Monodisperse Silica Particles Grafted with Concentrated Oxetane-Carrying Polymer Brushes: Their Synthesis by Surface-Initiated Atom Transfer Radical Polymerization and Use for Fabrication of Hollow Spheres

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ABSTRACT: An oxetane group-carrying methacrylate, 3-ethyl-3-(methacryloyloxy)methyloxetane (EMO), was polymerized via copper-mediated atom transfer radical polymerization (ATRP) initiated from the surface of monodisperse silica particles (SiPs). The polymerization proceeded in a living manner producing SiPs grafted with well-defined poly(EMO) (PEMO) of target molecular weight up to about 400K with a graft density as high as 0.36 chains/nm^2. The surface-initiated ATRP of methyl methacrylate (MMA) with PEMO-grafted SiPs as macroinitiator afforded SiPs grafted with block copolymer of the type PEMO-*b*-PMMA ((PEMO-*b*-PMMA)-SiPs). The PEMO layer of (PEMO-*b*-PMMA)-SiPs, located between the PMMA shell and the SiP core, was cross-linked by cationic ring-opening reaction of the oxetane groups of the EMO moieties. The removal of the SiP core of the cross-linked (PEMO-*b*-PMMA)-SiPs by HF etching gave polymeric hollow spheres having size uniformity and good dispersibility in organic solvents.

Introduction

Surface-initiated living radical polymerization (LRP) has been rapidly developed for its excellent controllability over the molecular weight, polydispersity, and chain-end functionality of the graft polymers and its capability of affording an exceptionally high graft density with the robustness and versatility of LRP retained.[1,2] In particular, atom transfer radical polymerization (ATRP)[3] is widely used for this purpose[4−11] and applied to a variety of solid surfaces of different shapes and materials.[12−33]

We recently developed a useful route to the modification of silica particle (SiP) by surface-initiated ATRP and synthesized hybrid nanoparticles with a monodisperse SiP core of diameter between 100 and 1500 nm and a well-defined, concentrated poly(methyl methacrylate) (PMMA) brush with graft chain molecular weight up to about 500K.[34] The perfect dispersibility of these hybrid particles allowed us to fabricate their two-dimensional ordered arrays formed at the air−water interface by simply depositing the particle suspension of an appropriate concentration onto a water surface,[35] and more notably in suspension, to construct a new type of colloidal crystals, which we call "semi-soft" colloidal crystals.[36] In these crystals, the interparticle potential is exerted by the steric or excluded-volume interaction between the highly extended concentrated polymer brushes, and thus the lattice and other parameters of the colloidal crystals are widely and easily controlled by manipulating the core, brush, and solvent properties.[36]

To broaden the applicability of the mentioned chemistry and technology, we, in this work, have employed a functional methacrylate monomer, 3-ethyl-3-(methacryloyloxy)methyloxetane (EMO, Figure 1), having a four-membered cyclic ether, i.e., oxacyclobutane (oxetane). Oxetanes are readily polymerized by various cationic initiators such as boron trifluoride (BF_3) to yield polyesters through a ring-opening process,[37] and they exhibit higher reactivity than frequently used, three-membered cyclic ethers of oxiranes, e.g., ethylene oxide, in cationic ring-opening polymerization.[38] Vinyl monomers carrying a pendent oxetane group have been synthesized by several researchers, who obtained desirable results in both radical and cationic polymerizations.[39,40] Sato et al. reported that radical polymerization of EMO proceeded through the reaction of the vinyl group and the subsequent cationic polymerization of thus-obtained poly(EMO) (PEMO) proceeded through the ring-opening of the oxetane moiety to provide a cross-linked polymer.[40] Attempts were made to carry out ATRP of monomers carrying a pendent cyclic ether: Srinivasan et al.[41] and Singha et al.[42] carried out the ATRP of glycidyl methacrylate and 3-ethyl-3-(acryloyloxy)methyloxetane, respectively, to provide well-defined polymers with the cyclic ether groups remaining unaffected. It will be described below that PEMO and related block copolymers with narrow molecular weight distribution are readily grafted on SiP surfaces by surface-initiated ATRP, producing monodisperse hybrid particles having a spherical silica core and a shell of well-defined, oxetane-holding polymer brush.

