Synthesis of Monodisperse Silica Particles Coated with Well-Defined, High-Density Polymer Brushes by Surface-Initiated Atom Transfer Radical Polymerization

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ABSTRACT: Monodisperse silica particles (SiPs) of diameter between 100 and 1500 nm were surface-modified in a mixture of ethanol/water/ammonia with a newly designed triethoxysilane having an atom transfer radical polymerization (ATRP) initiating site, (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane. The surface-initiated ATRP of methyl methacrylate (MMA) mediated by a copper complex was carried out with the initiator-fixed SiPs in the presence of a "sacrificial" (free) initiator. The polymerization proceeded in a living manner in all examined cases, producing SiPs coated with well-defined PMMA of a target molecular weight up to 480K with a graft density as high as 0.65 chains/nm^2. These hybrid particles had an exceptionally good dispersibility in organic solvents. Transmission electron microscopic and atomic force microscopic observations of their monolayers prepared at the air−water interface revealed that they formed an ordered 2-dimensional lattice extending throughout the monolayer.

Introduction

Surface-initiated living radical polymerization (LRP) has been rapidly developing for its excellent controllability over the molecular weight and polydispersity of the graft polymers and its capability of affording an exceptionally high graft density with the robustness and versatility of LRP retained. This technique was applied to a variety of solid surfaces including flat substrates,[1−10] fine particles,[11−37] and porous[38] or tubelike structures.[39−41] Strategies have been developed to tailor silica particle (SiP) surfaces with polymers by surface-initiated LRP techniques, in particular, atom transfer radical polymerization (ATRP).[11−23] Patten et al. first succeeded in surface-initiated ATRP of styrene and methyl methacrylate (MMA) on SiPs with an average diameter of 75 and 300 nm.[11,12] Matyjaszewski et al. synthesized an initiator-functionalized SiP with a diameter about 20 nm via the sol−gel chemistry and grafted homo and block polymers on the SiP surface by ATRP.[13] Carrot et al. used a commercially available SiP with an even smaller average diameter of 12 nm and carried out ATRP of *n*-butyl acrylate from its surface.[16] Müller et al. synthesized a hybrid particle with a SiP core and the shell of a hyperbranched polymer by surface-initiated ATRP copolymerization of *n*-butyl acrylate and an ATRP initiating group-holding acrylic monomer.[17]

In search for a better route to the modification of SiP by surface-initiated ATRP, we synthesized a new triethoxysilane derivative to introduce ATRP initiation sites onto SiP surfaces without causing any aggregation of the particles. This initiator system afforded polymer-grafted SiPs with an excellent dispersibility in organic solvents. We confirmed the versatility of the developed system by successfully synthesizing SiPs of diameter between 100 and 1500 nm coated with well-defined, high-density PMMA brushes with molecular weights up to about 500K.

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Experimental Section

Materials. Ethyl 2-bromoisobutyrate (2-(EiB)Br, 98%) was used as received from Nacalai Tesque Inc., Osaka, Japan. 4,4′-Dinonyl-2,2′-bipyridine (dNbipy, 97%) was purchased from Aldrich and used without further purification. Copper(I) chloride (Cu(I)Cl, 99.9%) was purchased from Wako Pure Chemicals, Osaka, Japan. Methyl methacrylate (MMA, 99%) was obtained from Nacalai Tesque Inc. and purified by distillation over calcium hydride under reduced pressure. Platinum catalyst (Karstedt's catalyst) solution (Pt-114, platinum content: 3 wt %) was received from Johnson Matthey Catalysts, Royston, UK. Triethoxysilane (99%) was obtained from Chisso Corp., Tokyo, Japan, and distilled before use. SiPs (SEAHOSTER, 20 wt % suspension of SiP in ethylene glycol) were kindly donated by Nippon Shokubai Co., Ltd., Osaka, Japan. The average diameters of the SiPs were 130 (KE-E10), 290 (KE-E30), 740 (KE-E70), and 1550 nm (KE-E150) with relative standard deviations less than 10%, as measured with transimission electron microscopy (TEM). Water was purified by a Milli-Q system (Nihon Millipore Ltd., Tokyo, Japan) to a specific resistivity of ca. 18 MΩ·cm. All other reagents were used as received from commercial sources.

