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Communications

Polystyrene-Grafted Magnetite Nanoparticles Prepared through Surface-Initiated Nitroxyl-Mediated Radical Polymerization

Ryosuke Matsuno, Kazuya Yamamoto,
Hideyuki Otsuka, and Atsushi Takahara*

Institute for Fundamental Research of Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

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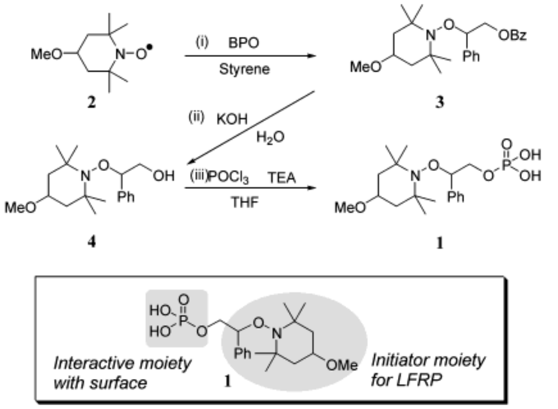
Surface modification of nanoparticles allows for the dispersion and stability of these nanoparticles in various solvents or polymer matrixes while they still maintain their physical characteristics. The modification technique frequently employed makes use of the interaction between the nanoparticle surface and functional groups of organic molecules, for example, silica particles and silane coupling agent[1] and gold particles and a functionalized thiol group.[2] Since the surface of metal oxide particles consists of metal−OH groups, a widely applicable surface modification technique is required. Recently, the authors reported on surface modification using the specific interaction between Al−OH groups of an inorganic nanofiber surface and *n*-octadecylphosphonic acid.[3] The interaction between the metal−OH and the phosphonic acid groups[4] is a strong candidate as an approach for surface modification of metal oxide nanoparticles, in general.[5] In this communication, we describe the preparation and properties of polystyrene-grafted magnetic magnetite nanoparticles based on both the interaction between metal−OH and the phosphonic acid groups and subsequent surface-initiated radical polymerization.

To realize direct polymerization of styrene from the surface of magnetite, a surface modifier with a nitroxyl-mediated initiator group known for living free radical polymerization (LFRP) was employed. As shown in Scheme 1, the designed modifier **1** has both a LFRP moiety as reported by Hawker[6] and a phosphonic acid moiety which can be expected to interact with metal−OH groups. Surface modifier **1** was synthesized from precursor **4**[7] through treatment with $POCl_3$ in the presence of triethylamine (TEA).[8] The structure of **1** was confirmed by ^1H NMR and IR spectra.

Scheme 1. Molecular Design and Synthesis of Surface Modifier with Living Free Radical Polymerization Initiator Moiety



Adsorption of **1** onto the magnetite surface was conducted as follows. Magnetite (d = 10 nm) and **1** (1:1, w/w) were added to tetrahydrofuran (THF) and the suspension was sonicated for 24 h with cooling, then centrifuged, decanted, and rinsed with ethanol several times to remove the nonchemisorbed **1**. The amount of adsorbed **1** on the nanoparticle surfaces was evaluated by thermogravimetric analysis (TGA).[9]

As shown in Scheme 2, polymerization of styrene on the surface of magnetite nanoparticles was carried out by heating a mixture of modified magnetite particle (3.0 mg) and styrene monomer (200 μL) at 125 °C. After polymerization, unreacted styrene monomer was removed by washing with chloroform and the magnetite dispersed solution was collected by applying a magnetic field.

To evaluate the dependence on reaction time of number-averaged molecular weights (M_n) and polydispersities (M_w/M_n) of the grafted polystyrene, polystyrene-

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* To whom correspondence should be addressed. Tel: +81-92-642-2721. Fax: +81-92-642-2715. E-mail: takahara@cstf.kyushu-u.ac.jp.

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(7) The synthesis of compound **4** was conducted following the methods described in ref 6 and in Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373.

