



Surface Charge Controlled Magnetic Nanoparticles with Grafting of Poly(4-vinylpyridine)

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Poly(4-vinylpyridine)-grafted magnetic nanoparticles were prepared by the “graft to” method. Surface-modified magnetic particles are covered with a hydrophobic layer because it can be dispersed in organic solvents such as methanol, toluene, benzene, and chloroform, but not in water. Surface charge control with magnetic nanoparticles of various isoelectric point was achieved by quaternization of pyridyl groups, and the positively charged particles can be dispersed in water within a wide range of pH.

Keywords: Maghemite, Poly(4-vinylpyridine), Telomerization, Quaternization, Silane Coupling, Polymer Grafting, Surface Modification, ζ -Potential.

The preparation of magnetic nanoparticles has been motivated because of their possible applications in the scientific, clinical, and industrial fields.¹ The techniques for uniform size-control² and surface modification of magnetic nanoparticles have been described by many research groups in a last decade. We have reported the preparation of polymer-grafted magnetic nanoparticles by using the “graft to” method in a previous report.³ Our polymer “graft to” method includes two steps, which are synthesis of polymer with a trimethoxysilyl terminal group at the one side of the polymer chain and grafting onto magnetic nanoparticles. The advantages compared to “graft from” methods are that polymer characterization is relatively easy because it can be done before immobilization and thus it is also possible to use a tailor-made polymer for grafting. In this paper, we report the surface charge control of magnetic nanoparticles by grafting of poly(4-vinylpyridine) with the graft-to method followed by quaternization of the pyridyl group (Fig. 1). The surface charge property of magnetic particles is an important feature, which influences their characteristics, such as affinity with substances and dispersibility in solvents. Surface charge control

of magnetic nanoparticles will expand their possible applications.

The polymer was synthesized by the modified telomerization method.⁴ 4-Vinylpyridine (10 mL, 92.7 mmol), 3-mercaptoptrimethoxysilane (0.91 mL, 4.64 mmol), and AIBN (100 mg) were mixed at 60 °C for 6 h under N₂ atmosphere. The obtained light yellow viscous solution was cooled and dissolved in chloroform (20 mL). The solution was added to 200 mL of hexane and the precipitates were collected by filtration. The reprecipitation procedure was repeated 3 times and the precipitate was collected by filtration. The obtained white powder was dried in vacuo (9.87 g (91%)). The polymerization degree (n) of the resultant polymers (4VP)_{*n*}, n is the average degree of polymerization) was estimated by ¹H NMR spectroscopy to be 22. 4VP₂₂: ¹H NMR (CDCl₃) δ 0.55–0.70 (m, 2H, SiCH₂), 1.2–1.7 (m, 44H, CH₂ (polymer main chain)), 1.7–2.2 (m, 22H, CH-Py (polymer main chain)), 3.54 (s, 9H, CH₃OSi), 6.2–6.9 (m, 44 H, C–CH=C (pyridyl ring)), 8.1–8.6 (m, 44 H, N–CH=C). Anal. Calcd for C₁₆₀H₁₇₀N₂₂O₃SiS: C, 76.6; H, 6.83; N, 12.3; C/N, 6.24. Found: C, 76.3; H, 6.80; N, 12.2; C/N, 6.26.

The 4VP₂₂ was agitated with γ -Fe₂O₃ nanoparticles in a methanol/toluene (2:8) mixture at reflux temperature, and then the particles were successively washed

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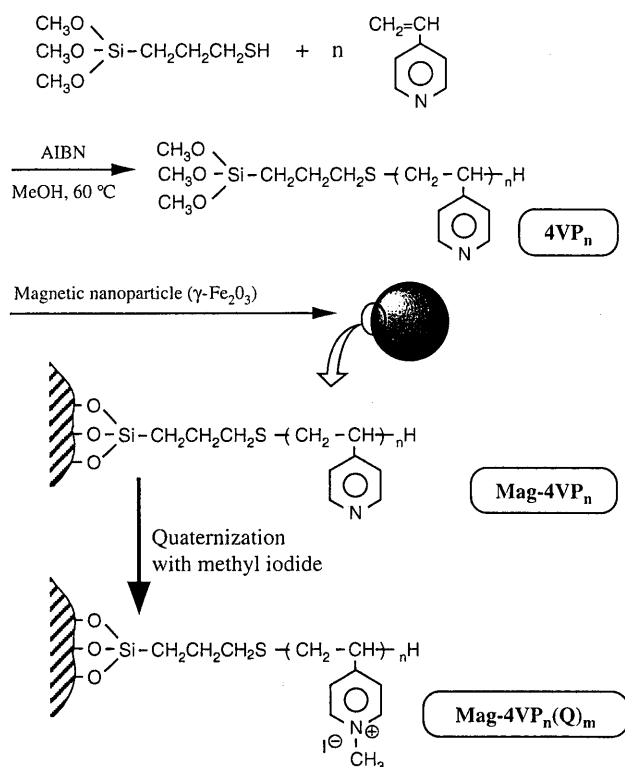


Fig. 1. Preparation scheme of polymer-grafted magnetic nanoparticles.