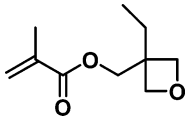

Figure 1. Chemical structure of 3-ethyl-3-(methacryloyloxy)methyloxetane (EMO).

The other aspect of this work concerns the fabrication of perfectly dispersive, monodisperse polymeric hollow spheres. Much effort has been made to design and fabricate polymeric hollow spheres for their potential utility for the encapsulation and controlled release of various substances including drugs, cosmetics, and dyes and for the use as confined reaction vessels. Key technologies for the fabrication of polymeric hollow spheres include micelle formation of block copolymer,[43] seed polymerization,[44] emulsion polymerization,[45] and layer-by-layer technique.[46] Strategies based on surface-initiated LRP have also been

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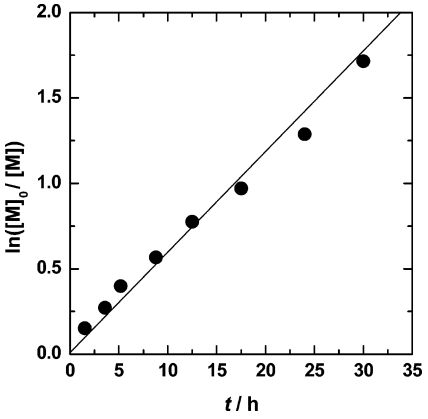


Figure 2. Plot of ln([M]$_0$/[M]) vs *t* for the solution polymerization of 3-ethyl-3-(methacryloyloxy)methyloxetane (EMO, 50 wt %) in anisole at 60 °C with initiator-coated silica particle of diameter 130 nm (2 wt %): [EMO]$_0$/[ethyl 2-bromoisobutyrate]$_0$/[Cu(I)Cl]$_0$/[4,4′-dinonyl-2,2′-bipyridine]$_0$ = 3000/1/5/10.

developed: Mandal et al. carried out surface-initiated ATRP of benzyl methacrylate on SiP and then etched out the silica core by hydrofluoric acid (HF) treatment to produce a hollow sphere with a shell of poly(benzyl methacrylate) (PBzMA) brush layer.[47] This hollow sphere is dissolved into individual free chains in good solvent for PBzMA because the grafting points between the polymer chains and SiP surface no longer exist after etching the silica core. To overcome this drawback, polymeric hollow spheres with a cross-linked shell were produced: Hawker et al. used the strategy based on cross-linking of the polymer chains end-grafted on SiP by surface-initiated nitroxide-mediated LRP.[48] Cross-linking reaction was achieved either thermally by the incorporation of benzocyclobutene groups in the polymer chains or chemically by the reaction of maleic anhydride units incorporated in the polymer chains with 2,2′-(ethylenedioxy)bis(ethylamine) as a cross-linker. Kang et al. prepared SiPs grafted with a block copolymer of the type of polystyrene (PS)-*b*-PMMA by surface-initiated ATRP stepwise copolymerization of styrene and MMA.[49] Ultraviolet (λ = 254 nm) exposure of the hybrid particles resulted in cross-linking of the PS intermediate layer and decomposition of the PMMA outermost layer, and subsequent removal of the silica core with HF etching provided cross-linked PS hollow spheres. These authors claimed that the sacrificial PMMA layer played an important role to prevent interparticle cross-linking and aggregation, while they presented no clear evidence showing the dispersibility of the obtained hollow sphere particles.

We in this work will prepare hallow spheres from the monodisperse SiPs grafted with oxetane-holding polymer brushes by making use of the ring-opening reactivity of oxetane for the shell cross-linking. To be highlighted are the high productivity of the developed strategy and the high dispersibility of the resultant hollow spheres.

