

Synthesis of Silica Hybrid Nanoparticles Modified with Photofunctional Polymers and Construction of Colloidal Crystals

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ABSTRACT: Photofunctional polymer as silane coupling agent (PFD) was prepared by free radical copolymerization of 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) and methyl methacrylate (MMA) in the presence of (3-mercaptopropyl)trimethoxysilane (MPMS) as chain transfer agent. Next, silane (SiO₂; the average diameter D_n = 192 nm) nanoparticles was surface-modified with PFD and 3-(trimethoxysilyl)propyl methacrylate (γ -MPS) by covalent bond formed between silanol groups and silane coupling agents. The PFD and γ -MPS functionalizations changed the silica surface into hydrophobic nature and

provided grafting initiation sites and methacrylate terminal groups respectively. We performed the construction of hybrid nanocomposites by using these modified SiO₂ nanoparticles. It was found from electron microscopy observations that SiO₂ particles were packed into repeating cubic arrangements in a poly(methyl methacrylate) (PMMA) matrix such as colloidal crystals. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2434–2440, 2009

Key words: silica particle; photofunctional polymer; silane coupling agent; colloidal crystal

INTRODUCTION

Recently, there has been a lot of work on the elaboration of nanocomposite systems by embedding of inorganic particles into polymer matrices.^{1–10} These materials represent a new class of polymeric materials which combine the unique physical properties of the inorganic particles with the processability and flexibility of the organic polymer matrix. Silica (SiO₂) nanoparticles received recent attention because of their superior properties over the microsize particles.^{11,12} However, its nanocomposites with organic polymers, SiO₂ generally exists as agglomerates. It becomes important to disperse the SiO₂ particles in the nanocomposites with other polymers for utilizing the synergic properties and fluid applications. On the other hand, the unique ability of photonic crystals to manipulate the transmission of light may lead to potential applications ranging from simple optical switches to an optical computer.¹³ Opals are naturally occurring three dimensional photonic crys-

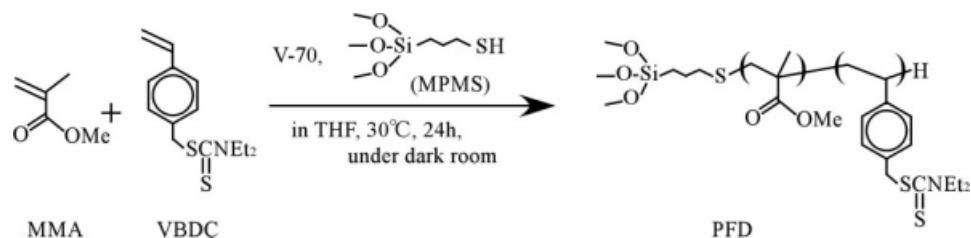
tals: their microstructure consists of SiO₂ spheres of about 150–300 nm in diameter, which are tightly packed into repeating hexagonal or cubic arrangements.¹⁴ Synthetic opals (colloidal crystals) use this same pattern, although they can be made from different materials.

The silica surface consists of two types of functional groups, siloxane (Si–O–Si) and silanol (Si–OH),^{15,16} which provide functionalization with different functional groups. Thus, silica modification can occur via the reaction of particular molecules with either the siloxane or the silanol. Modification of the surface is mostly done by using an appropriate molecule designated as precursor silane coupling agent. Thus, a covalent bond can be formed between the silica surface and the silane coupling agent to give a new modified silica surface with an anchored functionality. More recently, Park and coworkers¹⁷ have prepared poly(methyl methacrylate) (PMMA)-SiO₂ core-shell nanocomposite particles from the dispersion polymerization in supercritical carbon dioxide. In their approach, 3-(trimethoxysilyl) propyl methacrylate-functionalized SiO₂ were first dispersed in the reaction medium, followed by the polymerization with methyl methacrylate (MMA). The polymer-grafted SiO₂ was also prepared as reported previously.^{18,19} For example, the PMMA-grafted SiO₂ particles were synthesized as follows¹⁹: (1) Radical polymerization of MMA was carried out in the