Measurements. Gel permeation chromatographic (GPC) analysis was carried out at 40 °C on a Shodex GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30 cm mixed columns (Shodex GPC KF-806L, exclusion limit = 2×10^7), and a differential refractometer (Shodex RI-101). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.8 mL/min. Poly(methyl methacrylate) (PMMA) standards were used to calibrate the GPC system. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a JEOL/AL300 spectrometer. Dynamic light scattering (DLS) measurements were made in ethanol or THF solvent at 30 °C on a DLS-7000 photometer (Otsuka Electronics, Japan) with a He−Ne laser (wavelength 633 nm and power 10 mW) as a light source. The scattering light intensity was measured at a scattering angle of 90°. Data analysis was made with the histogram method including the nonnegative least-squares analysis. TEM observation was made on a JEOL transmission electron microscope JEM-1010

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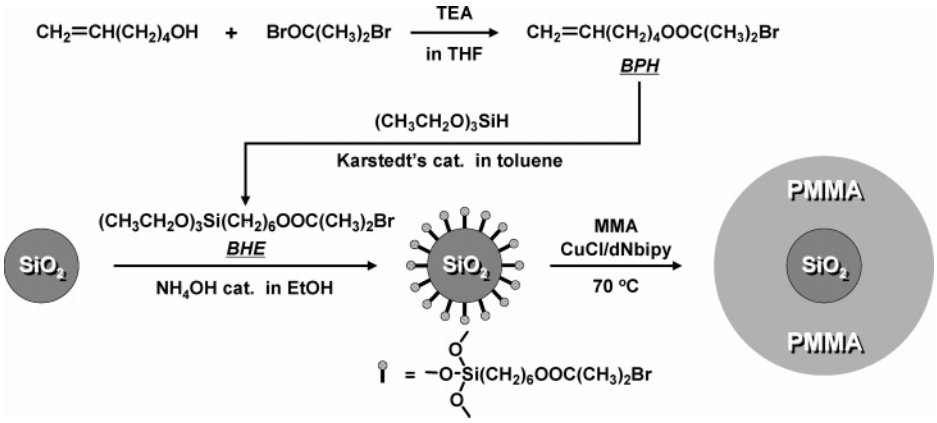
Scheme 1. Schematic Representation for the Synthesis of Polymer-Coated Silica Particle by Surface-Initiated ATRP



operated at 100 kV. Tapping-mode atomic force microscopy (AFM) analysis was carried out by a SPA-400 Multi-Function Unit (Seiko Instruments Inc.). The image was acquired in air with standard silicon OMCL-AC160 probe (Olympus Optical Co., Ltd., Japan; nominal spring constant and resonance frequency are 42 N/m and 300 kHz, respectively).

Synthesis of the Surface Initiator, (2-Bromo-2-methyl)propionyloxyhexyltriethoxysilane (BHE). BHE was synthesized via a two-step reaction (Scheme 1). First step: 2-bromoisobutyryl bromide (63 mL, 510 mmol) was added dropwise to a cold solution of 5-hexen-1-ol (43 g, 430 mmol) in dry THF (1 L) with triethylamine (71 mL, 510 mmol) at 0 °C. The mixture was magnetically stirred for 3 h at 0 °C and then for another 10 h at room temperature. The system was passed through a filter paper, and the filtrate was evaporated to dryness under reduced pressure. The residue was diluted with chloroform (500 mL) and washed twice with 1 N HCl aqueous solution (2 × 500 mL), twice with saturated $NaHCO_3$ aqueous solution (2 × 500 mL), and with water (500 mL). Drying over Na_2SO_4, filtration, and removal of the solvent gave a brown oil, which was purified by flash chromatography on a column of silica gel with a mixture of *n*-hexane/ethyl acetate = 15/1 as an eluent to yield 1-(2-bromo-2-methyl)propionyloxy-5-hexene (BPH) as a transparent liquid (95 g, 90%). ^{1}H NMR ($CDCl_3$): δ 1.47 and 1.68 (m, 4H, CH_2), 1.90 (s, 6H, CCH_3), 2.08 (q, 2H, CH_2=CHCH_2), 4.16 (t, 2H, CH_2O), 4.93−5.04 (m, 2H, CH_2=CH), 5.79 (m, 1H, CH_2=CH). ^{13}C NMR ($CDCl_3$): δ 25.0, 27.8, and 33.2 (*C*H_2), 30.8 (*C*CH_3), 55.9 (*C*Br), 65.9 (*C*H_2O), 114.9 (*C*H_2=CH), 138.2 (CH_2=*C*H), 171.7 (*C*=O). Anal. Calcd for $C_{10}H_{17}O_2Br$: C, 48.20; H, 6.89; O, 12.84. Found: C, 48.30; H, 7.00; O, 12.99.

