

# Novel Synthesis of Poly(methyl methacrylate) Brush Encapsulated Silica Particles

Koji Ishizu,<sup>1</sup> Dong Hoon Lee,<sup>1</sup> Yoko Tokuno,<sup>1</sup> Satoshi Uchida,<sup>1</sup> Masaaki Ozawa<sup>2</sup>

<sup>1</sup>Department of Organic Materials and Macromolecules, International Research Center of Macromolecular Science, Tokyo Institute of Technology, 2-12-1-H-133, Ookayama, Meguro-Ku, Tokyo 152-8552, Japan

<sup>2</sup>Chemical General Division, Nissan Chemical Industries, Limited, 722-1, Tsuboi-Cho, Funabashi-City, Chiba 274-8507, Japan

Received 28 January 2008; accepted 24 March 2008

DOI 10.1002/app.28510

Published online 10 June 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Silica (SiO<sub>2</sub>)-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 SiO<sub>2</sub> (diameter = 20 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. The particle sizes of such core-shell structures [number-average particle diameter ( $D_n$ ) = 35–40 nm] were controlled by the variation of the feed amounts of the

monomers and surfactant, or emulsion system. The size distributions were relatively narrow (weight-average particle diameter/ $D_n \approx 1.05$ ). These particles had DC groups on their surface. Subsequently, poly(methyl methacrylate) brush encapsulated SiO<sub>2</sub> particles were synthesized by the grafting from a photoinduced atom transfer radical polymerization approach of methyl methacrylate initiated by SiO<sub>2</sub>-crosslinked PS particles as a macroinitiator. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109:3968–3974, 2008

**Key words:** atom transfer radical polymerization (ATRP); emulsion polymerization; hyperbranched

## INTRODUCTION

Recently, there has been a lot of work on the elaboration of nanocomposite systems by the embedding of inorganic particles into polymer matrices.<sup>1–10</sup> These materials represent a new class of polymeric materials that combine the unique physical properties of the inorganic particles with the processability and flexibility of the organic polymer matrix. Silica (SiO<sub>2</sub>) nanoparticles have received recent attention because of their superior properties over microsize particles.<sup>11,12</sup> However, in its nanocomposites with organic polymers, SiO<sub>2</sub> particles generally exists as agglomerates. It becomes important to disperse the SiO<sub>2</sub> particles in the nanocomposites with other polymers for use in synergic properties and fluid applications. Because of the many uses of SiO<sub>2</sub>,<sup>11,12</sup> various polymer–SiO<sub>2</sub> composites have been studied. Tang et al.<sup>13</sup> reported the phase morphology and

particle structure of a poly(ethyl acrylate)–SiO<sub>2</sub> composite. Poly(ethylene-2,6-naphthalate)–SiO<sub>2</sub>,<sup>14</sup> polyimide–SiO<sub>2</sub>,<sup>15</sup> ethylene–propylene–diene terpolymer/SiO<sub>2</sub>,<sup>16</sup> and polypyrrole–SiO<sub>2</sub><sup>17</sup> hybrids and so on have been prepared. More recently, Park et al.<sup>18</sup> prepared poly(methyl methacrylate) (PMMA)–SiO<sub>2</sub> core-shell nanocomposite particles from dispersion polymerization in supercritical carbon dioxide. In their approach, 3-(trimethoxysilyl) propyl methacrylate functionalized SiO<sub>2</sub> was first dispersed in the reaction medium, followed by polymerization with methyl methacrylate (MMA). We also established a new synthetic method for crosslinked polystyrene (PS) particles possessing photofunctional *N,N*-diethyldithiocarbamate (DC) groups on their surface by the free-radical emulsion copolymerization of a mixture of styrene (St), divinylbenzene (DVB), and 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) with a redox system as an initiator under UV irradiation.<sup>19</sup> In this copolymerization, the inimer VBDC had the formation of hyperbranched structures by living radical photopolymerization. Subsequently, core-shell particles were synthesized by the photoinduced atom transfer radical polymerization (ATRP) of MMA initiated by photofunctional PS particles as a macroinitiator. We expected that this method would be applied for the synthesis of poly(methyl methacrylate) brush encapsulated silica (SPM) particles.

Correspondence to: K. Ishizu (kishizu@polymer.titech.ac.jp).

