

Architecture of Colloidal Crystals Constructed by Silica Hybrid Nanoparticles

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ABSTRACT: Silica (SiO₂)-crosslinked polystyrene (PS) particles possessing photofunctional *N,N*-diethyldithiocarbamate (DC) groups on their surface were prepared by the free-radical emulsion copolymerization of a mixture of SiO₂ (diameter $D_n = 192$ nm), styrene, divinyl benzene, 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC), and 2-hydroxyethyl methacrylate with a radical initiator under UV irradiation. In this copolymerization, the inimer VBDC had the formation of a hyperbranched structure by a living radical mechanism. These particles had DC groups on their surface. Subsequently, poly(methyl methacrylate) brushes encapsulated SiO₂ particles were synthesized by

the grafting from a photoinduced atom transfer radical polymerization (ATRP) approach of methyl methacrylate initiated by SiO₂-crosslinked PS particles as a macroinitiator. We constructed the colloidal crystals using these photofunctional particles. Moreover, the SiO₂ particle array of colloidal crystals was locked by radical photopolymerization with vinyl monomer as a matrix. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 43–49, 2011

Key words: silica particle; atom transfer radical polymerization (ATRP); hyperbranched structure; polymer brushes; colloidal crystal

INTRODUCTION

Very interesting applications of multiphase materials can be found in the biomedical field,^{1,2} in optic,³ microelectronic and automotive industries. Among the large number of strategies which have been developed for the synthesis of multiphase systems, microencapsulation technologies provide a variety of methods which are largely used in agriculture, food and pharmaceutical areas, for instance. A particular category of encapsulated materials is fillers or pigments. Although a lot of procedures exist, emulsion polymerization is by far the technique most frequently used for the encapsulation reaction of minerals with polymers. One difficulty, however, of encapsulation reactions through emulsion polymerization resides in the fact that inorganic surfaces are hydrophilic, while polymers are hydrophobic. To promote polymerization on the inorganic surface, modification of the mineral can be carried out by using, for instance, silane or titanate molecules reac-

tive in free-radical polymerization.⁴ To overcome these problems, we have recently established new synthesis methods of polymer brushes encapsulated silica (SiO₂) particles.^{5,6} The first method is as follows.⁵ SiO₂-crosslinked polystyrene (PS) particles possessing photofunctional *N,N*-diethyldithiocarbamate (DC) groups on their surface were prepared by the free-radical emulsion copolymerization of a mixture of SiO₂ (average diameter $D_n = 20$ nm), styrene, divinyl benzene (DVB), 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC), and 2-hydroxyethyl methacrylate (HEMA) with a radical initiator under UV irradiation. In this copolymerization, the inimer VBDC had the formation of a hyperbranched structure by a living radical mechanism. These particles had DC groups on their surface. Subsequently, poly(methyl methacrylate) (PMMA) brushes encapsulated SiO₂ particles were synthesized by the grafting from a photoinduced atom transfer radical polymerization (ATRP) approach of methyl methacrylate (MMA) initiated by SiO₂-crosslinked PS particles as a macroinitiator. On the other hand, the second method is as follows.⁶ Photofunctional polymer as silane coupling agent (PFD) was prepared by free-radical copolymerization of VBDC and MMA in the presence of (3-mercaptopropyl)trimethoxysilane (MPMS) as chain transfer agent. Next, SiO₂ nanoparticles ($D_n = 192$ nm) was surface-modified with PFD and 3-(trimethoxy-silyl)propyl methacrylate (γ -MPS)

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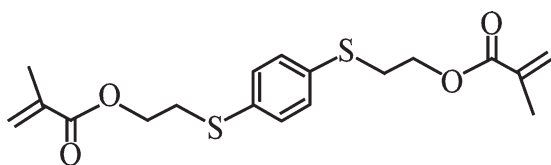


Figure 1 Chemical structure of UV3000.

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.