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Scheme 1 Polymerization scheme for the synthesis of photofunctional polymers (PFD) as silane coupling agent.

presence of (3-mercaptopropyl)trimethoxysilane as chain transfer agent to obtain PMMA-Si(OMe)₃. (2) the PMMA-grafted SiO₂ was prepared by coupling of SiO₂ particles with PMMA-Si(OMe)₃. Moreover, colloidal crystals formed by PMMA-grafted SiO₂ particles were immobilized by a procedure consisting of gelation by radical copolymerization. Recently, we have also established a new synthetic method for crosslinked polystyrene (PS) particles possessing photofunctional *N,N*-diethyldithiocarbamate (DC) groups on their surface by free-radical emulsion copolymerization of a mixture of styrene (St), divinylbenzene (DVB), and 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) with redox system as an initiator under UV irradiation.²⁰ In this copolymerization, the inimer VBDC acted the formation of hyperbranched structures by living radical photopolymerization. Subsequently, core-shell particles were synthesized by photo-induced atom transfer radical polymerization (ATRP) of MMA initiated by photofunctional PS particles as a macroinitiator. Moreover, we have extended this idea to the synthesis of PMMA brushes encapsulated SiO₂ particle.²¹ That is, SiO₂-crosslinked PS (possessing photofunctional DC groups on their surface) core-shell particles were synthesized first by free-radical emulsion copolymerization of a mixture of St, DVB, VBDC, and 2-hydroxyethyl methacrylate (HEMA) with a radical initiator under UV irradiation. At the same time, this system also led to the formation of hyperbranched structure by living radical mechanism of inimer. Subsequently, SiO₂-PMMA core-shell particles (PMMA brushes encapsulated SiO₂ particle) were prepared by grafting from photo-induced ATRP approach of MMA initiated from DC groups of crosslinked PS particle surface as a macroinitiator.

The objective of this study is to synthesize the silica hybrid nanoparticles (diameter $D_n = 192$ nm) modified with photofunctional polymer or monofunctional silane coupling agents. In addition, we dispersed such functional SiO₂ particles in MMA monomer and performed the construction of SiO₂ hybrid nanocomposites by grafting from DC groups under UV irradiation.

EXPERIMENTAL

Materials

VBDC was synthesized by the reaction of *p*-chloromethylstyrene (Seimi Chemical Industry, Tokyo,

Japan) with *N,N*-diethyldithiocarbamate sodium (Tokyo Kasei Organic Chemicals, Tokyo, Japan) in acetone. Details concerning synthesis and purification of VBDC have been given elsewhere.²² MMA (Tokyo Kasei Organic Chemicals, Tokyo, Japan) was distilled under high vacuum. SiO₂ sol (particle diameter = 192 nm, density $d_{\text{SiO}_2} = 1.74$ g/cm⁻³, MP-2040; 30 wt % alkaline aqueous solution, Nissan Chemical Industries, Tokyo, Japan), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70; Wako Pure Chemical Industries, Tokyo, Japan), (3-mercaptopropyl)trimethoxysilane (MPMS), 3-(trimethoxy-silyl)propyl methacrylate (γ -MPS), decahydronaphthalene, toluene, tetrahydrofuran (THF), tributyltin hydride (Bu₃SnH; Tokyo Kasei Organic Chemicals, Tokyo, Japan), and hydrofluoric acid (HF: 48 wt % in water, Kanto Reagent Division, Tokyo, Japan) were used as received.

Synthesis of photofunctional polymer (PFD) as silane coupling agent

PFD was prepared by free radical copolymerization of VBDC (0.93 g, 3.51 mmol) and MMA (3 mL, 28 mmol) in the presence of MPMS (0.1 mL) as chain transfer agent initiated by V-70 (0.7 wt % for total monomer) in THF (42 mL) at 30°C for 24 h in a dark room. Scheme 1 shows the reaction scheme for the synthesis of PFD. After polymerization, the copolymer was precipitated with a large excess of methanol. The yield of copolymer was 41% from gravimetric measurement. The content of DC groups of PFD was determined from the integration ratio of the methoxy protons ($\delta = 3.59$ ppm) of MMA units to methylene protons (4.04 ppm) of the DC groups by a proton nuclear magnetic resonance (¹H-NMR) spectra. ¹H-NMR spectroscopy (300 MHz, Bruker GPX300 NMR spectrometer, Germany) for PFD was performed in CDCl₃.