Contract grant sponsor: Ministry of Education, Culture, and Sports (Grant-Aid for Science Research); contract grant number: 19550119.

Contract grant sponsor: Fund of Nissan Chemical Industry, Ltd.

*Journal of Applied Polymer Science*, Vol. 109, 3968–3974 (2008)  
© 2008 Wiley Periodicals, Inc.

In this article, silica-crosslinked polystyrene (SPS) core-shell particles (possessing photofunctional DC groups on their surfaces) were synthesized first by the 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 a hyperbranched structure by the living radical mechanism of the inimer. Subsequently, SiO<sub>2</sub>-PMMA core-shell particles (SPM particles) were prepared by grafting from a photoinduced ATRP approach of MMA initiated from the DC groups of the crosslinked PS particle surfaces as a macroinitiator.

## EXPERIMENTAL

### Materials

VBDC was synthesized by the reaction of *p*-chloromethylstyrene (Seimi Chemical Industry, Tokyo) with *N,N*-diethyldithiocarbamate sodium (Tokyo Kasei Organic Chemicals, Tokyo) in acetone. Details concerning the synthesis and purification of VBDC were given elsewhere.<sup>20</sup> St, DVB (55% *m*-isomer/*p*-isomer = 2, and 45% mixture of ethylstyrene and diethylstyrene), and HEMA (Tokyo Kasei Organic Chemicals) were distilled under high vacuum. SiO<sub>2</sub> sol (particle diameter = 20 nm, density = 1.36 g/cm<sup>-3</sup>, MEK-ST-MS; 65% methyl ethyl ketone solution, Nissan Chemical Industries, Ltd. Tokyo), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70; Wako Pure Chemical Industries, Ltd., Tokyo), dodecylbenzenesulfonic acid sodium salt (SDBS), tributyltin hydride (Bu<sub>3</sub>SnH), decahydronaphthalene, tetrahydrofuran (THF), methanol, ethanol (EtOH), 2,2'-bipyridine (bpy; Tokyo Kasei Organic Chemicals), HCl, and copper(I) chloride (CuCl; Kanto Chemicals, Tokyo) were used as received.

### Synthesis of the SPS particles

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<sub>2</sub>, VBDC, St, DVB, HEMA, V-70, and the surfactant SDBS was added to the water or a mixture of water and EtOH. An Iuchi W-113 multiwave ultrasonic generator (Tokyo, Japan) was used for the ultrasonic irradiation and was operated at 45 kHz with an input power of 100 W for 15 min, and the resulting mixture was stirred under UV irradiation (SXUI 250 HAMQ 250-W high-pressure mercury lamp, Ushio Denki (Tokyo, Japan); UV intensity = 42 mW/cm<sup>2</sup>, irradiation distance = 20 cm). After copolymerization, the resulting solution was placed in dialysis tubes, dialyzed against distilled water for

4 days to remove the catalyst and unreacted monomers, and freeze-dried from water. The total monomer conversion was in the range 35–40%.

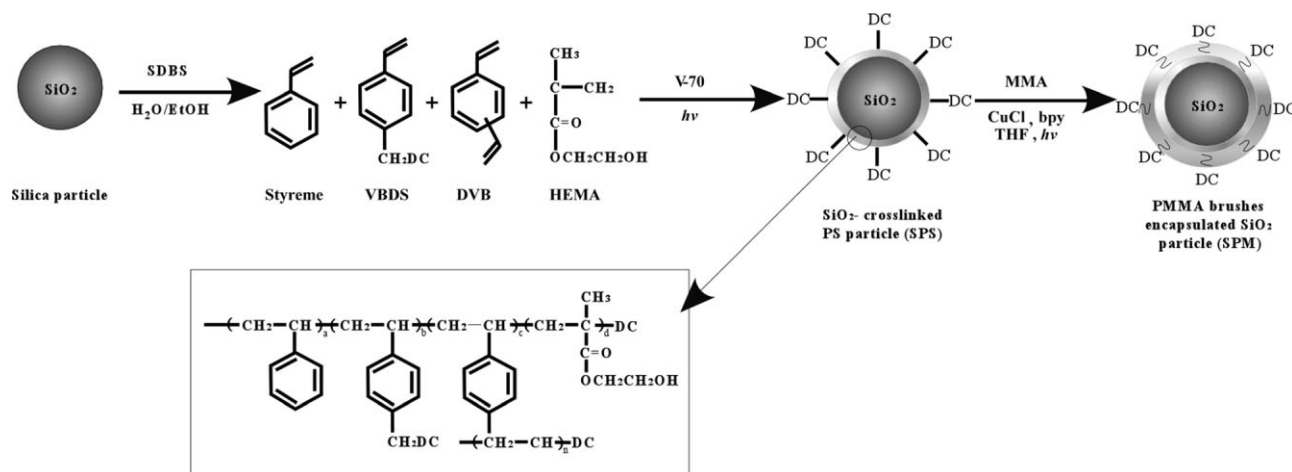
### Synthesis of the SPM particles by grafting from photoinduced ATRP