Second step: BPH (40 g, 160 mmol) and dry toluene (500 mL) were charged into a two-neck round-bottom flask equipped with a magnetic stir bar and a rubber septum, and the system was purged with argon. Triethoxysilane (500 mL, 2.7 mol) purged with argon was added dropwise into the flask through a cannula, and subsequently Karstedt's catalyst solution (450 μL) was added into the system by a syringe. The reaction mixture was magnetically stirred under an argon atmosphere for 12 h. Complete disappearance of BHP, and hence the completion of reaction, was confirmed by ^{1}H NMR spectroscopy. (If the reaction is not completed in 12 h, it should be continued by adding a suitable amount of the catalyst to the mixture.) Unreacted triethoxysilane and toluene were completely removed under vacuum by raising the temperature to 60 °C to yield the initiator BHE as a slightly yellow liquid in a quantitative yield. ^{1}H NMR ($CDCl_3$): δ 0.63 (t, 2H, SiCH_2), 1.22 (t, 9H, CH_3CH$_2$OSi), 1.32−1.50 and 1.60−1.75 (br, 8H, CH_2), 1.93 (s, 6H, CCH_3), 3.83 (q, 6H, CH_3CH_2OSi), 4.16 (t, 2H, CH_2O). ^{13}C NMR ($CDCl_3$): δ 10.3 (Si*C*H_2), 18.3 (SiOCH_2-*C*H_3), 22.6, 25.4, 28.2, and 32.6 (*C*H_2), 30.8 (C*C*H_3), 55.9 (*C*Br), 58.3 (SiO*C*H_2CH$_3$), 66.1 (*C*H_2O), 171.7 (*C*=O). Anal. Calcd for $C_{16}H_{33}O_5BrSi$: C, 46.48; H, 8.05. Found: C, 46.34; H, 8.11.

Synthesis of Initiator-Coated SiP. The commercially supplied SiP suspension in ethylene glycol was solvent-exchanged to ethanol. Namely, the suspension was diluted with ethanol and centrifuged. The collected SiP was redispersed in ethanol followed by centrifugation. This cycle was repeated three times to obtain a SiP suspension in ethanol. A mixture of ammonia solution (28% NH_3 aqueous solution, 13.9 g) and ethanol (175 mL) was added dropwise into the SiP suspension in ethanol (7.7 wt %, 30 mL) under magnetically stirring, and the system was stirred for 2 h at 40 °C. BHE (2 g, 4.8 mmol) dissolved in ethanol (10 mL) was added dropwise into the system, and the reaction mixture was continuously stirred for another 18 h at 40 °C. Thus, modified silica particles were cleaned by consecutive centrifugation and redispersion in ethanol. Finally, the initiator-coated SiP suspension in ethanol was subjected to the solvent exchange treatment (see above) to obtain an anisole suspension to stock.

Surface-Initiated ATRP on SiP. Just before polymerization, the initiator-coated SiP in anisole was solvent-exchanged to MMA to obtain a 2 wt % suspension in MMA. A Pyrex glass tube was charged with a predetermined amount of Cu(I)Cl (solid). A mixture of the initiator-coated SiP suspension in MMA containing a prescribed concentration of 2-(EiB)Br and dNbipy was quickly added to the Pyrex glass tube. The system was immediately degassed by three freeze−pump−thaw cycles and subsequently sealed off under vacuum. The polymerization was carried out in a shaking oil bath (TAITEC Corp., Saitama, Japan, Personal H-10) thermostated at 70 °C and, after a prescribed time *t*, quenched to room temperature. An aliquot of the solution was taken out for NMR measurement to estimate monomer conversion and for GPC measurement to determine molecular weight and its distribution. The rest of the reaction mixture was diluted by THF and centrifuged to collect polymer-grafted SiP. This cycle of centrifugation and redispersion in THF was repeated five times to obtain polymer-grafted SiPs perfectly free of the unbound (free) polymer. To determine the molecular weight of the graft polymer, PMMA chains were cleaved from the surface as follows: the polymer-grafted SiP (50 mg) and tetraoctylammonium bromide (50 mg) as a phase transfer catalyst were dissolved in toluene (5 mL), to which a 10% HF aqueous solution (5 mL) was added. The mixture was vigorously stirred for 24 h. The cleaved polymer in the organic layer was isolated by precipitation from *n*-hexane, dried under vacuum, and then subjected to GPC measurement.