SiO_2 nanoparticles received recent attention because of their superior properties over the micro-size particles.^{7,8} However, its nanocomposites with organic polymers, SiO_2 generally exists as agglomerates. It becomes important to disperse the SiO_2 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.⁹ Opals are naturally occurring three-dimensional (3D) photonic crystals: their microstructure consists of SiO_2 spheres of about 150–300 nm in diameters, which are tightly packed into repeating hexagonal or cubic arrangements.¹⁰ Synthetic opals (colloidal crystals) use this same pattern, although they can be made from different materials. We also tried to prepare the colloidal crystals by DC-mediated radical polymerization of MMA initiated by DC groups on SiO_2 hybrid nanoparticles modified with PFD.⁶ All the polymerization products provided transparent films and exhibited opal-like color. The texture of electron microscopy indicated that SiO_2 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.

In this article, SiO_2 ($D_n = 192$ nm)-crosslinked PS (SPS) core-shell particles (possessing photofunctional DC groups on their surfaces) and PMMA brushes

encapsulated SiO_2 particles (SPM) were prepared according to our previous work.⁵ We studied the construction of colloidal crystals using both SiO_2 hybrid particles.

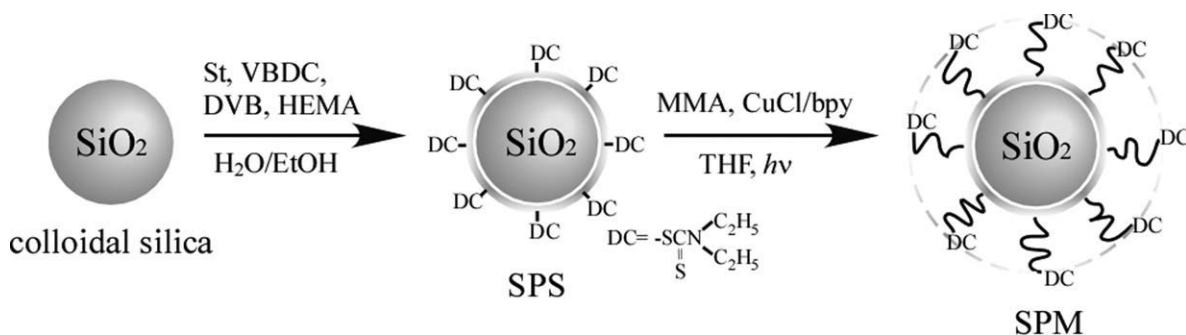
EXPERIMENTAL

Materials

VBDC was synthesized by the reaction of *p*-chloromethylstyrene (Seimi Chemical Industry, Tokyo) with *N,N*-diethyldithiocarbame sodium (Tokyo Kasei Organic Chemicals, Tokyo) in acetone. Details concerning synthesis and purification of VBDC have been given elsewhere.¹¹ Styrene (St), DVB (55% *m*-isomer/*p*-isomer = 2, and 45% mixture of ethylstyrene and diethylstyrene), and HEMA (Tokyo Kasei Organic Chemicals, Tokyo) were distilled under high vacuum. SiO_2 sol ($D_n = 192$ nm, density $d = 1.74$ g/cm³, refractive index $n_{\text{SiO}_2} = 1.49$, MP-2040; 30 wt % alkaline aqueous solution), [2-methylacrylic acid 2-4-[2-(2-methylacryloyloxy)ethylsulfanylmethyl]benzylsulfanyl ethyl ester] (UV3000: chemical structure is shown in Fig. 1) (Nissan Chemical Industries, Tokyo), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70; Wako Pure Chemical Industries, Tokyo), dodecylbenzenesulfonic acid sodium salt (SDBS), tributyltin hydride (Bu_3SnH), decahydronaphthalene, tetrahydrofuran (THF), methanol (MeOH), ethanol (EtOH), 2,2'-bipyridine (bpy; Tokyo Kasei Organic Chemicals, Tokyo), HCl, copper(I) chloride (CuCl), and hydrofluoric acid (HF; 48 wt % in water, Kanto Chemicals, Tokyo) were used as received.

Synthesis of SiO_2 -crosslinked PS particles (SPS)

The reaction scheme for the syntheses of SiO_2 -crosslinked PS particles and PMMA brushes encapsulated SiO_2 is shown in Scheme 1. Free-radical emulsion copolymerizations were carried out with stirring at room temperature for 4 h under a nitrogen atmosphere in a glass vessel. A mixture of SiO_2 (2.7 g), VBDC (0.12 g), St (0.12 g), DVB (0.03 g), HEMA (0.03



Scheme 1 Schematic illustration for the synthesis of PMMA brushed encapsulated SiO_2 .

g), V-70 (3 mg), and surfactant SDBS (60 g) was added to a mixture of water (50 mL)/EtOH (5 mL). Details concerning the synthesis and purification of SPS particles have been given elsewhere.⁵ The total monomer conversion was 40%.