The SPM particles were synthesized by photoinduced ATRP techniques with SPS particles as macroinitiators in high vacuum. For example, SPM1 particles were prepared by photopolymerization (under UV irradiation for 8 h) in THF under the feed of SPS3 (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 : 1.1 : 2.1 : 40, monomer concentration = 60 wt %), where [DC] indicates the DC concentration of SPS. After photoinduced ATRP, the polymer particles were recovered with an excess of methanol containing a small amount of HCl to remove the catalyst and dried *in vacuo* to a constant weight. The monomer conversion was in the range 18–24%.

### Measurements

The morphology and particle size of the polymer particles were investigated with a JEOL JSM7500-F scanning electron microscope (Tokyo, Japan). The number-average particle diameter ( $D_n$ ) and particle size distribution [weight-average particle diameter/ $D_n$ ] were determined by a survey of 300 samples picked from the photographs that were obtained. The hydrodynamic radius ( $R_h$ ) of the SPS and SPM particles was evaluated with the Stokes-Einstein equation:  $R_h = kT/6\pi\eta_0 D_0$ , where  $k$ ,  $T$ ,  $\eta_0$ , 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:wavelength ( $\lambda$ )<sub>0</sub> = 632.8 nm, 10 mW) data with a cumulant method at 25°C in a 2–10-mg/mL aqueous emulsion of SPS after dialysis or in a THF solution of SPM particles (scattering angle = 90°). Sample solutions were filtered through membrane filters with a nominal pore of 0.2 μm just before measurement.

DC groups on the surface of the SPS particles were reduced with Bu<sub>3</sub>SnH by radical transfer under 30 min of UV irradiation in a high vacuum (1 wt % SPS particles in THF solution). In previous works, the reduction of DC groups at the peripheral sites of hyperbranched polymers<sup>21</sup> and at the side chain ends of polymer brushes<sup>22</sup> was recognized from the disappearance of ethylene protons ( $\delta$  = 3.68 and 4.00 ppm) of DC groups by <sup>1</sup>H-NMR spectra. The content of DC groups on the surfaces of the SPS particles was measured as follows. Photolysis of SPS particles



**Scheme 1** Reaction scheme for the synthesis of the SPM particles.

was carried out in THF under UV irradiation with the addition of Bu<sub>3</sub>SnH and decahydronaphthalene. That is, photolysis of VBDC led to the initiating benzyl radical with the inactive DC radical, and such benzyl radicals were quenched with Bu<sub>3</sub>SnH. Then, the residual amount of Bu<sub>3</sub>SnH was measured by gas chromatography (Shimadzu, GC-14B, Kyoto, Japan) with decahydronaphthalene as an internal standard sample.

Fourier transform infrared (FTIR) spectra were performed with an FTIR-8700 (Shimadzu) instrument. The composition of SiO<sub>2</sub>-polymer particles was determined by thermogravimetric analysis (TGA). TGA was run in nitrogen atmosphere with a Seiko instrument (EXSTAR 6000, Tokyo). The heating rate was 20°C/min.

## RESULTS AND DISCUSSION

### Synthesis of the SPS macroinitiator particles

The reaction scheme for the synthesis of the SPM particles is shown in Scheme 1. The synthesis of well-defined core-shell structures by the method devised here required the architecture of the crosslinked PS shell parts to possess as many photofunctional DC groups as possible on the surface. In this study, the monomer-droplet (St, DVB, VBDC, and HEMA)-encapsulated SiO<sub>2</sub> particles were dispersed in the aqueous phases by means of a surfactant (SDBS), and a stable emulsion was produced. A small amount of HEMA that was miscible to the SiO<sub>2</sub> 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. The interaction between the crosslinked PS and SiO<sub>2</sub> was physical embedding. This reaction system formed a macroinitiator with highly localized DC groups attached chemically to the surfaces of the SiO<sub>2</sub> particles.