Experimental Section

Materials. Ethyl 2-bromoisobutyrate (2-(EiB)Br, 98%) and anisole (99%) were 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%) and copper(I) bromide (Cu(I)Br, 99.9%) were purchased from Wako Pure Chemicals, Osaka, Japan. Methyl methacrylate (MMA, 99%) was obtained from Nacalai Tesque Inc. and purified by passing through a column of activated basic alumina to remove inhibitor. 3-Ethyl-3-(methacryloyloxy)methyloxetane (EMO) was obtained from Osaka Organic Chemical Industry Ltd., Osaka, Japan, and purified by passing through a column of activated basic alumina and then by double distillation under reduced pressure before use. Boron trifluoride−diethyl etherate (BF_3OEt_2) was used as received from Aldrich. Anhydrous dichloromethane (99%) was purchased from Wako Pure Chemicals. SiPs (SEAHOSTER, 20 wt % suspension of SiPs in ethylene glycol) were kindly donated by Nippon Shokubai Co., Ltd., Osaka, Japan. The average diameters of the SiPs were 130 nm (KE-E10) and 740 nm (KE-E70) with relative standard deviations less than 10%, as measured by transmission electron microscopy (TEM). All other reagents were used as received from commercial sources.

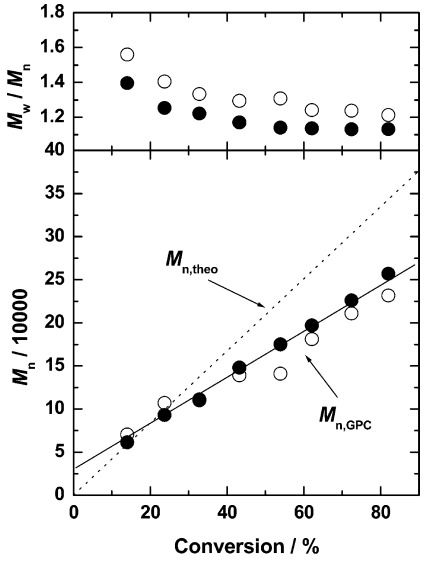


Figure 3. Evolution of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the graft (○) and free (●) polymers as a function of monomer conversion for the solution polymerization of 3-ethyl-3-(methacryloyloxy)methyloxetane (EMO, 50 wt %) in anisole at 60 °C with initiator-coated silica particle of diameter 130 nm (2 wt %): [EMO]$_0$/[ethyl 2-bromoisobutyrate]$_0$/[Cu(I)Cl]$_0$/[4,4′-dinonyl-2,2′-bipyridine]$_0$ = 3000/1/5/10.

