

Control of Interfacial Structure and Properties of Magnetite Nanoparticle through Surface-Initiated Nitroxide-Mediated Radical Polymerization of Styrene and 3-Vinylpyridine

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Polymer-grafted magnetite (Fe₃O₄) nanoparticles (diameter 10 ± 3 nm and 25 ± 5 nm) were prepared through a direct polymer grafting reaction from their surfaces. The chemisorbed initiator for nitroxide-mediated radical polymerization with a phosphoric acid group gave controlled polystyrene (PS) and poly(3-vinylpyridine) (P3VP) graft layers on the surface. The graft densities of polymers on the surfaces of magnetite particles were estimated at 0.12-0.20 chains/nm² by thermogravimetric analysis (TGA). PS-grafted magnetite was dispersed in organic solvents, whereas P3VP-grafted magnetite dispersed in acidic aqueous phase, by protonation, and by quaternization in neutral aqueous solution. The magnetic response against an external magnetic field was influenced to the dispersion state in solution and a magnetite particle size resulting from magnetic moments.

Key words: Magnetite, 3-Vinylpyridine, Surface modification, Living radical polymerization

1. INTRODUCTION

Since the dispersion of nanoparticles to the polymer matrix originates from the affinity between nanoparticle surface and matrix, appropriate surface modification method should be employed. This method achieves the stable dispersion of nanoparticles in a matrix by adsorbing the organic molecule with high affinity to matrix on nanoparticle surface. Recently, a 'grafted-from' system has been used to carry out the direct polymerization of polymers on the nanoparticle surface. [1,2] In this paper, 'grafted-from' surface modification of magnetic nanoparticles was performed, and the dispersibility of the polymer-grafted magnetite and in various solvents was investigated. Furthermore, magnetic response against an external magnetic field in various solvents was investigated.

2. EXPERIMENTAL

2.1 Materials

Styrene was obtained from WAKO Pure Chemical Industries, Ltd. and purified by distillation under reduced pressure over calcium hydride. 3-Vinylpyridine was synthesized by the method reported previously[3], and purified by distillation under reduced pressure over calcium hydride. Magnetite particles with diameters of approximately 10 ± 3 nm and 25 ± 5 nm were given by Prof. K. Enpuku (Kyushu University).

2.2 Measurements

Gel permeation chromatographic (GPC) analysis was carried out at 313 K on a Tosoh

HLC-8120GPC with a guard column (Shodex GPC KF-804L), and a differential refractometer RI-8020. Tetrahydrofuran (THF) was used as an eluent for PS analysis. THF containing 5 vol% *N,N,N',N'*-tetramethyl-ethylenediamine was used as an eluent for P3VP analysis. PS standards were used to calibrate the GPC system. Thermogravimetric analysis (TGA) was performed by Thermo Plus 2 (Rigaku Corporation), using aluminum pan with ca. 2 mg of the sample, under a nitrogen atmosphere and a heating rate of 10 K/min. Ultraviolet-visible (UV-vis) absorption spectra were recorded by Lambda 35 (Perkin Elmer Japan Co., Ltd.). Transmission electron microscopy (TEM) observation was made on an H-7500 (Hitachi) operated at 100 kV. Dynamic light scattering (DLS) measurement was performed by DLS-7000 (Otsuka Electronics CO., LTD.) at 13-20 mW of

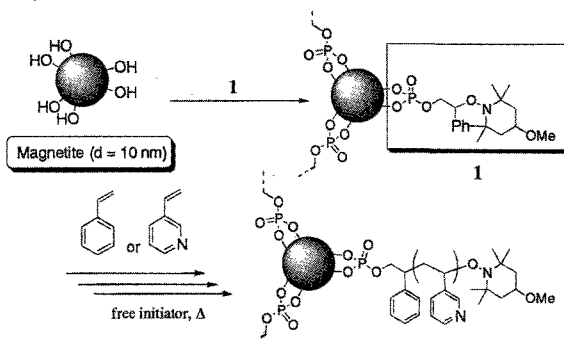


Figure 1. Scheme of the preparation of polymer graft chain on the nanoparticle surface.