The copolymerization conditions and results for the SPS macroinitiator particles are listed in Table I. The SPS1 and SPS2 particles were polymerized in the water phase only. The polymerization rate increased during the time in which the conversion reached 50–55% after 4 h. A typical scanning electron microscopy (SEM) photograph of the copolymerization product SPS2 is shown in Figure 1(a). The product provided large spherical particles ( $D_n \approx 50$  nm) and a broad size distribution [weight-average particle diameter ( $D_w$ )/ $D_n = 1.16$ ]. The result for SPS1 showed a similar trend. It was also found from both experiments that the particle diameter decreased gradually with increasing feed ratio of the surfactant SDBS to the total monomer. This was a reasonable result for an emulsion copolymerization. The thickness of crosslinked PS shell parts was too large because the particle diameter of the SiO<sub>2</sub> core used in this study was 20 nm.

Therefore, the SPS3 and SPS4 experiments were carried out with a small feed amount of total monomer in the water/EtOH phase. We expected that the addition of EtOH would promote uniform emulsion droplets in miscible water/monomer and the effect of the phase-transfer catalyst. Total monomer conversions were in the range 45–52% under 4 h of UV

TABLE I  
Emulsion Copolymerization Conditions and Results for the SPS Particles<sup>a</sup>

Code	SiO <sub>2</sub> (mg) <sup>b</sup>	Feed of monomer				SDBS (mg)	V-70 (mg)	Solvent (mL/mL)	Total monomer conversion (%) <sup>c</sup>	$D_n$ (nm) <sup>d</sup>	$D_w/D_n$ <sup>d</sup>
		St (mL)	VBDC (mg)	DVB (mL)	HEMA (mL)						
SPS1	140	1.2	400	0.2	0.2	200	50	H <sub>2</sub> O (30)	56	55	1.20
SPS2	140	1.2	400	0.2	0.2	300	50	H <sub>2</sub> O (30)	55	50	1.16
SPS3	140	0.3	100	0.05	0.05	278	50	H <sub>2</sub> O (45)/EtOH (5)	45	35	1.04
SPS4	140	0.6	300	0.1	0.1	278	50	H <sub>2</sub> O (45)/EtOH (5)	52	40	1.05

<sup>a</sup> Polymerized under UV irradiation at room temperature for 4 h in a nitrogen atmosphere.

<sup>b</sup>  $D_n = 20$  nm.

<sup>c</sup> Determined by the gravimetric method.

<sup>d</sup> Determined by a survey of 300 samples picked from SEM photographs.