In a typical run, the bulk polymerization of MMA was carried out at 70 °C for 14 h with the starting materials of MMA (9.8 g, 98 mmol), 2-(EiB)Br (3.2 mg, 0.016 mmol), Cu(I)Cl (16 mg, 0.16 mmol), dNbipy (134 mg, 0.32 mmol), and initiator-coated SiP of diameter 130 nm (200 mg; the amount of initiator molecules fixed on the SiP = 0.016 mmol), which gave a monomer conversion of 71% and a free polymer with the number-average molecular weight M_n = 314 000 and the polydispersity index M_w/M_n = 1.20 and a graft polymer with M_n = 317 000 and M_w/M_n = 1.20. The polymer-grafted SiP was purified by five cycles of centrifugation and redispersion in THF (5 × 40 mL).

Preparation of Monolayers of Polymer-Grafted SiP. A drop of the 10 wt % suspension of the polymer-grafted SiP in toluene, which was prepared by solvent-exchanging from THF to toluene (see above), was put on the surface of pure water in a Petri dish (i.d. 15 cm). The formed surface film was carefully transferred onto the TEM grid or the silicon wafer, which had been placed in the water horizontally to the water surface, by vertically lifting the grid or the wafer at a rate of 3 mm/min.

Results and Discussion

Synthesis of the Surface Initiator BHE. Various ATRP initiators that can be fixed on silicon oxide surfaces have been synthesized by several groups.[1,4−6,11−22] All of them were mono- or trichlorosilane derivatives, except the monoethoxysilane derivative synthesized by Patten et al. In this study, we synthesized an initiator carrying triethoxysilane group. Even though the chlorosilane group has the advantage of high reactivity, the reaction with it must be carried out in a dried aprotic solvent to prevent an unfavorable side reaction. On the other hand, the reaction with the triethoxysilane group can be carried out in protic solvent, *even in the presence of water*. This is a clear advantage for achieving a homogeneous modification of SiP surface because SiP exhibits a higher dispersibility in a protic solvent than in an aprotic one due to the hydrophilic character of the SiP surface with silanol groups. In addition, the reaction with triethoxysilane group forms a stable Si−O−Si network via the trivalent reaction.

The triethoxysilane derivative with an initiating site for ATRP was synthesized via the two-step reaction described above: in short, 5-hexen-1-ol was acylated with 2-bromoisobutyryl bromide to obtain BPH, the aryl group of which was subsequently hydrosilylated with triethoxysilane in the presence of Karstedt's catalyst to give the final product BHE. The overall yield exceeded 90%, and its high purity was confirmed by ^{1}H and ^{13}C NMR and elemental analysis.

Fixation of the Initiator BHE on SiP. The ATRP initiator BHE was fixed onto SiP surface in ethanol solution with NH_3 added as an alkaline catalyst. The NH_3 concentration is a key parameter in this reaction: if it is too high, it will cause particle aggregation due to the high ionic strength, while if it is too low, it will make the reaction too slow. We optimized the final NH_3 concentration to be 1 M in this work. In our case, 1.2 M NH_3 solution was added into the reaction system containing SiP to prevent particle aggregation (see Experimental Section). To estimate the amount of initiator fixed on SiP, we carried out an elemental analysis and determined the bromine content to be 0.63%, which, along with the known density (1.9 g/cm^3) and the diameter (130 nm) of the particle, led to a surface density of about 2 initiator molecules/nm^2. Compared to the surface density of hydroxyl groups on SiP (5 hydroxyl groups/nm^2),[12] the estimated initiator density suggests the formation of a monolayer nearly close-packed with the initiator molecules. The initiator-coated SiP suspension in anisole formed no aggregate and could be stably stored in a refrigerator without any change at least for 6 months.