several times with methanol to remove physisorbed polymer and impurities. The magnetic nanoparticles were purchased from Alfa Aesar (USA), and the average diameter and surface area of the particles were 28 nm and $40\text{ m}^2/\text{g}$, respectively. The resultant particles (Mag-4VP_{22}) were evaluated by diffuse reflectance FT-IR spectroscopy (FTS 6000 spectrometer (Bio-Rad Laboratories, USA)). The typical spectral features of poly(4-vinylpyridine) were observed on the resultant maghemite particles (Fig. 2). Elemental analysis showed that the immobilized amount of polymer was ca 8.0 wt% (0.62 mmol/g of pyridyl moieties were introduced to the particles). This corresponds to 0.43 chains/nm² on the surface. It has been reported by some research groups that alkoxy-silyl group can react with hydroxyl groups on the iron oxide surface and those chemical bonds are detectable by FT-IR and XPS spectroscopic measurements.⁵ However, distinct spectral change was not observed in XPS and FT-IR spectra of Mag-4VP_{22} before and after polymer grafting. To confirm chemical anchoring of polymer, the poly(4-vinylpyridine) without a terminal reactive group ($\text{C}_4\text{-4VP}_n$) was synthesized by telomerization with 1-butanethiol as a telogen. The $\text{C}_4\text{-4VP}_{24}$ (polymerization degree was determined to be 24) was mixed with magnetic nanoparticles under the same conditions and the obtained nanoparticles ($\text{Mag/C}_4\text{-4VP}_n$) were washed by same procedure. The ratio of KM (Kubelka-Munk) values at 638 cm^{-1} (Fe-O-H) and 1415 cm^{-1} (C=N) is useful to estimate the amount of pyridyl groups on the magnetic

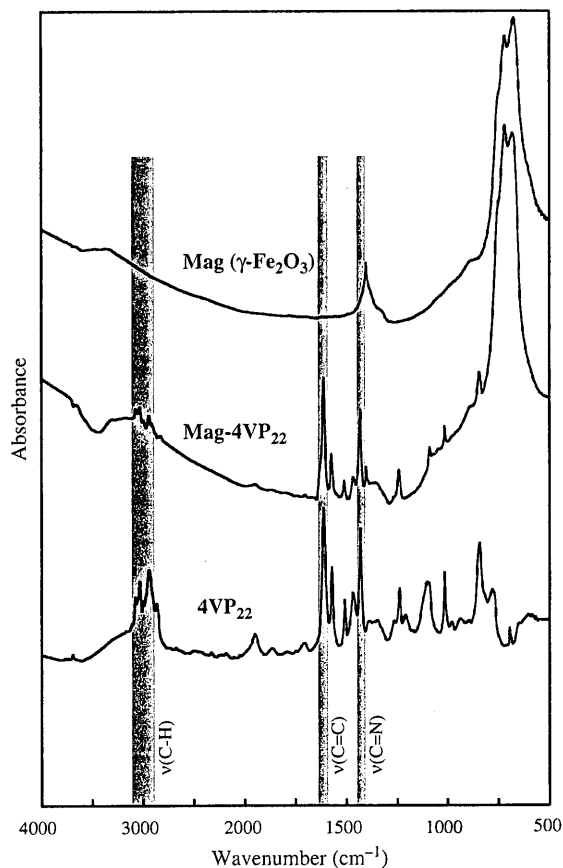


Fig. 2. FT-IR spectra of Mag, Mag-4VP_{22} , and 4VP_{22} .

particles. The $\text{KM}_{1415}/\text{KM}_{638}$ value for Mag-4VP_{22} was more than twice of that for $\text{Mag/C}_4\text{-4VP}_{24}$. And the $\text{KM}_{1415}/\text{KM}_{638}$ value showed almost no change in Mag-4VP_{22} after washing with acidic solution ($\text{pH} = 3.5$) but decreased to 40% in $\text{Mag/C}_4\text{-4VP}_{24}$. These results indicate that poly(4-vinylpyridine) physisorbs on the surface of magnetic nanoparticles by electrostatic attraction, but the physisorbed polymers are easily detached from the surface. The chemical anchoring by the terminal reactive group of 4VP_{22} significantly hinders their detachment and improves stability.

The Mag-4VP_{22} can be dispersed in organic solvents such as methanol, toluene, benzene, and chloroform, but not in water. This indicates that the immobilized polymer phases work as relatively hydrophobic layers. To increase the dispersity to water, the quaternization (alkylation) of 4-vinylpyridine moieties was investigated. Quaternization was carried out with methyl iodide and the degree of quaternization was estimated by diffuse reflectance FT-IR spectroscopy. Figure 3 shows the diffuse reflectance FT-IR spectra of Mag-4VP_{22} before and after quaternization. The peaks around 1599 cm^{-1} and 1640 cm^{-1} correspond to C=C bond stretching vibrations of the pyridyl ring before and after quaternization, respectively.⁶ Quaternization of pyridyl moieties can be controlled by additional amounts of methyl iodide as shown in Figure 3 ($\text{Mag-4VP}_{22}(\text{Q}_m)$),