Synthesis of SiO₂ hybrid nanoparticles modified with PFD (H-SiO₂)

Figure 1 shows schematic representation of the process for the synthesis of SiO₂ hybrid nanoparticles (H-SiO₂). SiO₂ particles with average diameter of 192 nm were used in this study. For the surface

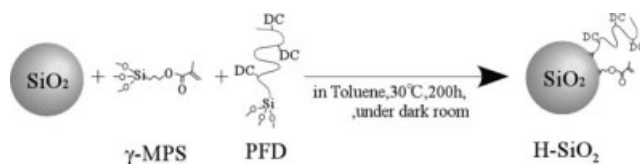


Figure 1 Schematic illustration for the synthesis of SiO₂ hybrid nanoparticles (H-SiO₂).

functionalization, PFD (1.3 g, 2.8×10^{-4} mol/L) and γ -MPS (0.03 mL, 1.3×10^{-4} mol/L) were added to 350 mg of SiO₂ particles dispersed in 15 mL of toluene and stirred for 200 h at 30°C in the sealed ampoule under a dark room. Modified SiO₂ was isolated by ultracentrifuge. Subsequently, this product was washed with toluene several times to remove the unreacted PFD and γ -MPS. The PFD and γ -MPS functionalizations change the silica surface into hydrophobic nature and provides grafting initiation sites (DC groups) and methacrylate terminal groups, respectively. To determine the introduction amounts of γ -MPS on silica surface, the supernatant solution after ultracentrifuge was measured by gas chromatography (Shimadzu, GC-14B, Kyoto, Japan) using decahydronaphthalene as internal standard sample.

The content of DC groups on SiO₂ surface was determined by the following method. As mentioned in a previous work (SiO₂-PMMA core-shell particles),¹⁹ photofunctional DC groups on the surface of PMMA brushes encapsulated SiO₂ particles were reduced with Bu₃SnH by radical transfer under 30 min of UV irradiation (SXUI 250 HAMQ 250-W high-pressure mercury lamp, Ushio Denki; UV intensity = 42 mW/cm², irradiation distance = 20 cm) in a high vacuum (1 wt % PMMA brushes encapsulated SiO₂ particles of THF solution). Then, we carried out also similar reaction using H-SiO₂ under the same conditions. Photolysis of VBDC leads to the initiating benzyl radical with inactive DC radical and such benzyl radical is quenched with Bu₃SnH. Then, the residual amount of Bu₃SnH was measured by gas chromatography using decahydronaphthalene as internal standard sample.

Construction of colloidal crystals

The prescribed MMA solution of H-SiO₂ (H-SiO₂; 84 wt %) was poured into a Petri dish. This weight percent was determined from calculation to give a body-centered cubic (BCC) packing structure. The calculation method will be mentioned later. The H-SiO₂ was dispersed in MMA under ultrasonic irradiation (Iguchi; 28 kHz, Tokyo) before polymerization. Radical photopolymerization was carried out in nitrogen atmosphere at 30°C under UV irradiation

for 6 h. This DC-mediated radical polymerization proceeded with living radical mechanism as proven previously by kinetic approaches.^{22,23} To observe the packing structures of SiO₂ particles, we prepared the microporous film by etching SiO₂ particles. That is, the composite film was broken in liquid nitrogen. Such composite film was immersed in HF aqueous solution to remove SiO₂ particles.

Measurements

The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of PFD were determined by gel permeation chromatography (GPC; Tosoh high-speed liquid chromatograph HLC-8120, Tokyo) using two TSK gel columns, GMH_{XL} [excluded-limit molecular weight ($M_{ELM} = 4 \times 10^8$)] and G2000H_{XL} ($M_{ELM} = 1 \times 10^4$), in series in THF as eluent (flow rate of 1.0 mL/min) at 40°C using calibration of PMMA standard samples.