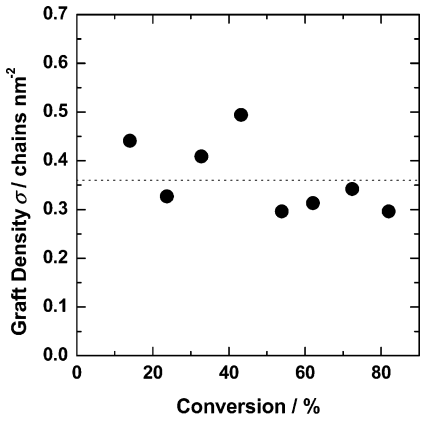
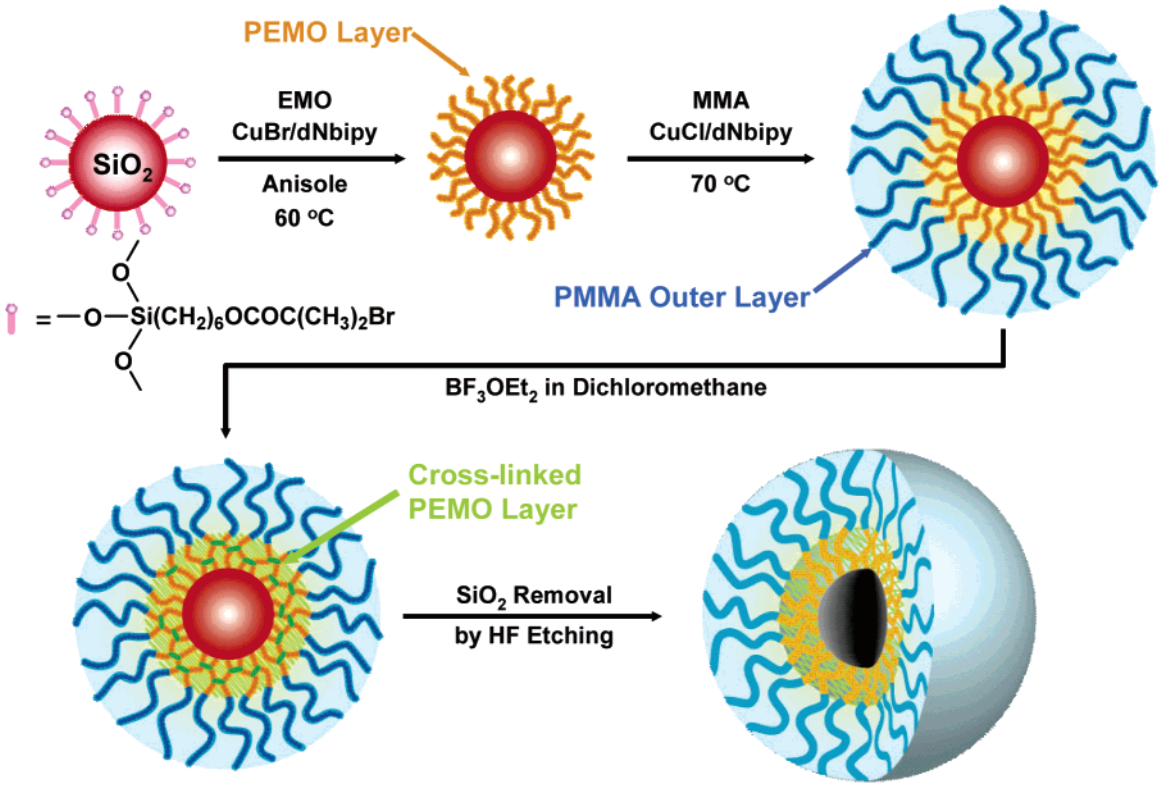


Figure 4. Evolution of the graft density of poly(3-ethyl-3-(methacryloyloxy)methyloxetane) grown from silica particles surface as a function of monomer conversion.

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. GPC analysis combined with light scattering measurement (GPC-LS) was carried out on Shodex GPC-101 equipped with a multiangle light scattering detector (Wyatt Technology DAWN EOS). TEM observation was made on a JEOL transmission electron microscope JEM-1010 operated at 100 kV. Scanning electron microscopic (SEM) observa-

Scheme 1. Schematic Representation for the Synthesis of Polymeric Hollow Spheres



tion was performed using a scanning electron microscope S-3400N (Hitachi, Japan) at an accelerating voltage of 30 kV. Sample was cast onto a cover glass mounted on an aluminum stub and sputter-coated with gold/palladium to minimize sample charging by a Hitachi ion sputter E-1010. Infrared (IR) spectra were recorded on a BioRad FTS 6000 Fourier transform spectrometer (Hercules, CA). Dynamic light scattering (DLS) measurement was made in chloroform solvent at 20 °C on a DLS-7000 photometer (Otsuka Electronics, Japan) equipped 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.

Polymerization. SiPs were surface-modified in a mixture of ethanol/water/ammonia with a triethoxysilane having an ATRP initiating site, (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane (BHE), as reported previously.[34] The surface-initiated ATRP of EMO was carried out with the initiator-coated SiPs as follows. In a typical run, a Schlenk tube was charged with EMO (15 g, 81.4 mmol), 2-(EiB)Br (5.5 mg, 0.027 mmol), dNbipy (111 mg, 0.27 mmol), and a suspension of initiator-coated SiPs (0.6 g) in anisole (14.9 g), and the mixture was deoxygenated by purging with argon for 10 min. In a glovebox purged with argon, Cu(I)Cl (13 mg, 0.14 mmol) or Cu(I)Br (20 mg, 0.14 mmol) was added to this mixture, and a three-way stopcock was attached to the Schlenk tube. The polymerization was carried out in a shaking oil bath thermostated at 60 °C, and after a prescribed time *t*, an aliquot of the solution was taken out for NMR measurement to estimate monomer conversion and for GPC measurement to determine the molecular weight and its distribution of the free chains produced in solution from the free initiator 2-(EiB)Br. The main reaction mixture was diluted by acetone and centrifuged to collect polymer-grafted SiP. The cycle of redispersion in acetone and centrifugation was repeated five times to obtain polymer-grafted SiP (PEMO-SiP) perfectly free of the unbound (free) polymer. To determine the molecular weight of the graft polymer, PEMO chains were cleaved from the surface as follows: the polymer-grafted SiP (18 mg) was dissolved in acetone (17.5 g), to which a 40 wt % HF aqueous solution (2.5 g) was added. The mixture was stirred for 3 h. The cleaved polymer in the mixture was isolated by precipitation from water and then subjected to GPC measurement.