(8) The synthesis of compound **1** was carried out by the following method. The mixture of **4**, triethylamine (TEA), and THF was added to THF solution with $POCl_3$ under iced water. The mixture was stirred for 2 h at room temperature. The solvent was then evaporated and chloroform was used for extraction. Surface modifier **1** was separated by silicagel chromatography (chloroform−ethyl acetate−methanol). **1**: ^1H NMR (400 MHz, DMSO) ppm: 0.64 (s, 3H), 1.14 (s, 3H), 1.29 (s, 3H), 1.46 (s, 3H), 1.14−1.98 (m, 4H), 3.28 (s, 3H), 3.75 (s, 1H), 4.03 (s, 1H), 4.37 (s, 1H), 4.88 (t, J = 6 Hz 1H), 7.40−7.43 (m, aromatic). FT-IR (KBr, cm^{-1}): 3424, 2979, 2945, 2815, 2605, 1172, 763, 700.

(9) The amount of absorbed **1** was 0.055 mg per 1 mg of magnetite particles. The calculated amount of **1** at the complete monolayer coverage of the magnetite surface was estimated to be 0.067 mg. The degree of coverage of **1** onto the magnetite surface was 82%. The measurement condition was 10 K/min program temperature rates under a nitrogen atmosphere.

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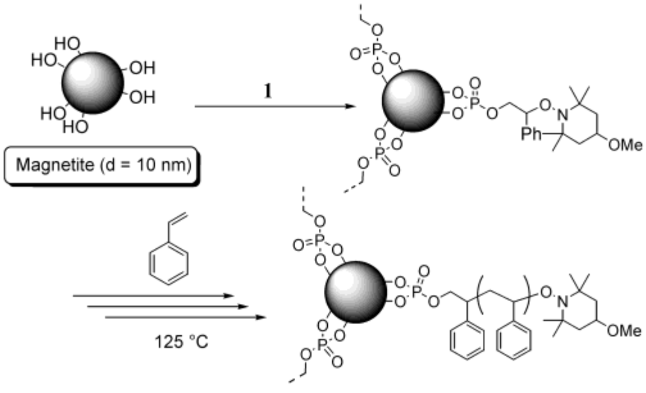
Scheme 2. Surface Modification of Magnetite with 1 and Surface-Initiated LFRP



grafted magnetite nanoparticles were added to hydrochloric acid (37%) to dissolve the iron oxide core and chloroform was then used to extract the desorbed polystyrene. The harvested polystyrene was recovered by reprecipitation in ethanol.

Figure 1 shows M_n and M_w/M_n of polystyrene grafted from the magnetite surface based on reaction time. It was confirmed by GPC measurement that polystyrenes with a high molecular weight and low polydispersities (M_w/M_n < 1.25) were grafted onto the magnetite particle surface and that polydispersity did not depend on reaction time. These results show that the nitroxyl-mediated initiator adsorbed on the magnetite surface by the interaction between Fe−OH and phosphonic acid groups successfully initiated the radical polymerization of styrene.

To examine the dispersibility and stability of the polystyrene-grafted magnetite in organic solvents, these modified magnetite nanoparticles were added to chloroform and dispersed by ultrasonic wave for 10 min. The dispersibility and stability were evaluated by ultraviolet−visible (UV−vis) absorption spectroscopy and transmission electron microscopy (TEM) observation.

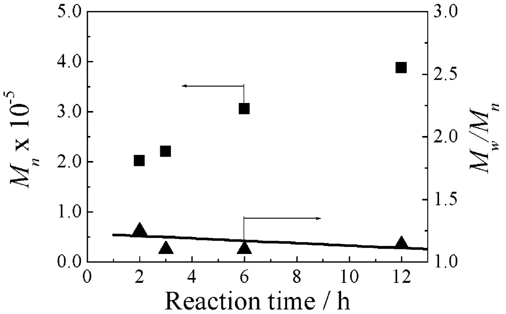


Figure 1. Dependence on reaction time of molecular weights (square) and polydispersities (triangle) of polystyrene grafted from the magnetite surface (2 h: $M_n = 202\,000$, $M_w/M_n = 1.25$; 3 h: $M_n = 221\,000$, $M_w/M_n = 1.12$; 6 h: $M_n = 306\,000$, $M_w/M_n = 1.12$; 12 h: $M_n = 388\,000$, $M_w/M_n = 1.14$).