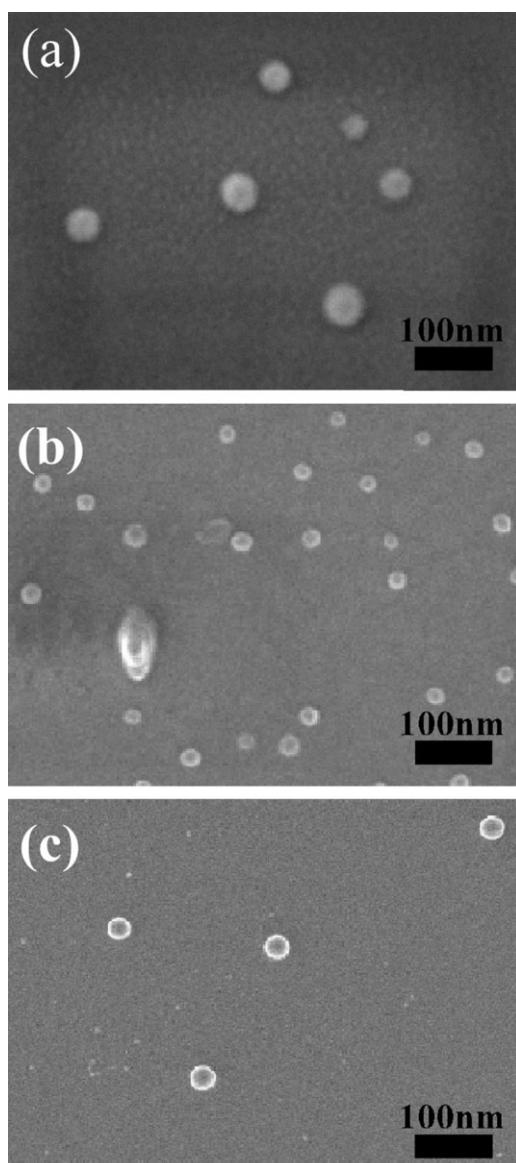


Figure 1 SEM photographs of the (a) SPS2, (b) SPS3, and (c) SPM1 particles.

irradiation. A typical SEM photograph of SPS3 is shown in Figure 1(b). From this texture, we found that small spherical particles ( $D_n = 35$  nm) were clearly visible and exhibited a narrow size distribution ( $D_w/D_n = 1.04$ ). Figure 2(a) shows the size distribution for the DLS data of SPS3 in an emulsion aqueous solution. The profile showed unimodal distribution, and the hydrodynamic diameter ( $D_h$ ) was 38 nm. This value was well in agreement with that observed from SEM. The result for the SPS4 particles showed almost the same trend.

We performed FTIR measurements for the SPS3 particles [see Fig. 3(a)]. This spectrum exhibited the absorbances at 1600 and 750  $\text{cm}^{-1}$  of the aromatic ring, the  $-\text{C}=\text{O}$  bond at 1730  $\text{cm}^{-1}$ , and the VBDC

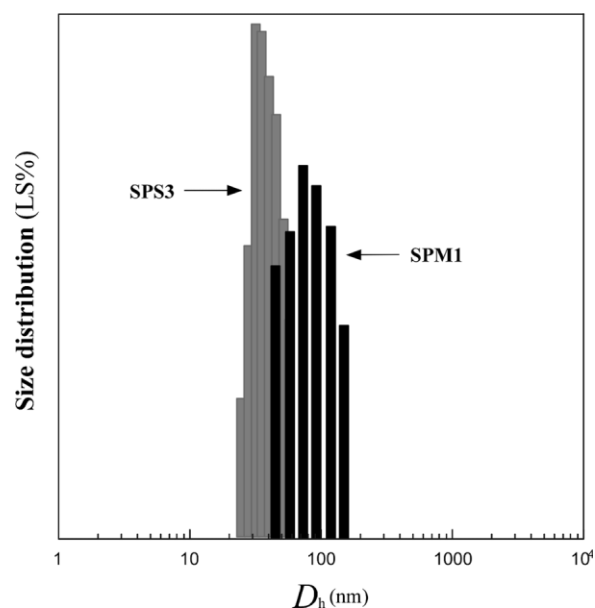


Figure 2 Size distributions of the DLS data for the SPS3 particles in an emulsion aqueous solution and the SPM1 particles in THF.

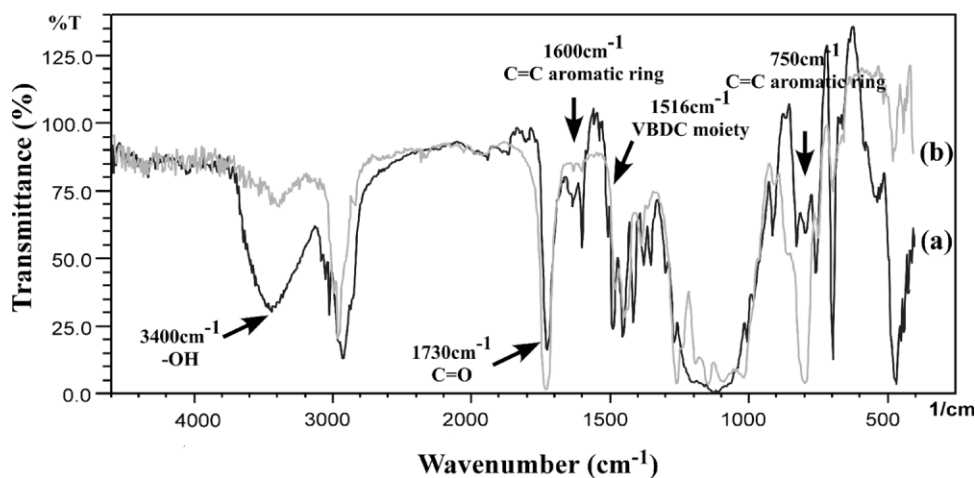


Figure 3 FTIR spectra of the (a) SPS3 and (b) SPM1 particles.