The morphology and particle size of the polymer particles were investigated with a JEOL JSM7500-F scanning electron microscope (SEM). The number-average particle diameter (D_n) and particle size distribution [weight-average particle diameter/number-average particle diameter (D_w/D_n)] were determined by a survey of 300 samples picked from the photographs that were obtained. The hydrodynamic radius (R_h) of SiO₂ and H-SiO₂ particles were evaluated with Stokes–Einstein equation: $R_h = kT/6\pi\eta_0F_0$, where k , T , η_0 , and F_0 are the Boltzmann constant, the absolute temperature, the viscosity of the solvent, and the diffusion coefficient, respectively. F_0 was determined by dynamic light scattering (DLS; Photal DLS-8000PNA: Otsuka Electronics, Tokyo, He–Ne laser: $\lambda_0 = 632.8$ nm, 10 mW) data with cumulant method at 25°C in 2–10 mg/mL aqueous solution of SiO₂ or THF solution of H-SiO₂ particles (scattering angle = 90°). Sample solutions were filtered through membrane filters with a nominal pore of 0.5 μ m just before measurement.

The composition of H-SiO₂ particles was determined by thermogravimetric analysis (TGA). TGA was run in nitrogen atmosphere using a Seiko Instrument (EXSTAR 6000, Tokyo, Japan). Heating rate was 20°C/min.

RESULTS AND DISCUSSION

Synthesis of PFD as silane coupling agent

In the previous work,²⁰ we carried out free radical homopolymerization of VBDC initiated by V-70. As a result, the probability that a propagating polystyryl radical led to chain transfer was negligible. We synthesized PFD as silane coupling agent by free radical copolymerization of VBDC and MMA using

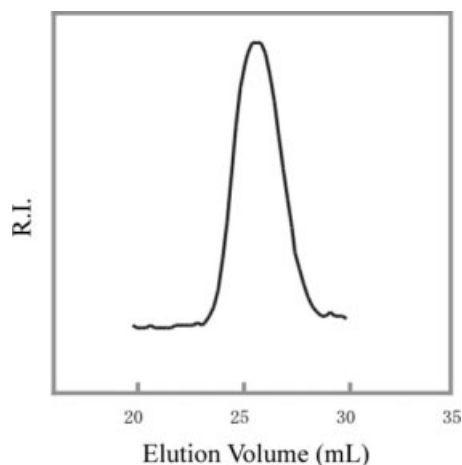


Figure 2 GPC profile of PFD photofunctional polymer as silane coupling agent.

MPMS as chain transfer agent. A typical GPC profile of PFD is shown in Figure 2. The GPC curve showed a unimodal distribution ($M_n = 4500$) and relatively broad polydispersity ($M_w/M_n = 1.55$). The $^1\text{H-NMR}$ spectrum also gives support to polymeric silane coupling agent having formed (see Fig. 3). The spectrum displays the expected resonances for aromatic protons (g, h; $\delta = 6.94\text{--}7.26$ ppm), methylene protons (j; 4.04 and 3.71 ppm), and methyl protons (k; 1.27 ppm) of VBDC units, methoxy protons (n; 3.59 ppm) of MMA units, and methylene protons (d; 2.48 ppm) and methoxy protons [a; 3.59 ppm, this peak overlapped with methoxy protons (n) of MMA units] of MPMS fragment. The ratio of MMA to VBDC units was estimated to be 4/1 by the integration ratio of $(n/3) \div (j/2)$, where we used j signal at 4.04 ppm. Then, the number of DC groups for PFD was 6.4 number per molecule, because the molecular weight of PFD ($M_{n,\text{PFD}}$) was 4500.