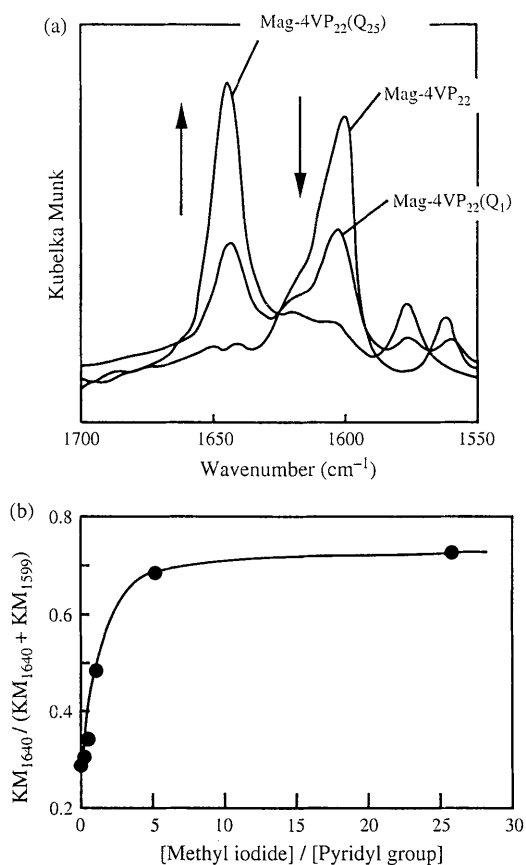


Fig. 3. FT-IR spectra and the peak ratio ($KM_{1640}/(KM_{1640} + KM_{1599})$) of Mag-4VP₂₂ before and after quaternization.

where m is the ratio of methyl iodide and pyridyl groups in the reaction mixtures). The quaternization of pyridyl groups was almost complete by mixing with 5 times the amount of methyl iodide, in spite of the fact that one end of the polymer is immobilized on the surface of the particle. With Mag-4VP₂₂(Q₁), well-dispersed particles in water were observed, the quaternization degree of which is less than half (shown in Fig. 3). The surface charges of magnetic nanoparticles were evaluated by using a Zetasizer 3000HSA (MALVERN Instruments Ltd., USA). The ζ -potentials of magnetic nanoparticles were measured in 1 mmol of NaCl background electrolyte solutions at a particular pH, which was adjusted by the addition of NaOH or HCl stock solutions. The aqueous dispersions of Mag-4VP₂₂ were prepared by adding concentrated methanol dispersion of Mag-4VP₂₂ to excess water. Figure 4 shows the ζ -potentials of Mag-4VP₂₂(Q _{m}) in aqueous dispersions within a pH range from 2 to 12. The isoelectric point (IEP) of magnetic nanoparticles without polymer was 6.9, and this value showed almost no change after grafting poly(4-vinylpyridine) Mag-4VP₂₂. However, the IEP of Mag-4VP₂₂(Q _{m}) shifted to a drastically higher pH with increase of the quaternization degree. Finally, the ζ -potentials of particles showed positive charge in a wide

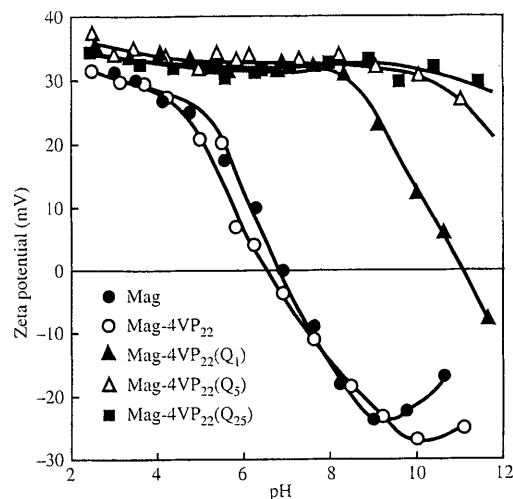


Fig. 4. ζ -Potentials of Mag-4VP₂₂ and Mag-4VP₂₂(Q _{m}) in aqueous solutions. NaCl solution (1 mmol L⁻¹) was used as background electrolyte solution and pH was adjusted by NaOH and HCl stock solutions.

range of pH, therefore the aqueous dispersion of Mag-4VP₂₂(Q₂₅) was stable in this pH range.

In conclusion, surface-modified magnetic γ -Fe₂O₃ nanoparticles can be prepared by a "graft to" method. It is estimated that the poly(4-vinylpyridine) chains chemically grafted on the surface of particles at the terminal and the flexible polymer chain acts effectively to cover the surface of particles. Furthermore, the quaternization of the pyridyl groups on the particles was successful, and their conversion ratio is readily controllable. The surface charge of Mag-4VP₂₂(Q _{m}) in aqueous dispersion was changed remarkably with quaternization. The fully quaternized particles (Mag-4VP₂₂(Q₂₅)) are stable in a wide range of pH. Poly(4-vinylpyridine)⁷ and quaternized poly(4-vinylpyridine)⁸ are known to form complexes with metal ions. These polymer-grafted particles have many applications, such as carriers and separation materials with magnetic properties.

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