency of the metal ions by Mag-Im₁₈ was found to be Cu²⁺ > Ni²⁺ > Co²⁺. The observed order is in line with the complexation equilibrium constants of poly(1-

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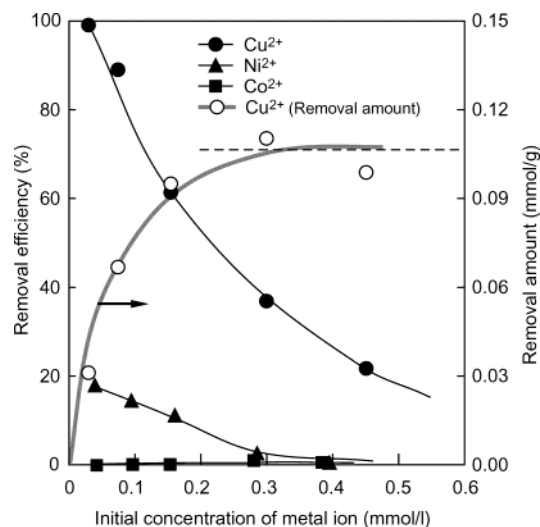


Figure 6. Removal efficiency of Cu²⁺, Ni²⁺, and Co²⁺ and loading capacity of on Mag-Im₁₈ for Cu²⁺. Metal ion solution/Mag-Im₁₈ = 10 mL/10 mg. Initial pH of solution = 5.3.

vinylimidazole) with these metal ions. According to Pekel et al.,³⁵ poly(1-vinylimidazole) forms a much more stable complex with Cu²⁺ than with other bivalent transition metals such as Co²⁺, Cd²⁺, and Pb²⁺.

It is well-known that the complexation of a Cu²⁺ with imidazole has a preferred coordination number of 4.³⁶ The coordination number of copper with poly(1-vinylimidazole) has been confirmed experimentally to be 4 by the molar ratio method with UV-vis spectroscopy.²⁴ As shown in Figure 6, the loading capacity of Mag-Im₁₈ for Cu²⁺ at pH 5.3 is 0.11 mmol g⁻¹, equivalent to 7.0 mg of Cu²⁺ ions per gram of Mag-Im₁₈. The imidazolyl groups among the grafted polymer on the magnetic particles are estimated by elemental analysis to be 0.44 mmol g⁻¹. These numbers not only suggest a coordination number of 4 for copper complexation with immobilized imidazolyl groups on the Mag-Im₁₈ but also indicate that almost all the imidazolyl groups on the magnetic nanoparticles are available to form complexes with copper ions in aqueous solutions. To account for all the imidazolyl groups accessible, the polymer chains on the surface of the particles have to be flexible, as schematically shown in Figure 1. This was possible since only one terminal silane group for each polymer molecule is immobilized on the particles through covalent siloxane bonds.

The equilibrium constant of poly(1-vinylimidazole) complexing with Cu²⁺ and Co²⁺ ions is well-documented to be 82×10^{18} and 7×10^{18} , respectively.³⁵ These thermodynamic numbers indicate that complexation of poly(1-vinylimidazole) with Cu²⁺ should be more stable than with Co²⁺. Although the equilibrium constant of poly(1-vinylimidazole) complexing with Co²⁺ suggests the complex formation, Co²⁺ ions do not load effectively on Mag-Im₁₈ from bulk solutions, as shown in Figure 6. It is known that complexation is not only influenced by the charge to ion radius ratio of metal ions but also influenced by acidic properties and steric effect. To account for the observed discrepancy in complexation