Ar laser.

2.3 Surface-Initiated polymerization of styrene and 3-vinylpyridine on nanoparticle

The surface of magnetite nanoparticles was modified by direct graft polymerization using a nitroxide-mediated radical polymerization initiator. Synthesis and adsorption of surface initiator **1** on magnetite surface were performed according to the previous report.[4] As shown in Figure 1, the designed surface initiator **1** has both an living free radical polymerization moiety that contains 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO) and a phosphoric acid moiety that can interact with Fe-OH groups on nanoparticle surface. Polymerization of PS and P3VP on the surface of nanoparticles was carried out by heating a mixture of surface initiator **1** modified magnetite particles, free initiator (4-hydroxy-1((2'-hydroxy-1'-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine)[5], and monomers, after degassing by four freeze-pump-thaw cycles. The number-average molecular weights (M_n) and polydispersities (M_w/M_n) were evaluated by GPC. The graft densities were calculated from the weight loss of the polymer measured by TGA, surface area of magnetite estimated assuming magnetite particle as a sphere with a diameter of 10 nm or 25 nm, and density 5.18 g/cm³ for a whole particle.

3. RESULTS AND DISCUSSION

3.1 Determination of graft density of surface polymer on magnetite

The M_n and M_w/M_n of the representative grafted polymer on magnetite (diameter 10 nm) were M_n 12300, M_w/M_n 1.27 (PS) and M_n 16500, M_w/M_n 1.46 (P3VP). The graft densities of magnetite particle were estimated to be 0.12-0.20 chains nm⁻². The density of surface initiator **1** was 0.73 chains nm⁻². Therefore it seems that 16-28 % of alkoxyamine initiator on magnetite surface participated in the polymerization. In the case of 25 nm in diameter, M_n 22000, M_w/M_n 1.37 (PS) and M_n 12600, M_w/M_n 1.45 (P3VP) were grafted as the representative polymers. The graft densities of the particles were estimated to 0.17-0.20 chains nm⁻². Since the density of surface initiator **1** was 0.68 chains nm⁻², 25-30 % of alkoxyamine initiator participated in polymerization.

3.2 The dispersibility of polymer-grafted magnetite

The dispersibility and stability of polymer-grafted nanoparticle were evaluated by UV-vis absorption spectroscopy, TEM and DLS measurements. To investigate the dispersibility and stability in solvents, PS-grafted magnetite (10 nm in diameter) nanoparticles were added to chloroform and dispersed by sonication for 10 min. UV-vis spectra showed that the absorption did not change over several hours. Furthermore, after centrifugation at 3500 rpm for 20 min, the

absorbance decreased slightly over several hours. In the case of other good solvents such as tetrahydrofuran (THF), toluene, and ethyl acetate, PS-grafted magnetite nanoparticles were also stably dispersed. In contrast, in poor solvents such as hexane and acetone, they were not stably dispersed. This means that the dispersibility and stability were influenced by solubility of the grafted PS on surface.

P3VP-grafted magnetite nanoparticle was dispersed into chloroform and weak acidic aqueous solution by sonication for 10 min. Figure 2 shows UV-vis spectra of P3VP-modified magnetite (d = 10 nm) dispersion (a) in chloroform and (b) in pH 3.0 aqueous solution. In chloroform, the spectrum was not changed over several hours. Even after centrifugation, absorbance did not reach 0. In pH 3.0 aqueous solution, UV-vis spectra were not changed over several hours as well as in chloroform. Even after the centrifugation, absorbance did not reach 0, either. This stable dispersion is due to the protonation of pyridine moieties in grafted P3VP chains.