moiety at  $1516\text{ cm}^{-1}$ . This means that the  $\text{SiO}_2$  particles were encapsulated effectively with crosslinked PS layers. However, it was impossible to determine the composition of the core-shell structure from such FTIR spectra. To determine the composition of the core-shell particles, we performed TGA measurements for the SPS particles. Figure 4 shows the TGA result for the SPS3 particles. A 65 wt % mass increase was observed after the emulsion copolymerization. Therefore, the volume ratio of  $\text{SiO}_2$  to crosslinked PS shell parts was estimated to be 1 : 2.43 with the core-shell densities:  $d_{\text{SiO}_2} = 1.36$  and  $d_{\text{shell}} = 1.04^{23}\text{ g/cm}^3$  (this value was assumed to that of PS because the crosslinked shell part was composed of a random structure of St, DVB, VBDC, and HEMA units). Then, the following relation was given;  $r_1^3 : (r_2^3 - r_1^3) = 1 : 2.43$ , where  $r_1$  (10 nm) and  $r_2$  are the radii of the  $\text{SiO}_2$

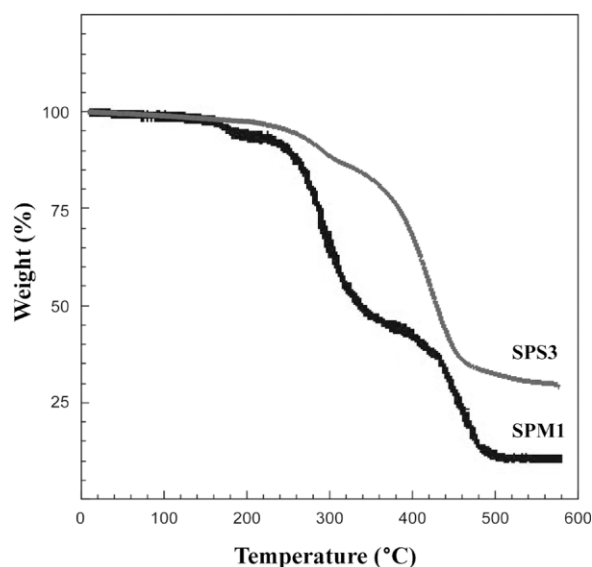


Figure 4 TGA results for the SPS3 and SPM1 particles. The heating rate was  $20^\circ\text{C}/\text{min}$ .

and SPS particles, respectively. The value of  $r_2$  was determined to be 15.1 nm. This value was in relative agreement with that observed from the SEM image (SPS3,  $D_n = 35\text{ nm}$ ) within experimental error. The thickness of shell part was estimated to be 5.1 nm.

The formation mechanism of the SPS macroinitiator particles can be speculated as follows. PHEMA-co-PS (PVBDC or PDVB) copolymer was formed in the initial stage because the propagation rate constant of HEMA was very rapid. These copolymers covered the surface of the  $\text{SiO}_2$  particles because of good affinity between the PHEMA units and silanol (Si-OH) groups on the  $\text{SiO}_2$  particles. Subsequently, the network and hyperbranched structures at shell part were generated during polymerization.

The content of DC groups for the SPS particles was determined with the radical transfer reaction. SPS3 (37.9 mg) was reduced with a lower excess of  $\text{Bu}_3\text{SnH}$  under 0.5–1.0 h of UV irradiation in THF. The consumed amount of  $\text{Bu}_3\text{SnH}$  ( $1.237 \times 10^{-5}\text{ mol}$ ) was constant for the previous irradiation times from gas chromatography with decahydronaphthalene as an internal standard sample. The molecular weight ( $M$ ) of the SPS3 particles was calculated to be  $5.47 \times 10^6$  with following equation:  $M = (4/3)\pi r_1^3 d_{\text{SiO}_2} N_0 + (4/3)\pi(r_2^3 - r_1^3) d_{\text{shell}} N_0$ , where  $N_0$  is Avogadro's number ( $6.025 \times 10^{23}\text{ mol}^{-1}$ ). Then, the feed amount (37.9 mg) of the SPS3 particles corresponded to  $6.93 \times 10^{-9}$  ( $0.0379/M$ ) of the particle number. The DC groups were estimated to be 1785 number/particle ( $1.237 \times 10^{-5}/6.93 \times 10^{-9}$ ).

