

Preparation of Micrometer-Sized, Monodisperse, Magnetic Polymer Particles

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ABSTRACT: Micrometer-sized, monodisperse, magnetic composite particles were prepared by heating micrometer-sized, monodisperse, hollow polystyrene/polydivinylbenzene composite polymer particles at 200°C for 4 h (particles had been dipped in pentacarbonyliron) and then washed in 12 N HCl and water. The hollow polymer particles were produced by seeded polymerization by the dynamic swelling method that was proposed by authors. The magnetic

composite particles contained Fe₃O₄, the content of which was 49% based on total weight, and were attracted easily in water by a 1650 G magnet. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 428–433, 2003

Key words: magnetic polymers; crosslinking; swelling; colloids; separation techniques

INTRODUCTION

Polymer particles with hollow structures have received much attention in many industrial fields. These particles are used as weight-saving thermal insulation, hiding and opaquifying agents, and as microcapsules. For example, submicrometer-sized thermoplastic styrene/acrylic polymer particles containing one hollow at the center were produced by alkali swelling of carboxylated polymer particles with a core-shell structure.¹ We have also prepared submicrometer-sized, monodisperse styrene-butyl acrylate-methacrylic acid terpolymer and styrene-methacrylic acid copolymer emulsion particles with many hollows in the inside by stepwise treatment with alkali and acid^{2–4} and by alkali treatment at temperatures higher than the glass transition temperature of the base polymer, followed by cooling to room temperature.^{5–7} Moreover, micrometer-sized, monodisperse, crosslinked polymer particles with a single hollow at the center have been produced^{8–10} by seeded polymerization of highly swollen particles (divinyl monomer/solvent). These particles were prepared by the “dynamic swelling method” (DSM), which was proposed for production of micrometer-sized, monodisperse polymer particles with >5- μ m-size diameter by the authors.^{11, 12}

Magnetic particles are attractive for wastewater treatment¹³ and for the area of biotechnology¹⁴ in

which enzymes and cells are separated and purified. The particles are desirable if they have a suitable size, narrow size distribution, and functionalized surface.

In this article, micrometer-sized, monodisperse magnetic composite particles with a vinyl group at their surfaces were prepared with the micrometer-sized, monodisperse, hollow particles just described.

EXPERIMENTAL

Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB; Nippon Steel Chemical Company Ltd., DVB-960; purity, 96%) was washed with 1N NaOH and deionized water to remove polymerization inhibitors before use. Regent grade benzoyl peroxide (BPO) and 2,2'-azobis(isobutyronitrile) (AIBN) were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Polyvinyl alcohol (PVA; Nippon Synthetic Chemical Industry Company, Ltd., Gohsenol GH-17; degree of polymerization, 1700; degree of saponification, 88%) and poly(acrylic acid) (PAA) were used as colloidal stabilizers. The PAA was prepared by solution polymerization of acrylic acid in 1,4-dioxane. Analytical grade *p*-xylene, reagent grade ethanol and hydrochloric acid, and pentacarbonyliron (Aldrich; purity, 99.999%) were used as received.

Preparation of PS seed particles

Micrometer-sized, monodisperse PS seed particles were produced by dispersion polymerization of styrene in an ethanol/water (7/3, w/w) medium in the

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TABLE I
Recipe for the Preparation of Micrometer-Sized Monodisperse PS Seed Particles by Dispersion Polymerization^a

Ingredient ^b	Amount, g
Styrene	140
AIBN	2.35
PAA	16.8
Ethanol	959
Water	280

^a Determined at 70°C, under N₂ atmosphere, for 24 h, with stirring at 60 rpm.