Synthesis of Pmma brushes encapsulated SiO₂ (SPM) particle by grafting from photoinduced Atrp

PMMA brushes encapsulated SiO₂ particle were synthesized by photoinduced ATRP techniques with SiO₂-crosslinked PS (SPS) particles as macroinitiators in high vacuum. For example, PMMA brushes encapsulated SiO₂ particle (SPS) were prepared by photopolymerization in THF under the feed of SPS (215 mg, DC groups 0.7 mmol), MMA (3 mL, 28 mmol), CuCl (0.08 g, 0.8 mmol), and bpy (0.24 g, 1.5 mmol) ([DC]/[MMA]/[CuCl]/[bpy] = 1 : 40: 1: 2, monomer concentration = 0.2 wt %), where [DC] indicates the DC concentration of SPS. Details concerning the synthetic procedures of SPM particles have been given elsewhere.⁵ The monomer conversion was 24%.

MEASUREMENTS

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 SPS and SPM particles was evaluated with Stokes-Einstein equation: $R_h = kT/6\pi\eta_0 D_0$, where k , T , η_0 , and D_0 are the Boltzmann constant, the absolute temperature, the viscosity of the solvent, and the diffusion coefficient, respectively. D_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 emulsion aqueous of SiO₂-crosslinked PS after dialysis or THF solution of PMMA brushes encapsulated SiO₂ particle (scattering angle = 90°). Sample solutions were filtered through membrane filters with a nominal pore of 0.5 μ m just before measurement.

DC groups on the surface of SiO₂-crosslinked PS particles (SPS) were reduced with Bu₃SnH by radical transfer under 30 min of UV irradiation in a high vacuum (1 wt % THF solution of SPS particles). In previous works, reduction of DC groups at the peripheral sites of hyperbranched polymers¹² and at the side chain ends of polymer brushes¹³ was recognized from the disappearance of ethylene protons (δ 3.68 and 4.00 ppm) of DC groups by ¹H-NMR spec-

tra. The content of DC groups on the surface of SPS particles was measured as follows. Photolysis of SPS particles was carried out in THF under UV irradiation with the addition of Bu₃SnH and decahydronaphthalene. That is, 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 (Shimadzu, GC-14B, Kyoto, Japan) using decahydronaphthalene as internal standard sample.

The composition of SiO₂ hybrid particles SPS was determined by thermogravimetric analysis (TGA). TGA was run in nitrogen atmosphere using a Seiko Instrument Inc. (EXSTAR 6000, Tokyo). Heating rate was 20°C/min. The reflection spectra of colloidal crystals were measured at the 90° position from the cell surface by a multichannel spectral analyzer, MK-300JW (Jasco, Tokyo, Japan), with a 150-W halogen lamp.

Construction of colloidal crystals (CC)

We employed following three methods for construction of colloidal crystals (CC). (1) Emulsion solution of SPS particles was dropped on the glass plate and then dried at room temperature for 1 day. Subsequently, this sample was dried *in vacuo*. Sample showed green due to structural color. A small amount of monomer UV3000 was dropped on these colloidal crystals. After maintaining for 1 day at dark room, radical photopolymerization was carried out in nitrogen atmosphere at 30°C under UV irradiation for 2 h. (2) We prepared the prescribed UV3000 solution of SPM particles [near the overlap concentration (C^*)] and diluted with THF to disperse homogeneously. The details of the feed conditions will be mentioned latter. Such solution was poured into a petri dish and THF solvent was evaporated slowly. Radical photopolymerization was carried out under the same conditions described in the method 1. (3) The prescribed UV3000 solution of SPM particles (more than C^*) was poured into a petri dish. The closed packing structure of SPM particles was formed by ultracentrifuge. After wiping up the supernatant UV3000 with paper filter, photopolymerization was carried out under UV irradiation. These CC films were broken in liquid nitrogen. Such CC films were immersed in HF aqueous solution to remove SiO₂ particles.