Surface-Initiated ATRP of MMA. The initiator-coated SiP was subsequently used for the copper-mediated ATRP of MMA in bulk (Scheme 1). To obtain a satisfactory result, the following points were important. First, the initiator-coated SiP should never be dried before the polymerization. Once dried, the particles are difficult to be homogeneously redispersed in the polymerization medium even by the aid of ultrasonication. In practice, we prepared a homogeneous polymerization solution via the solvent-exchange process mentioned above. Second, we carried out the polymerization in the presence of the "sacrificial" free initiator of 2-(EiB)Br. The role of the free initiator is to accumulate an appropriate amount of Cu(II) species via the termination of polymer radicals and thus to control the polymerization by the so-called persistent radical effect.[2,42]

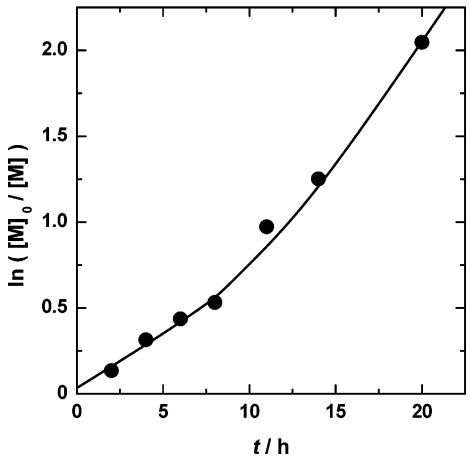


Figure 1. Plot of ln([M]$_0$/[M]) vs t for the polymerization of methyl methacrylate (MMA) in bulk at 70 °C with initiator-coated silica particle of diameter 130 nm (2 wt %): [MMA]$_0$/[ethyl 2-bromoisobutylate]$_0$/[Cu(I)Cl]$_0$/[4,4′-dinonyl-2,2′-bipyridine]$_0$ = 6000/1/10/20.

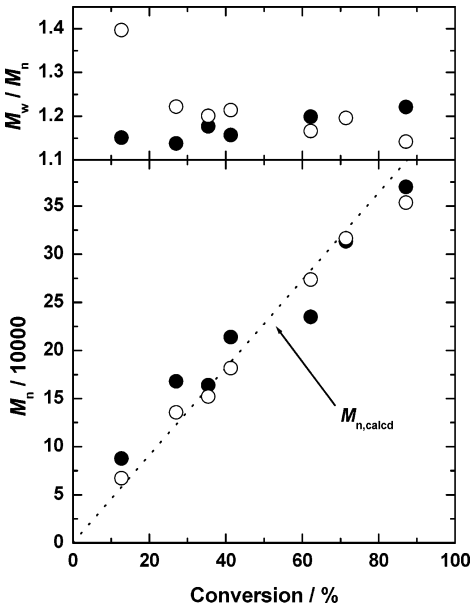


Figure 2. Evolution of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the graft (○) and free (●) polymers as a function of monomer conversion for the polymerization of methyl methacrylate (MMA) in bulk at 70 °C with initiator-coated silica particle of diameter 130 nm (2 wt %): [MMA]$_0$/[ethyl 2-bromoisobutylate]$_0$/[Cu(I)Cl]$_0$/[4,4′-dinonyl-2,2′-bipyridine]$_0$ = 6000/1/10/20.

Figure 1 shows the first-order kinetic plot of monomer concentration for the polymerization of MMA in bulk with the initiator-coated SiP of diameter 130 nm. The plot is concave upward with increasing polymerization time. In an ATRP with zero conventional initiation rate and zero Cu(II) concentration at $t = 0$, the polymeriza-

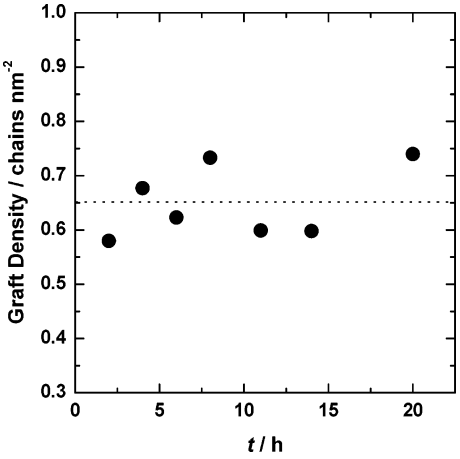


Figure 3. Time dependence of the graft density of poly(methyl methacrylate) grown from the silica particle surface.