Additionally, the P3VP-grafted magnetite was quarternized by iodomethane. The grafted magnetite and iodomethane were mixed and stirred 2 h in methanol under nitrogen atmosphere. The quarternized P3VP-grafted magnetite was successfully dispersed into neutral water. The

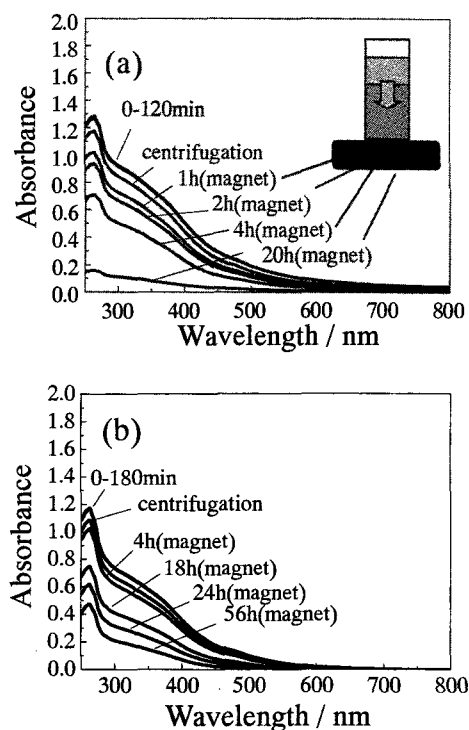


Figure 2. UV-vis spectra of P3VP-grafted magnetite (d=10nm) (a) in chloroform and (b) in water (pH 3.0) (0.1 mg/mL). Time (magnet) shows progressed time placed the magnet from the bottom of cell, after centrifugation.

stability were similar to those of P3VP-grafted magnetite dispersion in chloroform and in acidic aqueous solution.

The dispersibility and stability of polymer-grafted nanoparticle were also evaluated for diameter of 25 nm. The spectra did not change over several hours, even after centrifugation, absorbance did not reach 0 both in chloroform and pH 3.0 aqueous solution as well as the case for the magnetite with 10 nm in diameter.

3.3 Magnetic response

To estimate magnetic response against an external magnetic field, after the neodymium magnet was applied from the bottom of a cell, UV-vis spectra were measured as a function of time. Figure 2 shows decrease of the absorbance, after the neodymium magnet was applied from the bottom of a cell. Although the polymer-grafted magnetite particles did not aggregate under centrifugation, they were attracted by magnet. However, times collected by magnet were different among solutions. Figure 3 shows the rates of decrease of normalized absorbance as a function of time after centrifugation (a) $d = 10$ nm and (b) 25 nm at $\lambda = 350$ nm in various solution. As compared with pH 3.0 at P3VP-grafted magnetite, the rate of decrease of absorbance in CHCl_3 was faster than that of pH 3.0 both of 10 nm and 25 nm. It seems that steric and electrostatic repulsion between the protonated polymer chains is effective for dispersion in pH 3.0 aqueous solutions. In same solvent, the rates of decrease of absorbance for 25 nm were faster than that for 10 nm. Therefore, a magnetite particle size resulting from magnetic

moments are assumed to influence their magnetic response.

3.4 Aggregation state and model

To obtain further insight into the aggregation state of the nanoparticles, size distributions in solution were estimated by DLS measurements. Table I summarizes observed diameter in each solution and calculated diameter. The calculated diameters were obtained from a model discussed below. Because many theories[6-8] regarding grafted polymers on flat surface have been discussed, these theories were adapted for magnetite nanoparticles, as the surface is to be locally flat. Both 'mushroom' and 'brush' polymer grafts are known to exist on surfaces. The grafted polymer behaves as a statistical coil of typical size $R \sim aN^\nu$, where a is the Kuhn statistical segment length with $a = 0.67$ nm for a polystyrene monomer unit; N is the number of monomers; and the scaling exponent ν characterizes the solvent quality ($\nu \approx 3/5$ in good solvent and $1/2$ in θ -solvent)[9]. The graft density σ and the distance between the grafting site d on the surface are related as $\sigma \sim 1/d^2$. In the 'mushroom' regime, $d \gg R$ or $\sigma R^2 \ll 1$, where grafted chains do not interact, and in the 'brush' regime, $d \ll R$ or $\sigma R^2 \gg 1$, where the grafted polymers are strongly overlapping and stretch away from the grafting surface to avoid unfavorable monomer-monomer contacts. To investigate the 'mushroom' or 'brush' types, inserting the graft density and R into σR^2 , 25 and 23 are obtained for PS (M_n 12300) and P3VP (M_n 16500) (diameter 10 nm), respectively. Therefore, grafted polymers are assumed to adhere to the 'brush' regime. The height h of the grafted layer is given by[10]