RESULTS AND DISCUSSION

Synthesis of the SPS macroinitiator particles

The monomer-droplets (St, DVB, VBDC, and HEMA)-encapsulated SiO₂ particles were dispersed

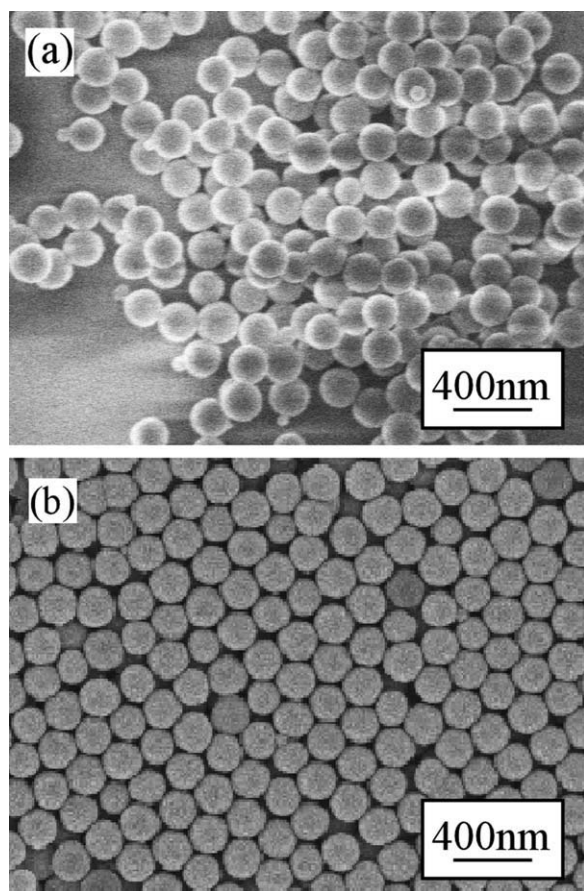


Figure 2 SEM photographs of (a) SiO₂ and (b) SPS particles.

in the aqueous phases by means of a surfactant (SDBS), and a stable emulsion was produced. As mentioned in the previous work,⁵ a small amount of HEMA that was miscible to the SiO₂ surface was also used to achieve the initial formation of the random copolymer composed of rich poly(2-hydroxyethyl methacrylate) (PHEMA) sequences because of the rapid propagation rate constant. An organic-solvent-soluble initiator (V-70) was used so that effective initiation occurred in the monomer droplets. At the same time, the photolysis of the inimer VBDC within the monomer droplets led to the initiating benzyl radical with the inactive DC radical. This benzyl radical could add to the vinyl groups of St, DVB, HEMA, or VBDC. By repeating these elementary reactions, this polymerization system proceeded to form the hyperbranched structures. This reaction system formed a macroinitiator with highly localized DC groups attached chemically to the surfaces of the SiO₂ particles.

A typical scanning electron microscopy (SEM) photograph of the copolymerization product SPS is shown in Figure 2(b), where Figure 2(a) shows starting SiO₂ particles ($D_n = 192$ nm). The product provided somewhat larger spherical particles ($D_n = 195$

nm) and a narrow size distributions [weight-average particle diameter (D_w)/ $D_n = 1.01$]. Figure 3 shows the size distribution for the DLS data of SPS in an emulsion aqueous solution and in THF. Both profiles showed unimodal distribution, and the hydrodynamic diameters (D_h) were 215 and 220 nm in water and in THF, respectively.