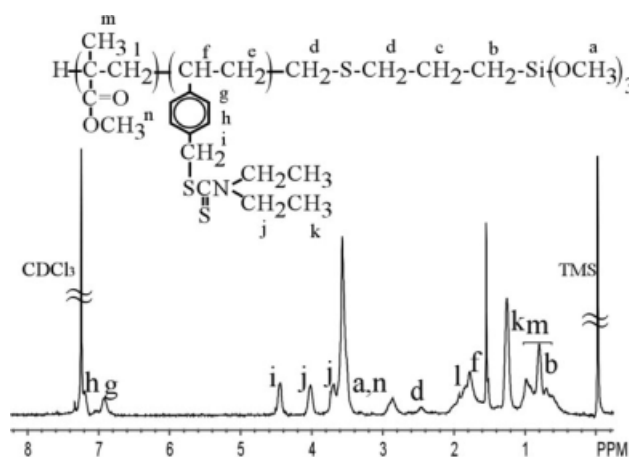


Figure 3 $^1\text{H-NMR}$ spectrum of PFD in CDCl_3 .

Synthesis of SiO_2 hybrid nanoparticles (H-SiO_2)

In preliminary experiment for the surface functionalization, only PFD was added to SiO_2 particles dispersed in toluene. We could not obtain stable emulsion of SiO_2 particles even for long reaction time (10 days). Therefore, we employed two kinds of silane coupling agents PFD and γ -MPS (low molecular weight silane coupling agent having methacrylate double bond). This reaction system gave stable emulsion of SiO_2 particles after 200 h. That is, modified- SiO_2 transferred to toluene phase, because the PFD and γ -MPS functionalizations changed the SiO_2 surface into hydrophobic nature.

A typical SEM photograph of H-SiO_2 hybrid particles shows in Figure 4(b), where Figure 4(a) shows SEM photograph of starting SiO_2 particles ($D_n = 192$ nm, $D_w/D_n = 1.01 \pm 0.05$). The product H-SiO_2 provided somewhat large spherical particles ($D_n = 198$ nm) and keeping narrow size distribution ($D_w/D_n = 1.01 \pm 0.06$). Figure 5 shows size distributions (D_n , hydrodynamic diameter) on DLS data of H-SiO_2 in THF and starting SiO_2 particles in water. Both

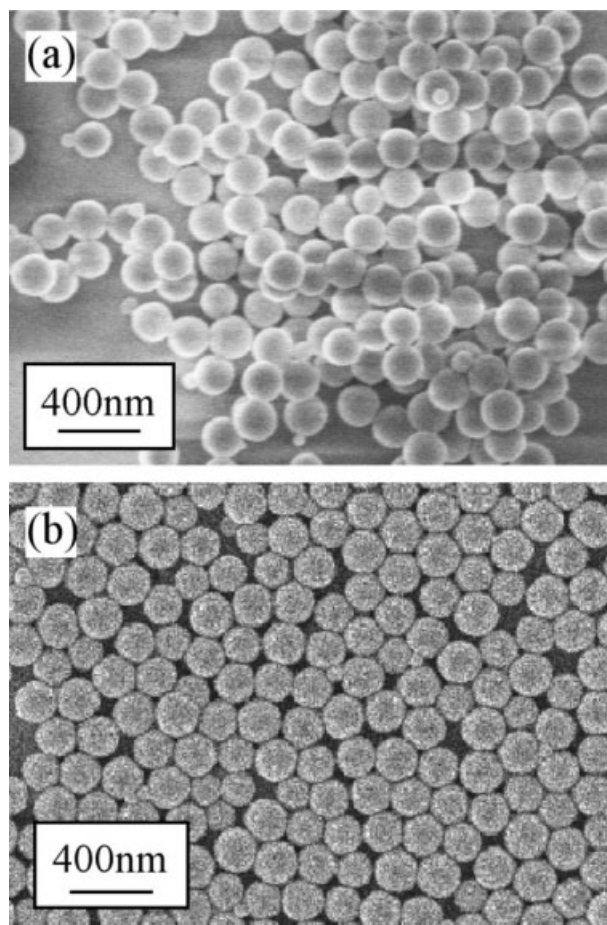


Figure 4 SEM photographs of (a) SiO_2 and (b) SiO_2 hybrid nanoparticle (H-SiO_2).