$$h = (12/\pi)^{1/3} N \sigma^{1/3} (\omega/\nu)^{1/3} \quad (1)$$

where ω is the excluded volume parameter, approximately $(2 \text{ \AA})^3$; N is the number of monomers; and $\nu = (a^3/3)^{-1}$. Inserting each value into Eq. (1), 11 nm and 13 nm are obtained for PS and P3VP, respectively. Therefore, the equilibrium diameters of polymer-grafted magnetite with diameters of approximately 10 nm are 32 nm for PS and 36 nm for P3VP in good solvents. The thickness L_d in the dry state could be estimated by

$$L_d = \sigma M_n / d N_A \quad (2)$$

where d is the bulk density of the polymer (for PS 1.04-1.065 g/cm³) and N_A is Avogadro's Number.

In the dry state, the polymer thicknesses grafted on magnetite nanoparticles were found to be 3.5-3.6 nm and 3.1-3.2 nm for PS and P3VP, respectively. Therefore, the heights of the grafted

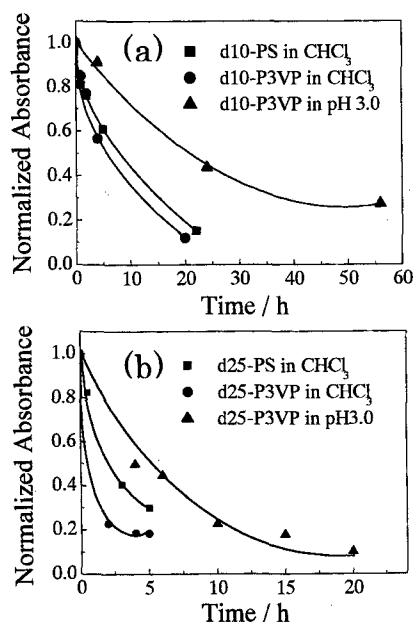


Figure 3. The rates of decrease in normalized absorbance as a function of time after centrifugation at $\lambda = 350$ nm. (a) diameter 10 nm, (b) diameter 25 nm.

Table I. Size distribution of polymer-grafted magnetite nanoparticles

diameter (nm)	graft polymer	M_n	M_w/M_n	solvents	diameter (nm) ^a	calculated diameter (nm) ^b
10	PS	12300	1.27	chloroform	110 ± 16	32
10	P3VP	16500	1.46	chloroform	194 ± 27	36
10	P3VP	16500	1.46	pH 3.0	65 ± 9	36
25	PS	22000	1.37	chloroform	475 ± 186	65
25	P3VP	12600	1.46	chloroform	151 ± 20, 481 ± 68	48
25	P3VP	12600	1.46	pH 3.0	85 ± 15, 215 ± 33	48

a: estimated by DLS measurement. b: calculated by assuming grafted magnetite particles as a sphere with 10 nm or 25 nm in diameter, and graft polymer length obtained from Eq. (1).

polymers in good solvents, as obtained by Eq. (1), on magnetite were approximately 3-4 times as long as those in the dry state, as obtained by Eq. (2). This elongation is good in agreement with the results of reference [11]. In that study, Fukuda et al. showed that the thickness of PMMA brushes with σ (0.14-0.42 chains/nm²) in toluene is approximately 4-7 times greater than that in the dry state estimated by an atomic force microscope (AFM).