The content of DC groups for the SPS particles was determined with radical transfer reaction. SPS (50.2 mg) was reduced with a lower excess of Bu₃SnH under UV irradiation in THF. The consumed amount of Bu₃SnH (1.7×10^{-6} mol) was constant for the previous irradiation time from gas chromatography. The DC groups were estimated to be 1.33×10^5 number/particle (1.1 molecule/nm²) or 3.26×10^{-3} mol/g. This calculation method has been given in elsewhere.⁵

Synthesis of the SPM particles by grafting from photoinduced Atrp

The graft polymerization of MMA initiated by the SPS macroinitiator under direct UV irradiation often led to macrogelation because of intermolecular radical couplings. The main reasons were (1) a high localized radical concentration on the particle surface and (2) a high propagation rate of PMMA radicals. Then, we used photoinduced ATRP for such a grafting process because the propagation rate, especially that of MMA with CuCl/bpy, was very slow compared to that without CuCl/byp. In a previous study,¹³ we proved from kinetic studies that this grafting from photoinduced ATRP proceeds with a

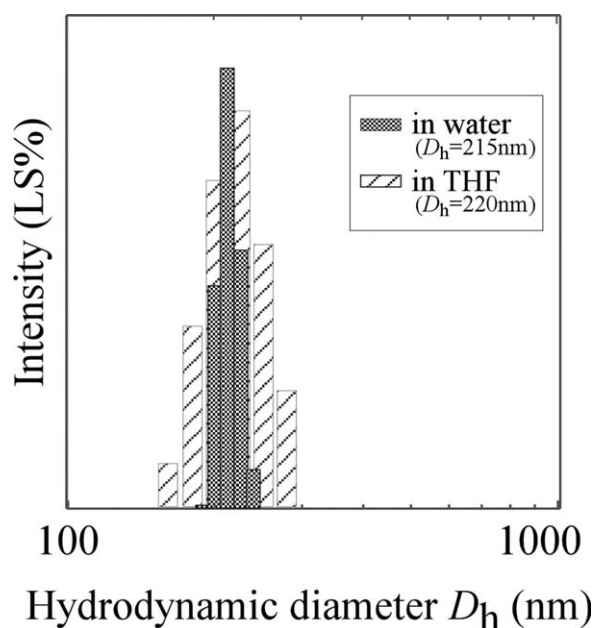


Figure 3 Size distributions of the DLS data for the SPS particles in emulsion solution and in THF.

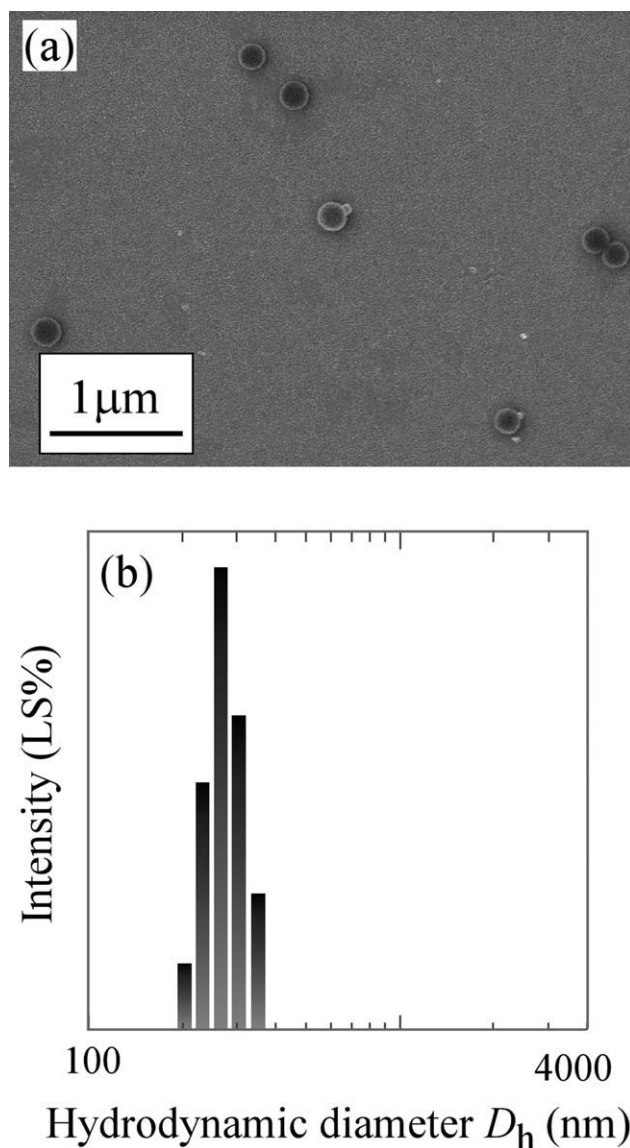


Figure 4 SEM photograph (a) of SPM particles and the size distribution (b) of DLS data in THF.

living radical mechanism. A typical SEM photograph of the PMMA brush encapsulated SiO_2 particle (SPM) is shown in Figure 4(a). Spherical particles ($D_n = 219$ nm) are clearly visible for the sample. This result supports the solution data from DLS. That is, the profile shows unimodal distribution, and D_h was 270 nm [see in Fig. 4(b)]. This means that the PMMA brush chains expanded in the THF solution because THF is a good solvent for PMMA.