The surface-initiated ATRP block copolymerization was carried out for 48 h at 70 °C in bulk MMA (29.5 g, 294.5 mmol) containing 2-(EiB)Br (10 mg, 0.049 mmol), dNbipy (402 mg, 0.98 mmol), Cu(I)Cl (49 mg, 0.49 mmol), and the macroinitiator PEMO-SiP (600 mg) to yield SiP coated with PEMO-*b*-PMMA block copolymer ((PEMO-*b*-PMMA)-SiP).

Preparation of Polymeric Hollow Sphere. (PEMO-*b*-PMMA)-SiPs (2 or 8 wt %) was dissolved in dichloromethane, and the mixture was deoxygenated by purging with dry argon for 10 min. To this mixture in a glovebox purged with argon, BF_3OEt_2 (1 wt %) was added, and the system was equipped with a stopcock and stirred for 24 h at ambient temperature. The suspension was diluted by toluene and washed by repeating centrifugation and redispersion in toluene. The SiP core in the hybrid particle was removed as follows: tetraoctylammonium bromide (500 mg) as a phase transfer catalyst was added in a polyethylene bottle containing the hybrid particle (250 mg) dissolved in toluene (50 g), to which, a 10% HF aqueous solution (50 g) was added. The mixture was vigorously stirred for 3 h. The treated particles suspended in the organic layer were collected by centrifugation and washed by five cycles of centrifugation and redispersion in acetone.

Results and Discussion

Surface-Initiated ATRP of EMO. As already mentioned above, we succeeded in the first synthesis of perfectly dispersive hybrid particles grafted with concentrated polymer brushes by surface-initiated ATRP, in which polymerization of MMA was achieved *in bulk* with initiator-coated SiP in the presence of a sacrificial (free) initiator.[34] According to this established technique, we, at first, attempted the surface-initiated ATRP of EMO *in bulk*. However, the system failed to give satisfactory results with respect to the predictability of the molecular weight and/or low polydispersity of the product, probably due to too fast reaction *in bulk*. We finally achieved a truly successful result with the solution polymerization of EMO in anisole.

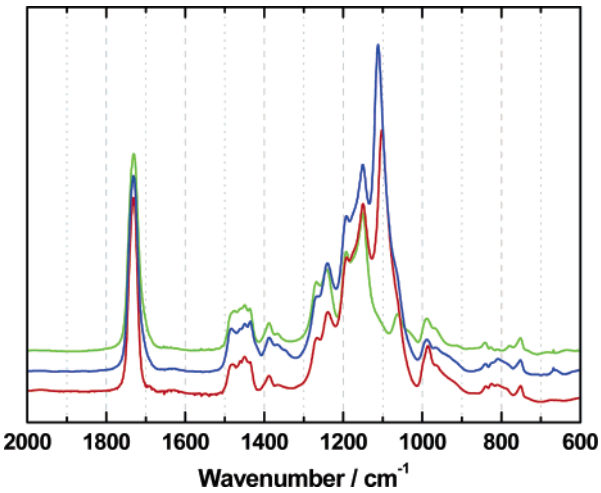


Figure 5. Fourier transform infrared spectra of the products at each step for the fabrication of the polymeric hollow spheres. The red and blue lines correspond to the hybrid particles before and after cross-linking of the poly(3-ethyl-3-(methacryloyloxy)methyloxetane) layer, respectively. The green line corresponds to the product after removal of silica cores by HF etching. The diameter of the silica particle core is 740 nm. Number-average molecular weight of the PMMA-*b*-PEMO block copolymers grafted onto silica particles is 832 000.