For this reason, the height h of the grafted layer obtained by Eq. (1) was adopted as the equilibrium diameter in good solvent.

Considering those equilibrium diameters, PS- and P3VP-grafted magnetite (diameter 10 nm) in chloroform were dispersed as aggregates of (a) approximately 3 or 4 particles, (b) 5 or 6 particles, or, on the other hand, as aggregates of (c) approximately 2 particles in pH 3.0 at the magnetic response measurement condition. In the case of diameter 25 nm, the results were similar to diameter 10 nm. From the rate of decrease of normalized absorbance and size distribution, it seems that magnetic response is influenced by the dispersion states in solutions and a magnetite particle size resulting from magnetic moments.

Additionally, TEM images supported the effect of grafted polymer. Although non-grafted magnetite nanoparticles were observed as aggregation states because of strong magnetic interaction, polymer-grafted magnetite nanoparticles were observed as fine dispersion, in spite of strong magnetic interaction.

4. CONCLUSION

In conclusion, the nitroxide-mediated radical polymerization initiator with a phosphoric acid group gave controlled polystyrene (PS) and poly(3-vinylpyridine) (P3VP) graft layers on the magnetite nanoparticles surfaces. PS- and P3VP-grafted magnetite nanoparticles were stably dispersed in good solvents for polymer chain due to the steric repulsion among grafted chains and affinity against solvents. Additionally, by protonation, P3VP-grafted nanoparticles were dispersed in acid solution, and by quarternization with iodomethane, they were dispersed in neutral aqueous solution. Finally, the dispersion state in

solution and a magnetite particle size resulting from magnetic moments are assumed to influence their magnetic response.

Acknowledgements

The authors would like to thank Prof. K. Enpuku (Kyushu University) for providing magnetite particles. R.M. acknowledges the financial support of Grant-in-Aid Scientific Research (A) (No(2)15205028) and Japan-Korea Basic Scientific Cooperation Program from Japan Society for the Promotion of Science. This work was partially supported by a Grant-in-Aid for the 21st century COE program "Functional Innovation of Molecular Informatics" from the Ministry of Education Culture, Sports, and Technology of Japan.

References

- [1] K. Ohno, K. -M. Koh, Y. Tsujii, and T. Fukuda, *Macromolecules*, **35**, 8989(2002).
- [2] K. Ohno, K. -M. Koh, Y. Tsujii, and T. Fukuda, *Angew. Chem. Int. Ed.*, **42**, 2751(2003).
- [3] X. Z. Ding, A. Fischer, A. Brembilla, and P. Lochon, *J. Polym. Sci., A. Polym. Chem.*, **38**, 3067(2000).
- [4] R. Matsuno, K. Yamamoto, H. Otsuka, and A. Takahara, *Chem. Mater.*, **15**, 3(2003).
- [5] C. J. Hawker, G. G. Barclay, and J. Dao, *J. Am. Chem. Soc.*, **118**, 11467(1996).
- [6] P. G. de Gennes, *Macromolecules*, **13**, 1069(1980).
- [7] S. T. Milner, *Science*, **251**, 905(1991).
- [8] C. Marques, J. -F. Joanny, and L. Leibler, *Macromolecules*, **21**, 1051(1988).
- [9] J. -L. Barrat and J. -F. Joanny, *Adv. Chem. Phys.*, **94**, 1(1996).
- [10] R. Jordan, A. Ulman, J. F. Kang, M. H. Rafailovich, and J. Sokolov, *J. Am. Chem. Soc.*, **121**, 1016(1999).
- [11] S. Yamamoto, Y. Tsujii, and T. Fukuda, *Macromolecules*, **33**, 5995(2000).

(Received October 11, 2003; Accepted October 25, 2003)