To determine the composition of the PMMA brush chains, we performed TGA measurements for SPS and SPM particles (see Fig. 5). It was found from TGA traces of SPS and SPM that 96.6 and 72.0 wt % mass, respectively, of SiO_2 remained after the decomposition of the polymer phases. Therefore, the weight ratio SiO_2/PMMA for SPM particle was estimated to be 72.0 : 24.6. The molecular mass (M_{SiO_2})

of SiO_2 core is given; $M_{\text{SiO}_2} = (4/3)\pi r_1^3 d_{\text{SiO}_2} N_A$, where r_1 (96 nm), d_{SiO_2} (1.74 g cm^{-3}), and N_A ($6.025 \times 10^{23} \text{ mol}^{-1}$) are the radius of SiO_2 , a SiO_2 density, and Avogadro number, respectively. The value of M_{SiO_2} was determined to be 3.88×10^9 . Then, the mass of the PMMA brush phase (M_B) was calculated to be 1.326×10^9 with following equation: $M_B = (24.6/72)3.88 \times 10^9$. Therefore, the molecular weight of the PMMA brush chain was estimated to be 1.0×10^5 , with the assumption that all of the DC initiation sites on macroinitiator SPS led to the propagation of MMA.

On the other hand, M_B can be also estimated from SEM images for SPS and SPM particles, neglecting the crosslinked PS layer. M_B was determined to be 1.28×10^9 with following equation: $M_B = (4/3)\pi(r_2^3 - r_1^3)d_{\text{PMMA}}N_A$, where r_2 (109.5 nm) and d_{PMMA} (1.19 g cm^{-3})¹⁴ are the radius of SPM and a PMMA density, respectively. This value was well agreement with that obtained from TGA data.

Construction of colloidal crystals (CC)

The prepared film (CC-SPS) from SPS particles deposited on the glass substrate showed green. This means that the CC-SPS film formed a colloidal crystal (CC). Figure 6 shows the reflection spectrum of CC-SPS under the condition of the incident angle $\theta = 90^\circ$. The Bragg equation is given by

$$\lambda_{\text{max}} = 2D_s \sqrt{(2/3)(n_{\text{eff}}^2 - \cos^2 \theta)}^{1/2} \quad (1)$$

which describes the bandgap position for light incident on the (111) face of a face-centered cubic (fcc) lattice, where λ_{max} , D_s , θ , and n_{eff} are the peak wavelength, diameter of spheres, angle between the

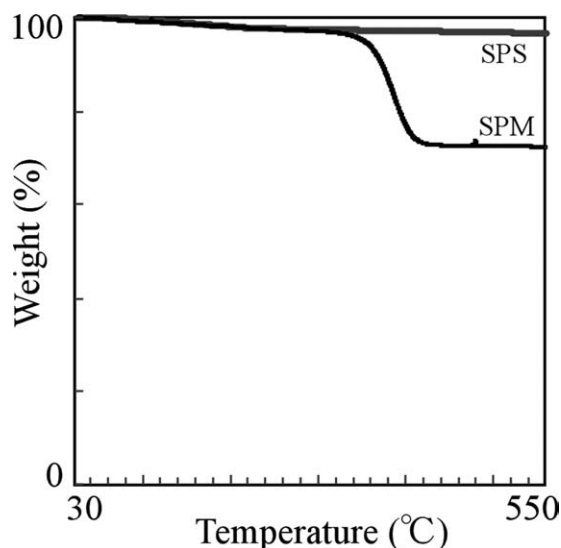


Figure 5 TGA results for SPS and SPM particles. Heating rate was $20^\circ\text{C}/\text{min}$.