Figure 2 shows the first-order kinetic plot of monomer concentration for the polymerization of EMO in anisole on the initiator-functionalized SiP with the diameter 130 nm using Cu(I)Cl/dNbipy as a catalyst. The plot can be approximated by a straight line passing through the origin, thus giving first-order kinetics with respect to monomer conversion. In the previously examined system for the surface-initiated ATRP of MMA in bulk, the first-order plot of monomer concentration was concave upward with increasing polymerization time, showing a gel effect most probably due to the large increase of the system viscosity.[34] Such a gel effect was not observed for the polymerization of EMO probably because the polymerization was carried out in anisole, which reduces the system viscosity.

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 3 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 produced from the free initiator. It can be seen that the M_n of the graft and free polymers are nearly the same,[5a,12b,34] both increasing in proportion to monomer conversion. The values of M_n estimated by PMMA-calibrated GPC ($M_{n,GPC}$) slightly deviated from the theoretical values $M_{n,theo}$ calculated with the initial molar ratio of EMO to the free initiator and the molar initiation sites available on the surface, as shown in Figure 3. This may be due to the difference in the hydrodynamic volume of the PMMA and the PEMO. To confirm this, GPC-LS measurement was made for the PEMO sample ($M_{n,GPC}$ = 204 000) prepared by the same method. The light scattering M_n value ($M_{n,LS}$) was 332 000, which is larger than the $M_{n,GPC}$ values and closer to the $M_{n,theo}$ value of 303 000. This may allow us to adopt the theoretical M_n values in the following discussion. As shown in Figure 3, the M_w/M_n ratio remains lower than 1.3 for most samples, although the ratio of the graft polymers is slightly larger than that of the free polymers for a still unclear reason. All these results confirm that the polymerization of EMO initiated from the SiP surface proceeds in a living fashion, affording SiPs grafted with well-defined PEMO (PEMO-SiP). It may be emphasized that we have for the first time succeeded in the synthesis of low-polydispersity, cyclic ether-containing polymers of molecular weights up to 400K by ATRP in both free and surface-confined media, while reported ATRP results for cyclic ether-carrying monomers, which all concerned a free medium, gave well-defined polymers no greater than 10K.[41,42]

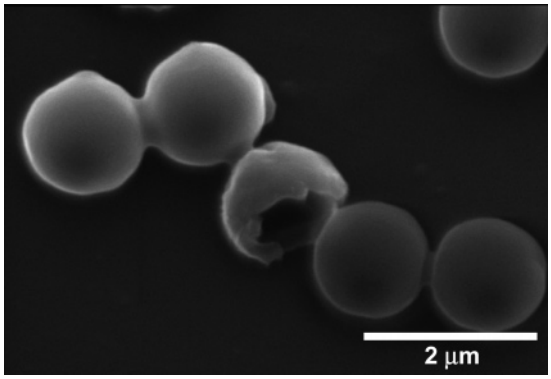


Figure 6. Scanning electron microscopic image of polymeric hollow spheres. The particles were treated by a mortar prior to the measurement for the direct observation of hollow structure. The diameter of the silica particle used for the fabrication of the hollow spheres is 740 nm.

Determination of Graft Density of PEMO-SiP. Elemental analysis for the PEMO-SiPs prepared above was carried out to estimate the amount of polymer grafted on the SiP. With the estimated amount of polymer, 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 4, the graft density σ is nearly constant, independent of conversion and approximately equal to 0.36 chains/nm^2. This density is lower than the value about 0.65 chains/nm^2 previously attained for the surface-initiated ATRP of MMA on SiP,[34] and the difference can be ascribed to the higher bulkiness of EMO unit compared to MMA unit. Incidentally, the volume ν_M per monomer unit, estimated from the molar mass of monomer and the bulk density (assumed, for simplicity, to be 1.0 g/cm^3 for both monomers) is 0.17 and 0.31 nm^3 for MMA and EMO, respectively, which suggests that the surface occupancy σ^*, i.e., the dimensionless graft density reduced by the monomer volume, is nearly the same for EMO ($\sigma^* = \sigma\nu_M/0.25 = 0.45$) and MMA (0.44).