^b Abbreviations: PS, polystyrene; AIBN, 2,2'-azobisisobutyronitrile; PAA, poly(acrylic acid).

presence of PAA colloidal stabilizer with AIBN initiator at 70°C for 24 h under a nitrogen atmosphere. The polymerization took place in a four-necked, round-bottomed flask according to the optimum conditions in a previous article.¹⁵

Production of composite particles with a single hollow at the center

Swelling of the PS seed particles produced by dispersion polymerization with DVB and xylene was carried out by DSM under the conditions listed in Table II according to the previous articles.⁸⁻¹⁰ Seeded polymerization for the (DVB/xylene)-swollen PS particles was carried out in sealed glass tubes under a nitrogen atmosphere at 70°C for 24 h. The particles were observed with a JEOL JEM-2010 transmission electron microscope (TEM).

Production of magnetic polymer particles

The dried hollow particles were dipped in pentacarbonyliron at room temperature for 20 h to allow the pentacarbonyliron to penetrate into the hollow. This

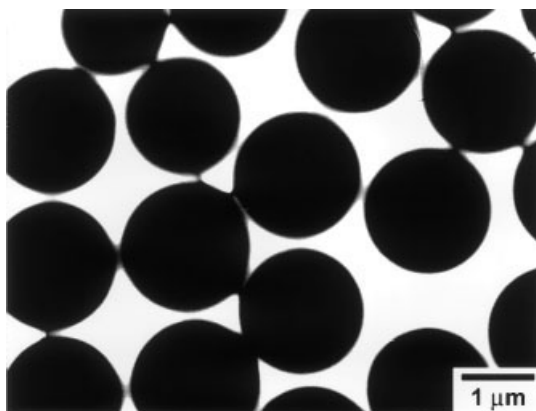


Figure 1 A TEM photograph of PS-seed particles produced by dispersion polymerization under the conditions listed in Table I.

TABLE II
Recipe for the Production of PS/PDVB Composite Particles by Seeded Polymerization^a for the Dispersion of (DVB/Xylene)-Swollen PS Particles Prepared by the Dynamic Swelling Method

Ingredient	Amount, g
PS particles ^b	0.3
DVB ^c	1.5
Xylene	4.5
BPO	0.03
PVA	0.15
Ethanol	70.0
Water	30.0 + 400 ^d

^a Determined at 70°C, under N₂ atmosphere, for 24 h, with stirring at 60 rpm

^b D_v 1.74 μm; C_v 3.4%.

^c Purity, 96%.

^d 400 g of water was post-added at the rate of 18 mL/h.

^e Abbreviations: PS, polystyrene; DVB, divinylbenzene; BPO, benzoylperoxide; PVA, poly (vinyl alcohol).

dispersion was placed in a 50-mL capacity stainless steel pressure-resistant vessel with a polytetrafluoroethylene inner container, and the vessel was dipped in an oil bath at 200°C for 4 h. After the treatment, the composite particles were washed with 12N HCl aqueous solution and water. Hereafter, these treatments will be called "inclusion treatment".

Observation of particles

Each particle was observed with a Nikon MICROPHOT-FXA optical microscope, TEM, and a Hitachi S-2500 scanning electron microscope (SEM).

Observations of ultrathin cross-sections of particles

Each dried particle was dipped in epoxy matrix, cured at room temperature for 24 h, and microtomed. The

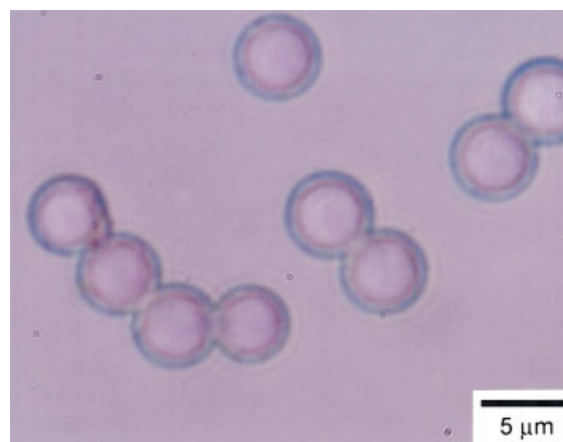


Figure 2 An optical micrograph of PS/PDVB composite particles produced by seeded polymerization of the dispersion of (DVB/xylene)-swollen PS particles prepared by the dynamic swelling method under the conditions listed in Table II.