tion rate should show the 2/3-order time dependence of conversion index $\ln([M]_0/[M])$.[43−45] However, many experimental results did not agree with this power law theory but showed a linear relationship of $\ln([M]_0/[M])$ vs t for several reasons, including the oxidation of Cu(I) in the air, the chain length dependence of termination reaction, and the solubility and reactivity change of the catalyst caused by polymerization. Agarwal et al. also observed the linear relationship of $\ln([M]_0/[M])$ vs t for the bulk polymerization of MMA under a similar polymerization condition to the one used in this work, except that SiP was not present in their system.[46] The unusual nonlinearity observed in Figure 1 may come from the large increase of the system viscosity due to the high molecular weight of polymer-grafted SiP. In a highly viscous reaction system, the polymer radicals are difficult to diffuse to undergo bimolecular termination, leading to reduced termination or enhanced polymerization rate, viz., a gel effect.

The SiP purified after the polymerization was treated with HF to cleave the graft polymer from the SiP surface, and the polymer was subjected to GPC. Figure 2 shows the evolution of the number-average molecular weight M_n and the polydispersity index M_w/M_n of the cleaved graft polymer and of the free polymer simultaneously produced from the free initiator. It can be seen that the M_ns of the graft and free polymers are nearly the same, both increasing in proportion to monomer conversion. These M_n values well agree with $M_{n,calcd}$, the value calculated with the initial molar ratio of MMA to the free initiator 2-(EiB)Br and the molar initiation sites available on the SiP surface, as will be described below. The M_w/M_n ratio remains lower than 1.2 for most samples. All these results confirm that the polymerization of MMA initiated from the SiP surface proceeds in a living fashion, giving SiPs coated with well-defined PMMA (PMMA−SiP).

Determination of Graft Density of PMMA−SiP. Elemental analysis for the PMMA−SiPs prepared above was carried out to estimate the amount of polymer grafted on the SiP, with which the graft density was calculated using the known density and surface area of the SiP and the M_n of the graft polymer. As can be seen in Figure 3, the graft density is nearly constant independent of time and approximately equal to 0.65 chains/nm^2. This figure means that PMMA chains have grown from about one-third of the initiation sites close-packingly fixed on the SiP surface. The graft density is as high as those previously attained on silicon wafer surfaces.[2,3]

Application to Various Sizes of SiPs. These results have encouraged us to extend this grafting technique to SiPs of various sizes. There are few reports on

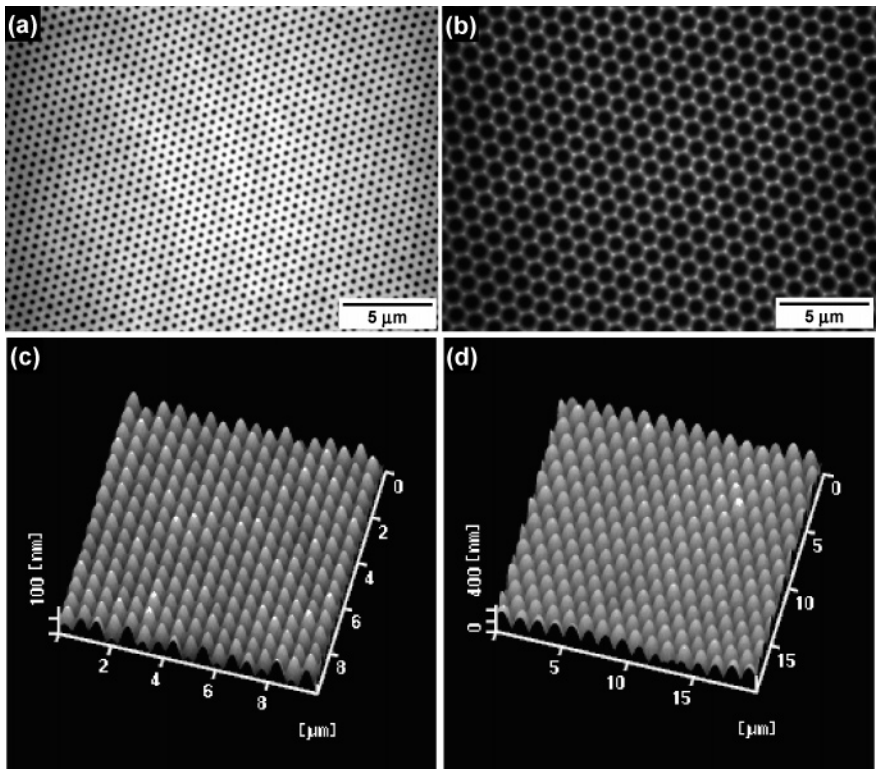


Figure 4. Transmission electron microscopic and atomic force microscopic images of the transferred films of silica particles coated with poly(methyl methacrylate) bruses (PMMA−SiPs): the diameters of the silica particle cores are (a, c) 290 and (b, d) 740 nm. Number-average molecular weights of the graft polymers are (a, c) 337 000 and (b, d) 407 000.