Block Copolymerization of MMA Initiated from PEMO-SiP. As is well-known, the halogen exchange reaction using alkyl bromide and copper chloride as initiator/catalyst works very well in block copolymerization based on ATRP mechanism, giving an excellent block efficiency.[50] This strategy was employed to obtain SiP grafted with well-defined block copolymer of the type PEMO-*b*-PMMA ((PEMO-*b*-PMMA)-SiP). The surface-initiated ATRP of EMO using Cu(I)Br proceeded in a living manner as in the case of polymerization with Cu(I)Cl, providing PEMO-SiP having a bromine end group. In a typical run, the solution polymerization of EMO (50 wt %) in anisole with the initial molar ratio of $[EMO]_0/[2\text{-}(EiB)Br]_0/[Cu(I)Br/2dNbipy]_0$ = 3000/1/5 in the presence of initiator-coated SiP of diameter 740 nm was carried out at 60 °C for 14 h and gave a PEMO graft with $M_{n,GPC}$ = 304 000 and M_w/M_n = 1.25 and a monomer conversion of 85%. The PEMO-SiP with bromine end groups was used as a macroinitiator for surface-initiated atom transfer block copolymerization of MMA at 70 °C for 48 h. The polymerization gave a monomer conversion of 95% and a block copolymer PEMO-*b*-PMMA with $M_{n,GPC}$ = 823 000 and M_w/M_n = 1.32 (Supporting Information).

Preparation of Polymeric Hollow Nanosphere. We have used the (PEMO-*b*-PMMA)-SiP as a starting material to fabricate a polymeric hollow sphere. The strategy is shown in

Table 1. Results of Dynamic Light Scattering Measurements[a]

entry	sample	d^b (nm)	s^c (%)
1	(PEMO-*b*-PMMA)-SiP	3090	5.2
2	cross-linked (PEMO-*b*-PMMA)-SiP (2 wt %)[d]	3200	5.3
3	cross-linked (PEMO-*b*-PMMA)-SiP (8 wt %)[d]	3180	4.9
4	hollow sphere	3210	4.6

[a] Measured in chloroform. The diameter of the silica particle used for the fabrication of the hollow spheres is 740 nm. [b] Average hydrodynamic diameter. [c] Relative standard deviation. [d] Cross-linking reactions were carried out using BF_3OEt_2 at the particle concentration described in parentheses.

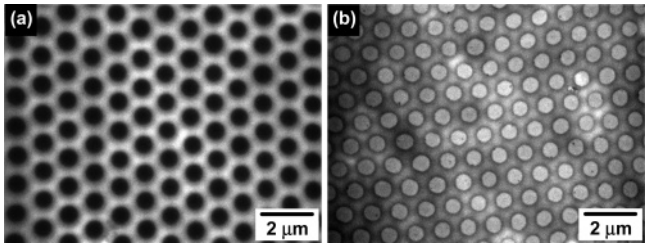


Figure 7. Transmission electron microscopic images of the transferred monolayers of (a) hybrid particles and (b) hollow spheres. The diameter of the silica particle core is 740 nm. Number-average molecular weight of the PMMA-*b*-PEMO block copolymers grafted onto SiPs is 832 000.

Scheme 1: First, block copolymers of the type PEMO-*b*-PMMA are grafted on SiP by surface-initiated ATRP, as described above. Second, the PEMO layer of the block copolymer shell is cross-linked through the ring-opening reaction of the oxetane groups using BF_3OEt_2 in dichloromethane, forming linear ether linkages, while the outermost PMMA layer is expected to work as protective layer preventing interparticle cross-linking during the reaction of the PEMO layer. Third, the SiP core is removed by HF etching.