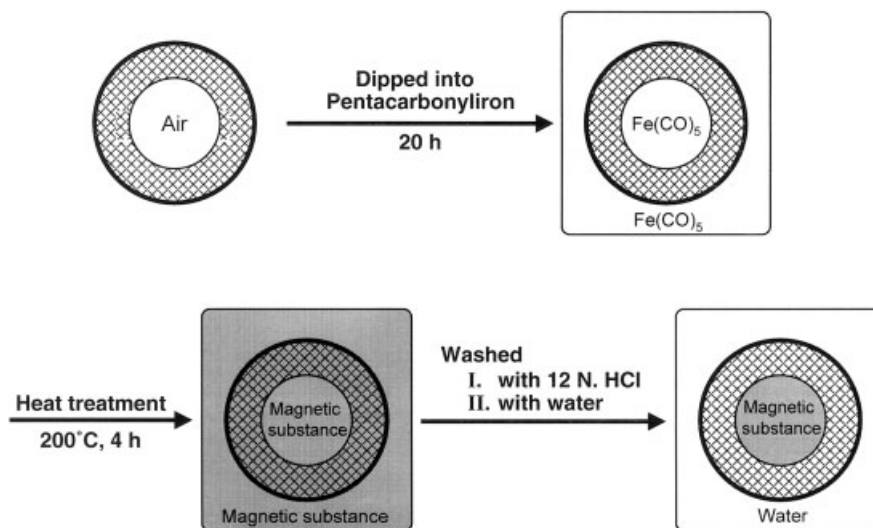


Figure 3 Schematic diagram for the inclusion of magnetic substance in the hollow of PS/PDVB composite particle.

ultrathin cross-sections were put on copper grids and observed with a TEM. They were also observed with an X-ray electron probe microanalyzer (JEOL, JXA-8900) to analyze distribution states of iron and oxygen atoms.

X-ray diffraction (XRD)

XRD spectra of the magnetic polymer particles were measured with a Rigaku RINT 2100 diffractometer, using Cu K α (40 kV, 20 mA).

Measurement of magnetite content in the magnetite particle

The content of magnetite in the magnetic polymer particles was evaluated by measuring weight loss by thermogravimetry (Seiko Instrument TG/DTA 220U). The dried particles were placed on platinum pan (φ 5 mm), and temperature was raised to 750°C at 10°C/min under N₂ flow.

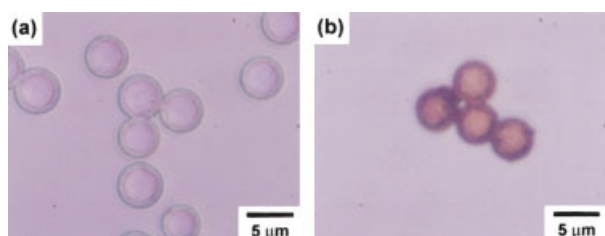


Figure 4 Optical micrographs of the PS/PDVB composite particles (a) before and (b) after the inclusion treatment of the magnetic substance.

Introduction of sulfate groups at the surface of the composite particle

Chemical modification of vinyl groups at the surface of the composite particle, which were derived from DVB units, was carried out with concentrated sulfuric acid for 2 h at 0° to introduce a sulfate group. The particle was washed repeatedly by centrifugation with water after the modification.

X-ray photoelectron spectroscopy (XPS)

XPS data were obtained with a Shimadzu ESCA-3400 using Mg K α (12 kV, 20 mA). The pressure in the measurement chamber was $\sim 5 \times 10^{-7}$ Pa. Dried particles were spread on an indium plate with a spatula.