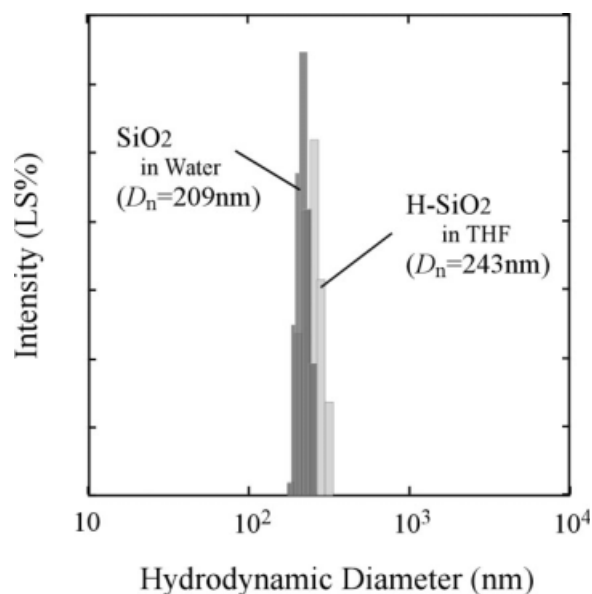


Figure 5 Size distribution of DLS data for SiO₂ in water and H-SiO₂ in THF.

profiles show unimodal distribution. Because H-SiO₂ particles were stabilized sterically with both PMMA grafted chains and γ -MPS fragments, these hybrid particles formed a single molecule in THF. Then, the hydrodynamic diameter of H-SiO₂ showed larger value ($D_h = 243$ nm) than that of starting SiO₂ particles ($D_h = 209$ nm) in solution.

To determine the composition of H-SiO₂ hybrid particles, we performed TGA measurements for H-SiO₂ particles. Figure 6 shows the TGA result for H-SiO₂ particles. A 6.6 wt % mass increase was observed after silane coupling reaction. Assuming that this organic layer is composed of PFD, the number (N_{PFD}) of grafted PFD on SiO₂ surface is calculated to be 6.09×10^4 mol/one H-SiO₂ particle, i.e., $(4/3)\pi r_1^3 d_{\text{SiO}_2} N_{\text{av}} (6.6/93.4 M_{\text{n,PFD}})$, where r_1 (96 nm), d_{SiO_2} (1.74 g/cm³), N_{av} (6.025×10^{23} mol⁻¹), and $M_{\text{n,PFD}}$ (4500) are radius of SiO₂, density of SiO₂, Avogadro number, and molecular weight of PFD silane coupling agent, respectively. Then, the number of DC groups on H-SiO₂ particle surface was estimated to be 3.2 mol/nm², i.e., $6.4N/4\pi r_2^2$, where r_2 (99 nm) is the radius of H-SiO₂ hybrid particles.

The content of DC groups for H-SiO₂ hybrid particles was determined by using the radical transfer reaction. H-SiO₂ (22.2 mg) was reduced with a less excess of Bu₃SnH under 30 min of UV irradiation in THF. The consumed amount of Bu₃SnH (9.85×10^{-7} mol) was constant for above irradiation times from gas chromatography using decahydronaphthalene as internal standard sample. The particle number of feed H-SiO₂ is calculated to be 5.339×10^{-12} number using the following equation: $(22.2 \times 10^{-3} \times 0.934) \div [(4/3)\pi r_1^3 d_{\text{SiO}_2} N_{\text{av}}]$, where $r_1 = 96$ nm, $d_{\text{SiO}_2} = 1.74$