Figure 5 shows the IR spectra of the products at each step for the fabrication of the polymeric hollow spheres. The peak at 1730 cm^{-1}, which is assigned to the C═O stretching of the ester bond of the methacrylates, remained unchanged through the overall synthesis. The peak at 980 cm^{-1}, which is assigned to the C−O−C antisymmetric stretching of the oxetane ring, decreased after the BF_3OEt_2 treatment in the presence of 2 wt % of the hybrid particles, indicating that the ring-opening reaction had taken place. The peaks around 800 and 1100 cm^{-1}, which is derived from the SiP core, decreased upon the HF treatment. Thermogravimetric analysis for the final product of hollow spheres revealed that no residual material was left after heating up to 500 °C under nitrogen, which also confirms that the SiP core was removed completely by the HF treatment.

To verify that the final product has a hollow structure, the spheres were treated by an earthenware mortar. Figure 6 shows the SEM image of thus-treated spheres. The image of the broken sphere shows that it has a cavity whose size corresponds to the diameter of the SiP core (740 nm). The shell thickness estimated by the same image is about 250 nm, which is nearly the same as the value (230 nm) theoretically calculated by assuming the PEMO-*b*-PMMA shell of its bulk density. Note that no broken particles were observed before the mortar treatment.

DLS measurements were carried out for the products at each step of the fabrication of the polymeric hollow spheres. The results are given in Table 1, which shows that all samples have nearly the same hydrodynamic diameter, about 3200 nm. Importantly, the relative standard deviation *s* remained nearly constant around 5% before and after the cross-linking of the PEMO layer and also before and after the removal of SiP core. Also notably, the *s* value remained unchanged before and after the cross-linking reaction of the PEMO layer with an even higher particle concentration of 8 wt %, which is the maximum possible concentration to achieve homogeneous stirring of the highly viscous solutions. These results mean that the particles have retained their high dispersibility throughout the experimental processes owing to the effective work of the PMMA block layer as a protective layer and that this system can potentially be used to produce monodisperse polymeric hollow spheres on a large scale.

Two-Dimensional Ordered Array of Polymeric Hollow Spheres. A monolayer of the polymeric hollow spheres was formed at the air−water interface by depositing a defined amount of the particle suspension in toluene (10 wt %) onto water surface, according to the method reported previously.[35] The hybrid particles before HF etching were also used for comparison. Figure 7a shows the TEM image of a monolayer of the hybrid particles. The SiP cores visible as dark circles are uniformly dispersed throughout the film with a constant interparticle distance, while the polymer chains, which should be forming fringes surrounding the SiP cores, are hardly seen because of their much lower electron density. The hollow spheres formed a uniform film on the surface of water, in a similar way as the hybrid particles. Its TEM image is shown in Figure 7b. The inner spaces corresponding to the SiP cores in Figure 7a appear as bright circles and are regularly distributed throughout the monolayer, which further indicates that the spherical cavities generated upon etching of the SiP cores form a two-dimensional ordered array. These polymer films featuring ordered arrays of spherical cavities could be used to fabricate highly ordered porous membranes.

Conclusions

An oxetane-carrying monomer EMO was successfully polymerized by surface-initiated ATRP to provide SiPs grafted with well-defined, concentrated PEMO brushes of a target molecular weight up to about 400K. The oxetane group can react with various functional groups.[51] Such chemistry will allow us to further functionalize PEMO brushes. Block copolymerization of MMA from PEMO-grafted SiPs as macroinitiator was achieved to afford (PEMO-*b*-PMMA)-SiPs, which was further used for the fabrication of perfectly dispersive, monodisperse polymeric hollow spheres. The thickness of the PEMO shell layer and of the PMMA brush layer and the size of cavity can be manipulated by changing the chain length of the grafted polymer and the size of SiP core, respectively, which enables access to polymeric hollow spheres of various structures. Also, because of the versatile applicability of ATRP to a large variety of monomers, this technique can be extended to the synthesis of many types of polymeric hollow spheres.

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Supporting Information Available: Detailed experimental procedures and data for the synthesis of block copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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