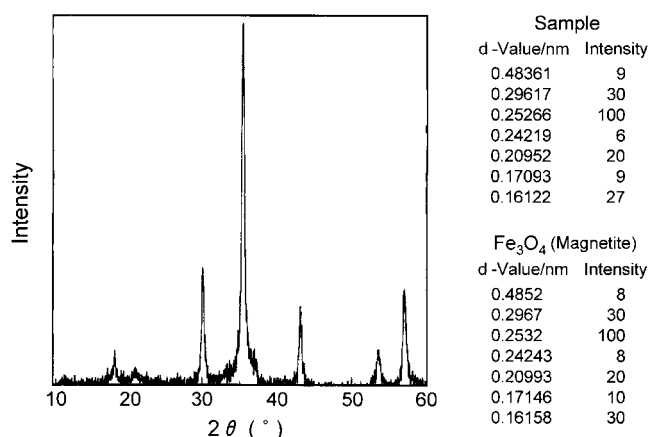


Figure 5 An X-ray diffraction pattern of the PS/PDVB/Fe₃O₄ composite particles after the inclusion treatment of the magnetic substance.

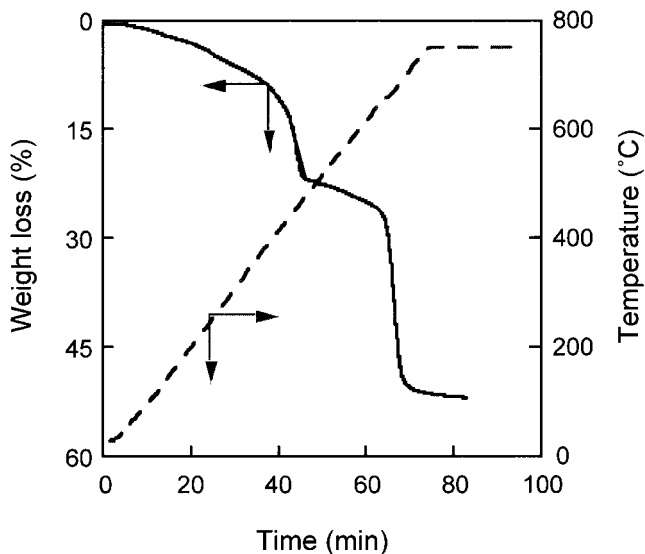


Figure 6 A TGA curve of the PS/PDVB/Fe₃O₄ composite particles.

Determination of the amount of sulfate groups at the particle surface

The amount of sulfate groups at the particle surface was determined by measuring the heat of the neutralization reaction between sulfate group and KOH with isothermal titration calorimetry (CSC Company, 4200 ITC) according to the optimum conditions given in a previous article.¹⁶

RESULTS AND DISCUSSION

A TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table I is shown in Figure 1. The PS particles were

spherical and monodisperse: the number-average diameter (D_n) and coefficient of variation (CV) were 1.74 μm and 3.4%, respectively, which were determined from the particle observation on TEM photographs with a Personal Image Analysis System (PIAS Company, Ltd., LA-525, Osaka, Japan).

An optical micrograph of the hollow PS/PDVB composite particles produced by seeded polymerization of the dispersion of (DVB/xylene)-swollen PS particles prepared by DSM under the conditions in Table II is shown in Figure 2. The D_n , CV, and number-average hollow diameter (D_h) were 4.8 μm , 6.1%, and 4.2 μm , respectively. The low CV means high monodispersity. All particles had a single hollow at the center.