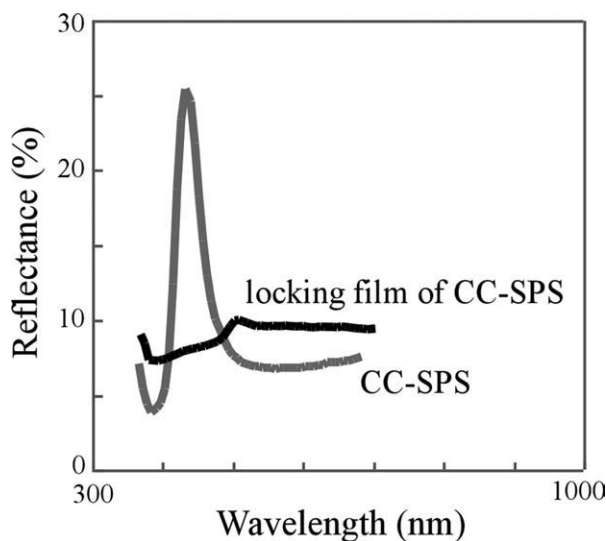


Figure 6 Reflection spectra of colloidal crystal CC-SPS and locking film of CC-SPS with UV3000 (incident angle $\theta = 90^\circ$).

incident light and the normal to the diffraction planes, and the mean effective refractive index of this crystalline array, respectively. The n_{eff} can be defined by

$$n_{\text{eff}}^2 = n_p^2 \phi_p + n_M^2 \phi_M \quad (2)$$

where n_p , n_M , ϕ_p , and ϕ_M are the refractive index of particles, refractive index of matrix, volume fraction of particles, and volume fraction of matrix, respectively.

The CC-SPS film is array composed of SiO_2 particles and air matrix. Then, n_{eff} is estimated to be 1.38 using $n_p = 1.49$ (SiO_2), $\phi_p = 0.74$, $n_M = 1.0$ (air), and $\phi_M = 0.26$. The calculated wavelength (λ_{cald}) from Eq. (1) is to be 439.4 nm using $D_S = 195$ nm. This value was well agreement with observed one ($\lambda_{\text{max}} = 437$ nm).

We locked the colloidal crystal CC-SPS with UV3000 possessing high refractive index ($n_{\text{PUV3000}} = 1.59$) by method 1. This locking film also maintained green color. The n_{eff} is estimated to be 1.52, with the assumption that UV3000 fills up in leaving gap on an fcc lattice instead of air. Then, λ_{cald} was calculated to be 483 nm. The reflection spectrum ($\theta = 90^\circ$) of locking film of CC-SPS is also shown in Figure 6. The peak wavelength (λ_{max}) is 510 nm and shifts to long wavelength side. This value is somewhat large compared to λ_{cald} , because the value of D_S (195 nm) employed in this sample may be underestimated. Moreover, the intensity of reflection decreases after locking treatment due to weak packing structure. Locking film of CC-SPS was then immersed in HF solution to etch away SiO_2 particles, yielding nanoporous poly(UV3000) (PUV3000) film. Figure 7(a)

shows SEM photograph of vertical section of locking film of CC-SPS after etching SiO_2 particles. SEM image shows a matrix with quite uniform nanopore voids. The average pore size was about 190 nm, which agrees well with the size of colloidal SiO_2 particles. Such pores seem to distribute with closed packing structure. The brilliant monochromatic colors were not prepared in the samples with structure of colloidal crystals. This means difficulty in controlling the size/structure during grafting.

The preparation conditions for locking method 2 are as follows. In general, the overlap concentration