#### Synthesis of the SPM particles by grafting from photoinduced ATRP

In a preliminary experiment, the graft polymerization of MMA initiated by the SPS3 macroinitiator under UV irradiation often led to macrogelation because of intermolecular radical couplings. The

TABLE II  
Grafting from Photoinduced ATRP Conditions and Results for the SPM Particles<sup>a</sup>

Code	SPS3 (mg)	[DC]/[CuCl]/[bpy]/[MMA]	Time (h)	Conversion (%) <sup>b</sup>	$D_n$ (nm) <sup>c</sup>	$D_w/D_n$ <sup>c</sup>	$D_h$ (nm) <sup>d</sup>
SPM1	215	1 : 1.1 : 2.1 : 40	8	24	65	1.03	95
SPM2	80	1 : 1 : 2 : 80	4	18	56	1.04	80

<sup>a</sup> Polymerized in THF (60 vol % monomer concentration) under UV irradiation at room temperature in high vacuum.

<sup>b</sup> Determined by the gravimetric method.

<sup>c</sup> Determined by a survey of 300 samples picked from SEM photographs.

<sup>d</sup>  $D_h$  was determined by DLS in THF at 25°C.

main reasons were the following: (1) a highly 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/bpy. In a previous study,<sup>23</sup> we proved from kinetic studies that this grafting from photoinduced ATRP proceeds with a living radical mechanism. Moreover, we applied this system to the architecture of nanocylinders consisting of graft block copolymers. The grafting from photoinduced ATRP conditions and results for the SPM particles are listed in Table II. The monomer conversion for SPM1 was 24% after 8 h of UV irradiation. A typical SEM photograph of the SPM1 core-shell particles is shown in Figure 1(c). Spherical particles ( $D_n = 65$  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 95 nm (see SPM1 in Fig. 2). This means that the PMMA brush chains expanded in the THF solution because THF is a good solvent for PMMA. We also performed FTIR measurements for the SPM1 core-shell particles. Figure 3(b) shows the FTIR spectrum for the SPM1 particles after PMMA growth. This spectrum exhibited the strong absorbance at  $1730\text{ cm}^{-1}$  for the  $-\text{C}=\text{O}$  bond. The ratio of optical density at  $1730\text{ cm}^{-1}$  [(OD)<sub>1730</sub> ( $-\text{C}=\text{O}$  moiety)] to the optical density at  $1600\text{ cm}^{-1}$  [(OD)<sub>1600</sub>; aromatic ring moiety] was calculated before and after grafting from photoinduced ATRP. The (OD)<sub>1730</sub>/(OD)<sub>1600</sub> value for SPM1 (1.71) increased more extremely than (OD)<sub>1730</sub>/(OD)<sub>1600</sub> for SPS3 (0.07), and PMMA propagated by grafting from the photoinduced ATRP from DC groups of the SPS3 macroinitiator.

To determine the composition of the PMMA brush chains, we also performed TGA measurements for SPM1 (see Fig. 4). It was found from TGA trace of SPM1 that a 8 wt % mass of SiO<sub>2</sub> remained after the decomposition of the polymer phase. Therefore, the volume ratio SiO<sub>2</sub>/PS shell/PMMA was estimated to be 1 : 2.43 : 11.04 with a PMMA density ( $d_{\text{PMMA}}$ ) of  $1.188\text{ g/cm}^3$ .<sup>24</sup> Then, the following relation is given;  $r_1^3 : (r_3^3 - r_2^3) = 1 : 11.04$ , where  $r_1 = 10$  and

$r_2 = 15.1$  nm and  $r_3$  is the radius of SPM1. The value of  $r_3$  was determined to be 24.9 nm. This value was in relative agreement with that observed from the SEM image (SPM1,  $D_n = 65$  nm). The thickness of the PMMA brush phase was estimated to be 9.8 nm in the solid state. The mass of the PMMA brush phase ( $M_B$ ) was calculated to be  $3.296 \times 10^7$  with following equation:  $M_B = (4/3)\pi(r_3^3 - r_2^3 - r_1^3)d_{\text{PMMA}}N_0$ . Then, the molecular weight of the PMMA brush chain was estimated to be  $1.85 \times 10^4$  ( $3.296 \times 10^7/1785$ ), with the assumption that all of the DC initiation sites on the macroinitiator led to the propagation of MMA.