A schematic diagram of the inclusion treatment of magnetic substance in the hollow of the PS/PDVB composite particle is shown in Figure 3. Because pentacarbonyliron existed both inside and outside of the hollow polymer particle, the decomposition products of pentacarbonyliron also existed on both surfaces after the treatment at 200°C for 4 h. To selectively remove the decomposition products at the outside surface, the particles were washed with 12N HCl aqueous solution. This time, HCl aqueous solution was hard to penetrate into the composite particle because of the hydrophobic shell.¹⁷

Optical micrographs photographs of the hollow PS/PDVB composite particles (a) before and (b) after the inclusion treatment are shown in Figure 4. The size and monodispersity after the treatment were, respectively, the same as those before the treatment. The contrast of the particles after the treatment was darker than that of ones before the treatment. This result seems to be based on a decomposition product of

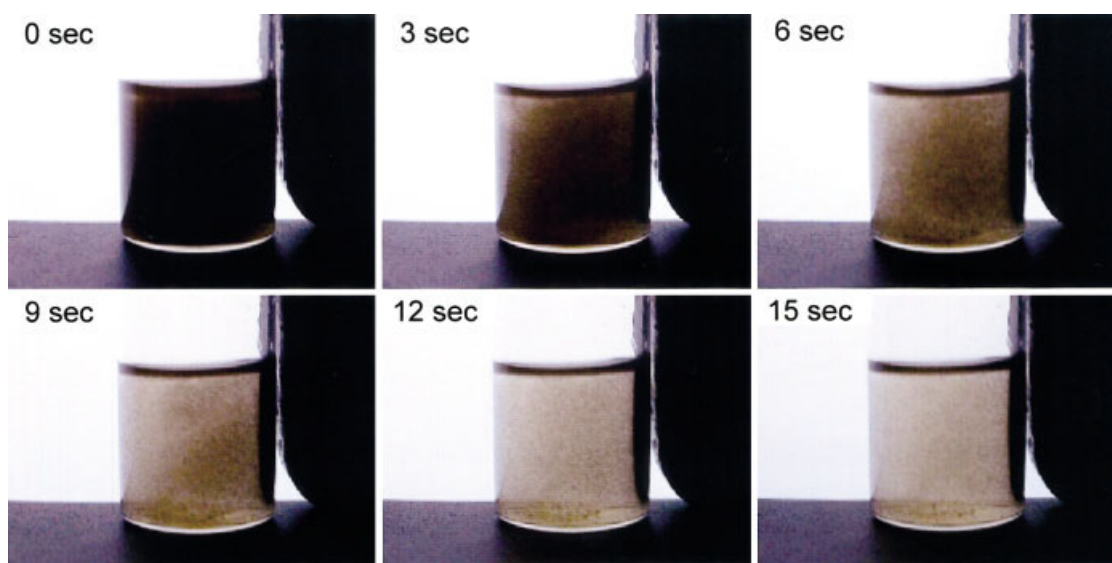


Figure 7 Consecutive photographs indicating the attraction of the PS/PDVB/Fe₃O₄ composite particles dispersing in water by a magnet (1650 G).

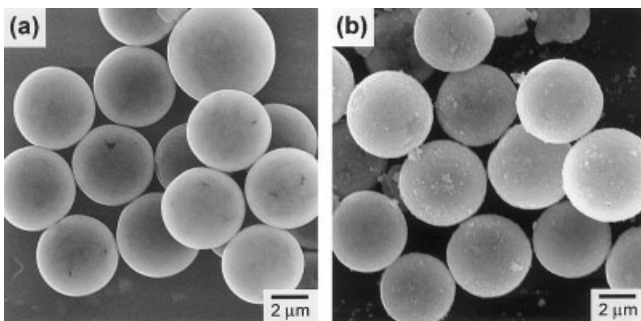


Figure 8 SEM photographs of the PS/PDVB/ composite particles (a) before and (b) after the inclusion treatment of the magnetic substance.

pentacarbonyliron. In other words, this result suggests that a magnetic substance was introduced into the hollow particles.

An X-ray diffraction pattern of the hollow PS/PDVB composite particles after the inclusion treatment is shown in Figure 5. All of the peak positions and intensity ratios, which were observed in 2θ range between 10° and 60° , respectively, agreed well with those of the Fe_3O_4 crystals.¹⁸ This result indicates that Fe_3O_4 was included in the composite particle as the decomposition product of pentacarbonyliron.