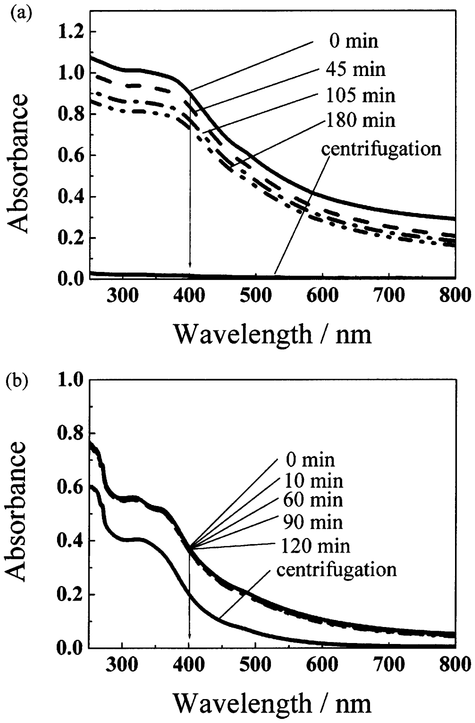


Figure 2. UV−vis spectra of (a) unmodified and (b) polystyrene-modified magnetite (M_n = 388 000, M_w/M_n = 1.14) particles in $CHCl_3$ (0.32 mg/mL).

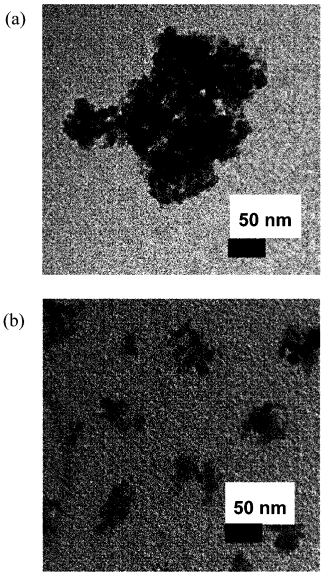


Figure 3. TEM images of (a) unmodified (×80 000) and (b) polystyrene-modified magnetite (×80 000), dispersed at 0.01 mg/mL in $CHCl_3$.

Figure 2 shows the UV−vis absorption spectra of (a) unmodified and (b) polystyrene-modified magnetite particles as a function of time. The centrifugal separation was 3500 rpm for 20 min. In the case of unmodified magnetite particles, absorbance (at λ = 400 nm) decreased from 0.90 to 0.73 over time because the magnetite particles coagulated by magnetic interaction and precipitated to the bottom of the UV cell. Finally, absorbance reached almost 0 by centrifugal separation over a longer period of time. On the other hand, in the case of polystyrene-modified magnetite, even after centrifugal separation, absorbance (at λ = 400 nm) was almost constant at 0.37. We believe that steric repulsion of a polystyrene chain on the magnetite surface blocks coagulation by magnetic interaction of the magnetite core and that the affinity of magnetite particles to chloroform was improved by the presence of polystyrene on the magnetite surface. The dispersibility and stability of magnetite in chloroform were thus improved by this surface modification using polystyrene. Toluene, ethyl acetate, and benzene are good solvents for the dispersion of modified particles besides chloroform. On the other hand, in water, methanol, and acetone, the modified particles aggregated and precipitated. The dispersion of the modified particles depends on whether the solvent is a good solvent or a poor solvent for polystyrene.

Figure 3 shows TEM images of (a) unmodified and (b) polystyrene-modified magnetite particles prepared by chloroform dispersion after sonication. Unmodified magnetite was observed as an aggregate over several hundred nanometers by strong interaction, that is, magnetic interaction. In contrast, polystyrene-modified magnetite was observed to have fine dispersion at 50 nm or less. These findings clearly reveal that the surface-initiated polymerization of styrene from magnetite nanoparticles allows dispersion and stability in organic solvents.

In summary, the authors successfully prepared the polystyrene-grafted magnetite particles using surface modifier **1** with both LFRP moiety and phosphonic acid groups which can interact with Fe−OH groups on the magnetite surface. With this method, it is possible to control the length of the polymer grafted onto the nanoparticle. Since the polystyrene-grafted magnetite particles disperse stably in organic solvents such as chloroform, toluene, ethyl acetate, benzene, and others (solvents for polystyrene), they can be used as nanofiller for polymer matrix. The present method of preparation can be highly useful for other metals or metal oxides that interact strongly with a phosphonic acid group.

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