The SPM particles exhibited one DC group at each PMMA brush end. SPM can be expected to be used in applications involving the construction of hybrid nanocomposites (continuous PMMA matrix) with such core-shell particles as fillers. These results will be reported in the near future.

## 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 emulsion copolymerization with SiO<sub>2</sub>, vinyl monomers, and the inimer VBDC as one component under UV irradiation. The inimer VBDC played an important role in the formation of the hyperbranched structure. The SPM particles were prepared by grafting from a photoinduced ATRP approach with MMA initiated by SPS particles as macroinitiators. Because of the promising combination of a nanostructured polymer with the properties of reactive particles, these SPM particles can be applied in the fields of hybrid nanocomposites and optic materials.

## References

- Luna-Xavier, L.; Bourgeat-Lami, E.; Guyot, A. *Colloid Polym Sci* 2001, 279, 947.
- Princen, L. H.; Stoip, J. A.; Zgol, R. J. *J Colloid Interface Sci* 1968, 28, 466.
- Lee, J.; Sena, M. *Colloid Polym Sci* 1995, 271, 76.

4. Furusawa, K.; Nagashima, K.; Anzai, C. *Colloid Polym Sci* 1994, 272, 1104.
5. Fleming, M. S.; Mandal, T. K.; Walt, D. R. *Chem Mater* 2001, 13, 3210.
6. Caruso, F. *Adv Mater* 2001, 13, 11.
7. Tiarks, F.; Landfester, K.; Antonietti, M. *Langmuir* 2001, 17, 5775.
8. Erdem, B.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. *J Polym Sci Part A: Polym Chem* 2000, 38, 4419.
9. Duguet, E.; About, M.; Morvan, F.; Maheu, P.; Fontanille, M. *Macromol Symp* 2000, 151, 365.
10. Stejskal, J.; Kratochvil, P.; Armes, S. P.; Lascelles, S. F.; Riede, A.; Helmstedt, M.; Prokes, J.; Krivka, I. *Macromolecules* 1996, 29, 6814.
11. Kageyama, K.; Tamazawa, J.; Aida, T. *Science* 1999, 285, 2113.
12. Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* 1998, 282, 1111.
13. Tang, X.; Tang, T.; Feng, Z.; Huang, B. *J Appl Polym Sci* 2002, 86, 3532.
14. Ahn, S. H.; Kim, S. H.; Lee, S. G. *J Appl Polym Sci* 2004, 94, 812.
15. Zhang, J.; Zhu, B. K.; Chu, H. J.; Xu, Y. Y. *J Appl Polym Sci* 2005, 97, 20.
16. Das, A.; De, D.; Naskar, N.; Debnath, S. C. *J Appl Polym Sci* 2006, 99, 1132.
17. La, H. S.; Park, K. S.; Nahma, K. S.; Jeong, K. K.; Lee, Y. S. *Colloids Surf A* 2006, 272, 22.
18. Park, E. J.; Kim, W. S.; Hwang, H. S.; Park, C.; Lim, K. T. *Macromol Symp* 2007, 249–250, 196.
19. Ishizu, K.; Kobayakawa, N.; Takano, S.; Tokuno, Y.; Ozawa, M. *J Polym Sci Part A: Polym Chem* 2007, 45, 1771.
20. Ishizu, K.; Mori, A. *Macromol Rapid Commun* 2000, 21, 665.
21. Ishizu, K.; Ochi, K.; Tomita, Y.; Furushima, K.; Odoi, K. *Designed Monomers Polym* 2006, 9, 403.
22. Ishizu, K.; Kakinuma, H.; Ochi, K.; Uchida, S.; Hayashi, M. *Polym Adv Technol* 2005, 16, 834.
23. Ishizu, K.; Kakimuma, H. *J Polym Sci Part A: Polym Chem* 2005, 43, 63.
24. *Polymer Handbook*, 4th ed.; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley: New York, 1999.