A thermogravimetric analysis (TGA) curve of the PS/PDVB/ Fe_3O_4 composite particles is shown in Figure 6. PS and PDVB in the composite particles were markedly decomposed around 400°C and 600°C , respectively. The content of Fe_3O_4 in the composite particle determined from the TGA curve was 49 wt %.

Consecutive photographs indicating the attraction of the PS/PDVB/ Fe_3O_4 composite particles dispersing in water by a magnet (1650 G) are shown in Figure 7.

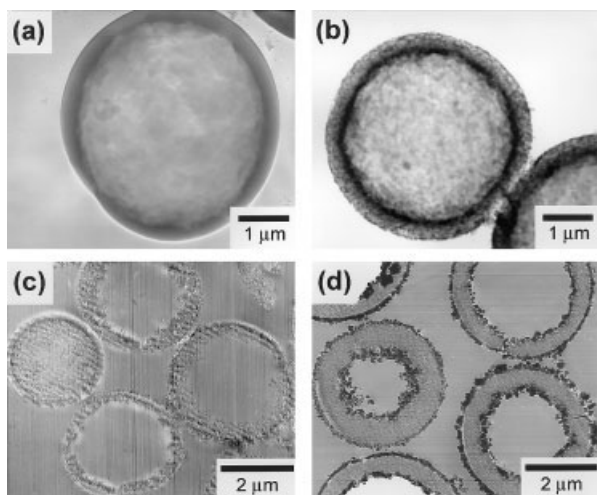


Figure 9 TEM photographs of the (a, b) PS/PDVB composite particles and of (c, d) ultrathin cross-sections of the particles before (a, c) and after (b, d) the inclusion treatment of the magnetic substance.

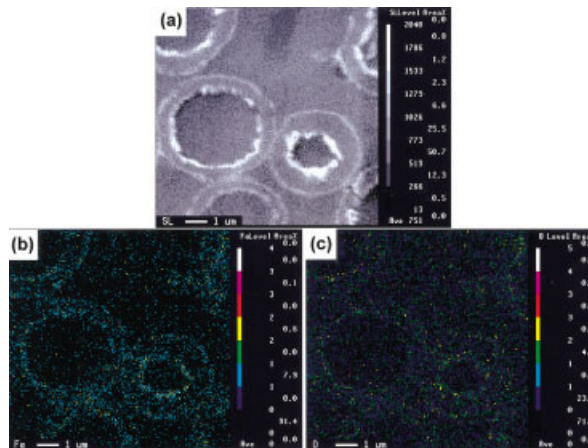


Figure 10 An (a) SEM photograph and distribution images of (b) iron and (c) oxygen in ultrathin cross-sections of the PS/PDVB/ Fe_3O_4 composite particles after the inclusion treatment of the magnetic substance, determined with an electron probe microanalyzer.

The composite particles were swiftly attracted by the magnet within 15 s.

SEM photographs of the (a) hollow PS/PDVB and (b) PS/PDVB/ Fe_3O_4 composite particles are shown in Figure 8. Almost all decomposition product (Fe_3O_4) was removed by washing with 12N HCl aqueous solution for a few minutes, although a small amount of the decomposition product was observed at the surfaces.

TEM photographs of the (a, b) hollow PS/PDVB composite particles and of (c, d) ultrathin cross-sections of the particles before (a, c) and after (b, d) the inclusion treatment are shown in Figure 9. In the TEM photographs of the composite particles after the treatment, a high contrast region was observed at the inner wall of the hollow that was not observed before the