Table 1. Results of Surface-Initiated Atom Transfer Radical Polymerization of Methyl Methacrylate on Various Silica Particles[a]

diameter of silica particle (nm)	time (h)	M_n(graft)[b]	M_w/M_n(graft)[b]	graft density (chains/nm^2)
130	4	135 700	1.22	0.68
130	20	354 000	1.14	0.75
290	4	79 400	1.30	0.69
290	23	337 000	1.19	0.90
740	4	78 600	1.28	0.63
740	20	407 000	1.22	0.85
1550	4	79 100	1.27	0.70
1550	42	475 000	1.27	0.88

[a] All reactions were carried out with 2 wt % of the initiator-coated silica particle in bulk at 70 °C: [methyl methacrylate]$_0$/[ethyl 2-bromoisobutylate]$_0$/[Cu(I)Cl]$_0$/[4,4′-dinonyl-2,2′-bipyridine]$_0$ = 6000/1/10/20. [b] Number-average molecular weight and polydispersity index of the cleaved graft polymer.

Table 2. Results of Dynamic Light Scattering Measurements of Silica Particles

sample	d[c] (nm)	σ[d] (%)
PMMA−SiP[a]	495	4.9
initiator-coated SiP[b]	154	5.0
bare SiP[b]	145	5.2

[a] Measured in tetrahydrofuran. [b] Measured in ethanol. [c] Average hydrodynamic diameter. [d] Relative standard deviation.

the surface-initiated ATRP on SiPs of diameter larger than 300 nm. We attempted graft polymerization with another three SiPs with diameter 290, 740, and 1550 nm. The results are summarized in Table 1. The polymerization was well controlled in all cases, as indicated by the low polydispersity of the graft polymers and the high graft density.

DLS Measurements of PMMA−SiP. The PMMA−SiPs obtained here are well dispersed in most common good solvents for PMMA. DLS measurement was carried out for the PMMA−SiP with a core diameter 130 nm (as determined by TEM) and graft polymer of M_n = 140 000 in dilute THF solution. For comparison, the corresponding initiator-coated and bare SiPs were also measured in ethanol. The results are given in Table 2, which shows that the average hydrodynamic diameter (d) of the PMMA−SiP was 495 nm, d of the initiator-coated SiP was 154 nm, and d of the bare SiP was 145 nm. Importantly, the relative standard deviation σ remained nearly constant around 5% before and after the initiator fixation and also before and after the graft polymerization. This means that the particles have retained their high dispersibility throughout the experimental processes.

Formation of Monolayer of PMMA−SiP at the Air−Water Interface. When a drop of 10 wt % suspension of PMMA−SiPs in toluene was deposited onto the surface of purified water, a surface film of the PMMA−SiP was formed at the air−water interface as the toluene was evaporated off. The film was transferred onto a TEM grid and a silicone wafer. Figure 4a,b shows the TEM images of the transferred films of the PMMA−SiPs with two different diameters of the SiP core and nearly the same molecular weight of the graft polymer (M_n = 400 000). The SiP cores visible as dark circles are uniformly dispersed throughout the film, while the PMMA chains, which should be forming fringes surrounding the SiP cores, are hardly seen because of their much lower electron density. The AFM images in Figure 4c,d exhibit the surface structure of the film transferred on the silicon wafer. It can be seen that the protrusions composed of SiP core and PMMA layer surrounding the core are standing with a constant spacing on the substrate. These results suggest that the lattice parameters could be easily and widely manipulated by changing the SiP diameter, the PMMA molecular weight, and the preparation condition of the surface film. Further studies are underway to address this issue.

Conclusions

A new silane coupling agent BHE was designed and used to prepare an initiator-coated SiP, with which hybrid particles of a SiP core and a well-defined, high-density PMMA brush were successfully prepared. These hybrid particles showed an exceptionally good dispersibility in organic solvents and, on the water surface, formed two-dimensional ordered arrays.

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