g/cm³, and $N_{\text{av}} = 6.025 \times 10^{23}$ mol⁻¹. Then, the number of DC groups per particle can be estimated to be 1.845×10^5 mol, i.e., $9.85 \times 10^{-7}/5.339 \times 10^{-12}$. Finally, the number of DC groups on H-SiO₂ particle surface was estimated to be 1.50 mol/nm², i.e., $1.845 \times 10^5/4\pi r_2^2$, where $r_2 = 99$ nm. This value is smaller than that (3.2 mol/nm²) calculated from TGA data, because the organic shell was consisted of PFD and γ -MPS silane coupling fragments. The number of grafted γ -MPS fragments ($N_{\gamma\text{-MPS}}$) can be estimated as follows. The molecular weight ($M_{\text{H-SiO}_2}$) of H-SiO₂ hybrid particle is given by the relation: $M_{\text{H-SiO}_2} = M_{\text{SiO}_2} + M_{\text{shell}}$, where M_{SiO_2} and M_{shell} are the molecular weights of SiO₂ core and organic shell part, respectively. From TGA data, the ratio of M_{SiO_2} to M_{shell} is given by $M_{\text{SiO}_2}/M_{\text{shell}} = 93.4/6.6$. Then, M_{shell} is estimated to be 2.744×10^8 using the relation: $M_{\text{SiO}_2} = (4/3)\pi r_1^3 d_{\text{SiO}_2} N_{\text{av}}$. This organic shell is composed of a mixture of PFD and γ -MPS fragments. Then, the mass of PFD grafted chains can be estimated to be 1.296×10^6 , i.e., $[(1.845 \times 10^5)/6.4] \times 4500$. So, the mass of grafted γ -MPS fragments is estimated to be 1.448×10^8 . Therefore, the number of grafted γ -MPS fragments was calculated to be 5.83×10^5 mol/one particle, i.e., $1.448 \times 10^8/248.35$.

Construction of colloidal crystals

We consider the space arrangement of the cubic lattice in colloidal crystals. The nearest-neighbor distance (D_s) of the spheres is related to the cell edge a_c of the cubic lattice as follows:

$$D_s = (\sqrt{3}/2)a_c \quad \text{for BCC} \quad (1)$$

A cubic lattice a_c^3 is occupied with two H-SiO₂ particles and MMA monomer. Then, the weight ratio of

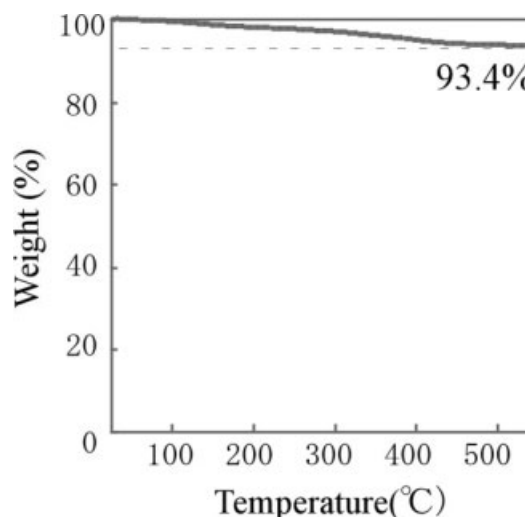


Figure 6 TGA result for SiO₂ hybrid nanoparticle (H-SiO₂). Heating rate was 20°C/min.