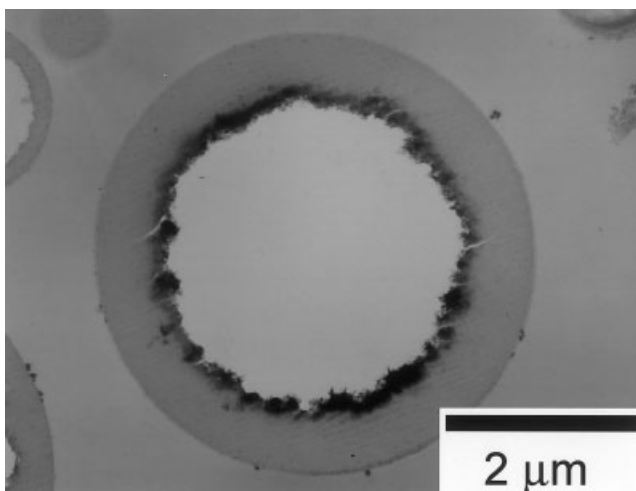


Figure 11 TEM photographs of ultrathin cross-sections of the PS/PDVB/ Fe_3O_4 composite particles after removing Fe_3O_4 at the outer surfaces.

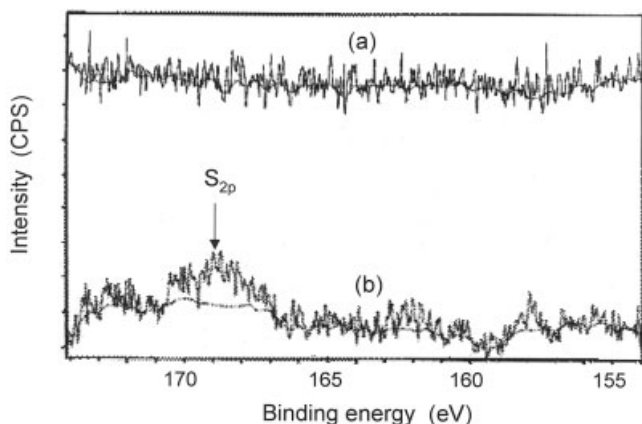


Figure 12 X-ray photoelectron spectroscopy spectrum of S_{2p} at the surface of the magnetic PS/PDVB/ Fe_3O_4 composite particles (a) before and (b) after sulfuric acid treatment.

treatment. In TEM photographs of ultrathin cross-sections of the composite particles, the high contrast region, which was due to Fe_3O_4 , was observed along the inner wall of the hollow of the composite particle after the treatment. It was observed at the outer surfaces of the composite particles.

An SEM photograph (a) and distribution images of iron (b) and oxygen (c) atoms in ultrathin cross-sections of the hollow PS/PDVB/ Fe_3O_4 composite particles after the inclusion treatment measured with X-ray electron probe microanalyzer are shown in Figure 10. The iron and oxygen atoms existed at the inner wall of the hollow structure and in the shell of the composite particles. This result indicates that Fe_3O_4 could be encapsulated in the hollow. It was also observed at the outer surfaces of the composite particles, but it was removed by the longer washing time, as shown in Figure 11. It is confirmed that the composite particles after removing Fe_3O_4 at the outer surfaces were attracted by the magnet.

The XPS spectra for (a) the PS/PDVB/ Fe_3O_4 composite particles and (b) those composite particles modified with sulfuric acid are shown in Figure 12. After the modification, the peak due to S_{2p} was observed at a binding energy of ~ 169 eV. This result indicates that the sulfate group was introduced by the reaction of vinyl groups with concentrated sulfuric acid at the surface of the composite particle. The amount of sulfate group at the surface was $0.7 \mu\text{mol}/\text{m}^2$ as deter-

mined by measurement by isothermal titration calorimetry. The occupied area of one sulfate group calculated from the value was 2.5 \AA^2 , although the value might include sulfate groups existing inside the shell of which the thickness is <10 nm. This occupied area was comparable to that (4 \AA^2) of vinyl group at the surface of the PS/PDVB composite particles produced by DSM.¹⁹

From the results just presented, it is concluded that an $\sim 5\text{-}\mu\text{m}$ -sized, monodisperse, magnetic polymer particle with a reactive vinyl group at its surface could be prepared.

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