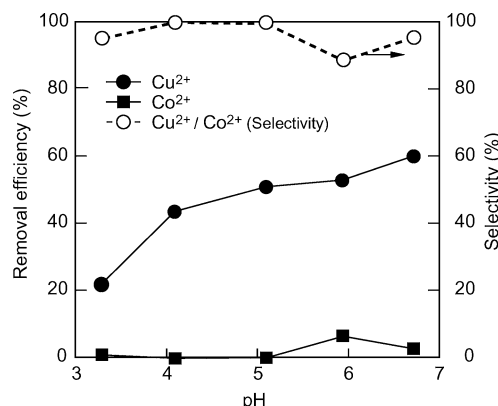


Figure 7. Removal efficiencies of Mag-Im₁₈ for Cu²⁺ and Co²⁺ and selectivity from a mixture of Cu²⁺/Co²⁺ solution. Metal ion solution/Mag-Im₁₈ = 10 mL/10 mg. Initial concentration: [Cu²⁺] = 0.157 mmol L⁻¹, [Co²⁺] = 0.170 mmol L⁻¹.

of Co²⁺ with poly(1-vinylimidazole) in solution and immobilized on particle surfaces, the steric effect of immobilized poly(1-vinylimidazole) has been considered.

Selective removal of metal ions from aqueous solutions was evaluated by loading tests from a mixture of Cu²⁺/Co²⁺ solutions. In this set of experiments, the initial concentration of Cu²⁺ and Co²⁺ was fixed at 0.157 mmol L⁻¹ (10 ppm) and 0.170 mmol L⁻¹ (10 ppm), respectively. As shown in Figure 7, the removal efficiency for Cu²⁺ increased with increasing solution pH. It is evident that the adsorption of copper ions on Mag-Im₁₈ is not significant below pH 3. The competitive adsorption of hydrogen ions with metal ions for imidazolyl groups at lower pH values accounts for the observed low removal efficiency. Since the imidazolyl groups are most likely protonated at a low pH, the magnetic particles are positively charged, resulting in a strong electrostatic repulsive force between the poly(1-vinylimidazole) on the magnetic particles and positively charged metal ions. This long-range repulsive force also contributes to the observed low removal efficiency. Co²⁺, however, cannot be removed by Mag-Im₁₈ in the pH range studied. The Mag-Im₁₈ showed a high selectivity for Cu²⁺ removal/recovery from a mixture of Cu²⁺ and Co²⁺. The selectivity ratio, defined as the removal efficiency of copper divided by the removal efficiency of cobalt, was more than 90% over the pH range from 3 to 7. The use of polymer-magnetic hybrid materials developed here offers a unique advantage in separation science and technology. The separation and/or recovery of a target species such as metal ions from a complex multiphase system can be accomplished without pretreatment, as the loaded hybrid materials can be isolated with an external magnetic field.

Conclusions

Poly(1-vinylimidazole) with a trimethoxysilyl terminal group was newly synthesized by telomerization. The DRIFTS measurement combined with elemental and thermal gravimetric analysis showed that immobilization of the synthesized polymer onto magnetic nanoparticles through siloxane bonds (Mag-Im₁₈) was successful. The Mag-Im₁₈ was well-dispersed in water and in organic solvents such as methanol, ethanol, and chloroform. The grafted polymer is stable over a wide

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solution pH range from 3.5 to 10.0. Removal of metal ions from solution by Mag-Im₁₈ is successful for copper. A loading capacity of 0.11 mmol g⁻¹ at pH 5.3 was determined. This capacity corresponds to a one-quarter amount of imidazolyl groups on the particles (0.44 mmol g⁻¹). This observation suggests a preferred coordination number of 4 for Cu²⁺ to complex with imidazolyl groups and confirms that the imidazolyl groups on the flexible polymer chain are effective at capturing copper ions. By comparison, the removal efficiency of Ni²⁺ and Co²⁺ was relatively low. The Mag-Im₁₈ showed an effective separation of Cu²⁺ from a Cu²⁺/Co²⁺ solution over a pH range of 3–7. Polymer-grafted magnetic particles can

provide vast potential applications given the wide selection of polymer functionality.

Acknowledgment. The financial support for this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan and Natural Sciences and Engineering Research Council of Canada (NSERC) is greatly appreciated. We would also like to thank Ms. Jie Dong for her help with magnetization measurements.

CM030334Y