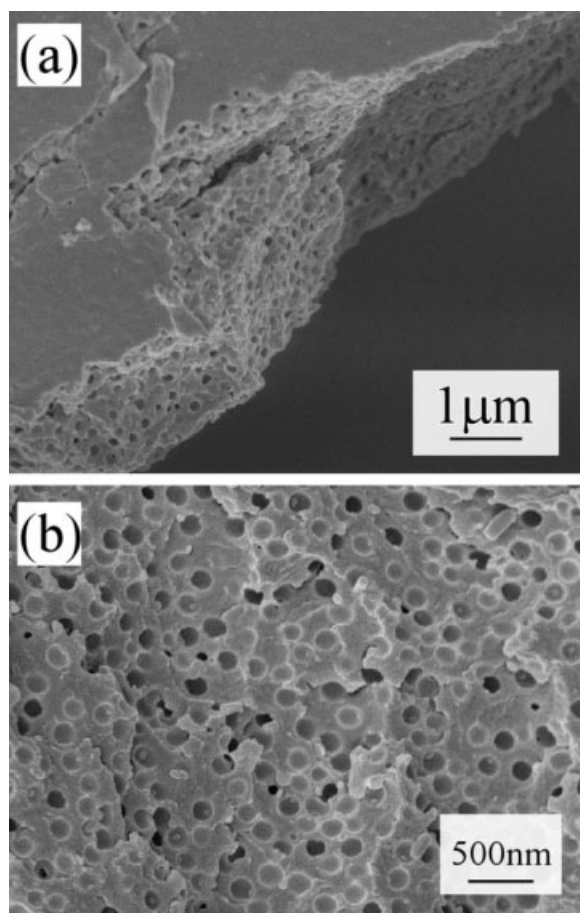


Figure 7 SEM photographs of (a) vertical section of composite film after etching SiO₂ particles and (b) enlarged image.

SiO₂ cores to MMA is given by SiO₂ : MMA = $2(4/3)\pi r_{\text{SiO}_2}^3 d_{\text{SiO}_2} : [a_c^3 - 2(4/3)\pi r_{\text{SiO}_2}^3] d_{\text{MMA}}$, where physical values are as follows: radius of SiO₂ core $r_{\text{SiO}_2} = 192/2$ (nm), densities of SiO₂ and MMA; $d_{\text{SiO}_2} = 1.74$ (g/cm³) and $d_{\text{MMA}} = 0.936$ (g/cm³), $a_c^3 = [(2/\sqrt{3})D_s]^3$ ($D_s = 243$ nm; this value is employed from D_h determined by DLS). As a result, we can estimate a following relation: SiO₂ : MMA = 0.75 : 1 (wt/wt). As mentioned earlier, a 6.6 wt % mass increase was observed after silane coupling reaction for the synthesis of H-SiO₂ (TGA results in Fig. 6). Therefore, the weight ratio of H-SiO₂ to MMA is given by H-SiO₂ : MMA = 0.75/0.934 : 1, i.e., 0.80 : 1 (wt/wt). Then, we employed 84 wt % H-SiO₂ concentration for the construction of colloidal crystals.

Composites films of the organic/inorganic hybrids were prepared by DC-mediated radical polymerization of MMA (H-SiO₂; 84 wt %) initiated by DC groups on SiO₂ particles. All the polymerization products provided transparent films and exhibited opal-like color. Such prepared samples were then immersed in HF solution to etch away SiO₂ particles, yielding nanoporous PMMA films. Figure 7(a)

shows SEM photograph of vertical section of composite film after etching SiO₂ particles. SEM image shows a matrix with quite uniform nanopore voids. On the other hand, Figure 7(b) shows an enlarged image of nanoporous films. The average pore size was about 190 nm, which agrees well with the size of colloidal SiO₂ particles. The nearest-neighbor distance D_s of SiO₂ particles was about 204 nm, which closes relatively to calculated value (243 nm) within experimental errors considering the effects of the volume shrinkage of PMMA matrix and the cutting angle of vertical section of composite film. This texture indicates that SiO₂ particles are locked in a state of molecular dispersion in a PMMA matrix, but that the two-dimensional long-range order such as colloidal crystals is not perfectly maintained. The photo-functional SiO₂ particles in this system undergo graft polymerization radially to form hybrid materials.

The target of our study is to create durable colloidal crystals that can withstand use for a long time. We will take the reflection spectra of SiO₂/PMMA colloidal crystals to determine the packing structure of SiO₂ particles. The results obtained will be reported in the near future.

CONCLUSIONS

We demonstrated a new strategy for the synthesis of SiO₂ hybrid nanoparticles modified with PED (H-SiO₂) by reaction between SiOH on SiO₂ surface and silane coupling agents. We dispersed these H-SiO₂ particles in MMA monomer and constructed hybrid nanocomposites by grafting reaction from DC groups. The SEM images indicated that SiO₂ particles were locked in a state of molecular dispersion in a PMMA matrix, but that the two-dimensional long-range order such as colloidal crystals was not perfectly maintained.

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