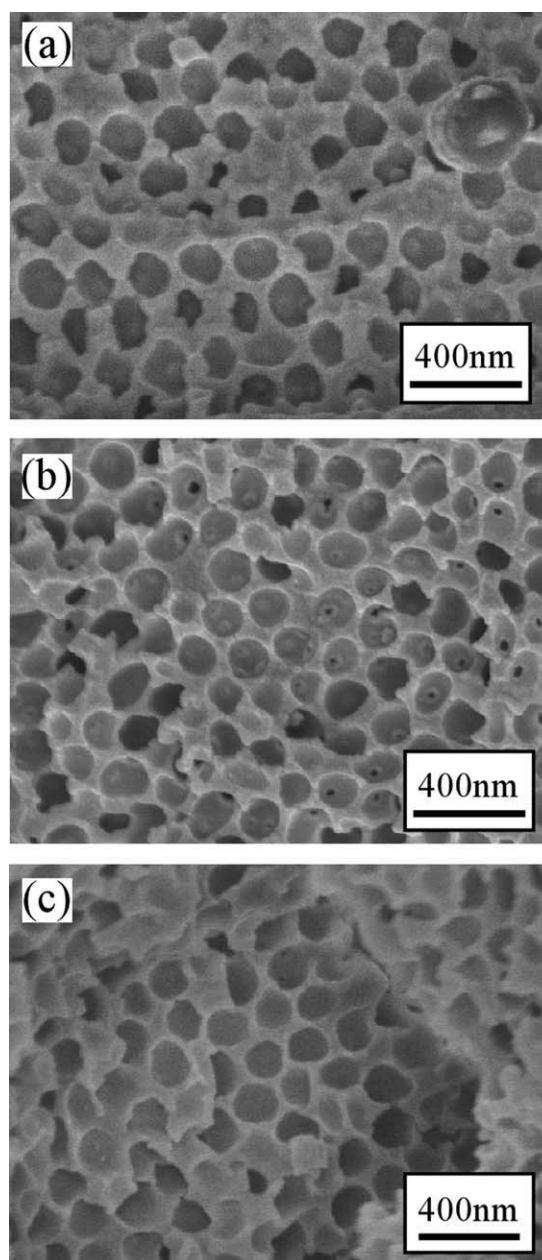


Figure 7 SEM photographs of vertical sections of locking films by method 1 (a), method 2 (b), and method 3 (c) after etching SiO_2 with HF.

(C^*) of polymer particles is given by following equation¹⁵:

$$C^* = M_w/D_h^3 N_A \quad (3)$$

where M_w and D_h are the molecular mass and hydrodynamic diameter of polymer particle, respectively. As mentioned earlier, the M_w (5.19×10^6) of SPM particle is given by following equation (neglecting the crosslinked PS layer):

$$M_w = M_{SiO_2} + M_B \quad (4)$$

where we employed M_B estimated from SEM images. Therefore, C^* can be estimated to be 43.5 wt % using $D_h = 270$ nm. We reported also from small-angle X-ray scattering (SAXS) measurements that near the C^* , brush-core particles and $(AB)_n$ stars formed the lattice of a body-centered cubic (bcc).¹⁶

On the basis of above information, the 45 wt % UV3000 solution of SPM particles was diluted with THF solvent. After evaporation of THF from such casting solution, free-radical photopolymerization was carried out under UV irradiation. Locking film showed somewhat turbid. Figure 7(b) shows SEM photograph of vertical section of locking film of SPM particles by means of method 2 after etching SiO_2 particles. The pores are not maintained perfectly with an bcc packing but are packed with irregular arrangement at places.

Figure 7(c) shows the SEM photograph of vertical section of locking film of SPM particles by means of method 3. This locking film also showed turbid. This texture indicates that SiO_2 particles are locked in a state of molecular dispersion in a PUV3000 matrix, but that the two-dimensional long-range order is not perfectly maintained. The photofunctional SiO_2 particles in these systems undergo graft polymerization radially to form hybrid materials.

CONCLUSIONS

We demonstrated a new strategy for the synthesis of inorganic core-organic shell hybrid particles via a

living radical mechanism. SPS particles possessing photofunctional DC groups on their surface were synthesized by encapsulation of SiO_2 core with vinyl monomers and the inimer VBDC under UV irradiation. The SPM particles were prepared by grafting from a photoinduced ATRP approach with MMA initiated by SPS particles as macroinitiators. The prepared film from SPS particles deposited on the glass substrate showed green. The peak wavelength (λ_{max}) in the reflection spectrum well agreed with the bandgap position for light incident on the (111) face of an fcc lattice according to Bragg law. This means that the prepared film CC-SPS formed colloidal crystals. Moreover, we succeeded to lock this CC-SPS with monomer UV3000 possessing high refractive index by photopolymerization.

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