

Production of Hollow Polymeric Microspheres by Surface-Confined Living Radical Polymerization on Silica Templates

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Uniform hollow polymer microspheres were prepared by coating silica microsphere templates with poly(benzyl methacrylate) using surface-initiated controlled/living radical polymerization and subsequently removing the core by chemical etching. Shell thickness was controlled by varying the polymerization time. Scanning electron microscopy was used to characterize the products and to demonstrate that the polymer microspheres were hollow. FTIR spectroscopy showed that the silica cores were completely removed by etching.

Introduction

A variety of structured particles have been prepared previously including core-shell,^{1–3} microdomain,⁴ hollow sphere,⁵ core-corona,⁶ and interpenetrating polymer networks.⁷ Hollow micro- and nanospheres represent unique classes of materials with applications in the fields of medicine and materials science. Potential applications include use as a product encapsulator for controlled-release drugs,^{5,8} dyes and inks,⁵ enzymes,⁸ and paints; as a protector of light-sensitive compounds,⁵ as heterogeneous catalysts.⁹

To fill the growing need for encapsulation materials, several different routes to hollow ceramic and polymeric nano- and microspheres have been developed recently. For example, vesicle-templated polymers,¹⁰ dendrimers,¹¹ block copolymers,¹² and template-synthesized microtubules¹³ have been produced. In some cases these are used as encapsulants for catalytic metal clusters, small molecules, and enzymes. Submicrometer-sized

spheres of yttrium compounds have been prepared by coating cationic polystyrene latex particles with yttrium basic carbonate followed by calcining.¹⁴ Silica hollow spheres have been synthesized by seeded polymerization of tetraethoxysilane on the surface of polystyrene particles followed by calcination.¹⁵ More recently, inorganic and hybrid inorganic-organic hollow microspheres have been prepared by coating colloidal core templates with alternating layers of oppositely charged nanoparticles and polymers.^{16,17} Cores were then removed by heat or chemical treatment.

In addition to these different approaches for making hollow ceramic spheres, a variety of novel techniques have evolved for producing polymeric hollow spheres or hollow latex particles. One of the earliest processes for making hollow latex particles was developed by Rohm and Haas.^{18–20} Their process involves copolymerizing an unsaturated monomer (e.g. acrylates and methacrylates) and a carboxyl group containing unsaturated monomer by emulsion polymerization to prepare seed particles (cores). These seed particles are covered with permeable polymer shells by copolymerizing an unsaturated monomer and small amount of unsaturated carboxylic acid in the presence of the core polymer dispersion. The carboxylated cores of the resulting core-shell particles are subsequently ionized with an aqueous volatile base. This procedure results in the expansion of the core by osmotic entry of water to produce hollow particles with water and polyelectrolyte in the interior.

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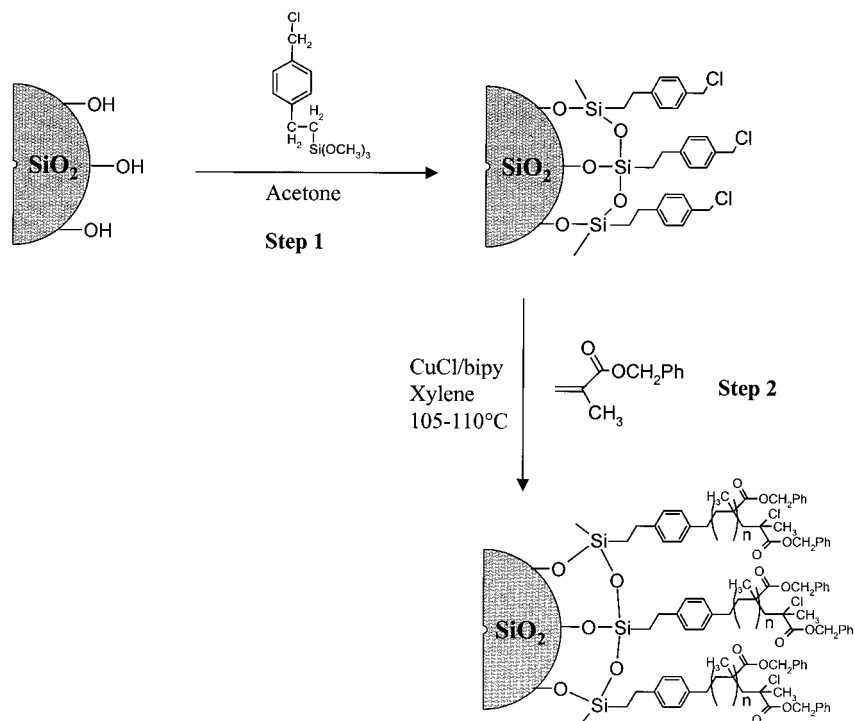
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Scheme 1



Several alternative procedures for the production of hollow polymer spheres have been patented. These processes are complex and consist of several steps employing different chemistries.^{21,22} A different approach for making hollow polymeric microspheres has been reported recently consisting of two steps.²³ The first step involves an emulsion polymerization of styrene containing a small amount of vinyl carboxylic acid in the presence of a hydrocarbon, surfactant, and a water-miscible alcohol. The hydrocarbon is a nonsolvent for the polymer being formed, and as monomer is consumed, the polymer becomes less compatible with the dispersed hydrocarbon/monomer mixture. As a result a phase-separated polymer particle forms by encapsulating hydrocarbon in the interior, which serves as a locus for further polymerization. In the second stage, styrene and divinylbenzene are used to form a cross-linked shell. After polymerization, the hydrocarbon nonsolvent is removed by vacuum or steam stripping, resulting in hollow polymer spheres. A more recent approach to the synthesis of hollow nanoscopic polypyrrole and poly(*N*-methylpyrrole) particles is to employ gold nanoparticles as a template from which to grow the polymer shell, followed by dissolution of the template.^{24,25} In most cases the formation of uniform and regular shell structures surrounding the particles, as well as control over the shell thickness, is difficult to achieve because the polymerization is not restricted to the surface of the templates.

In this work, we describe a process for making uniform hollow polymeric microspheres by using surface-confined living radical polymerization. Using the silica microsphere as a sacrificial core, hollow microspheres are produced following core dissolution. First, a controlled/living polymerization is conducted using an initiator attached to the surface of silica microparticles to initiate atom transfer radical polymerization (ATRP).^{26–30} This procedure yields core–shell microparticles with a silica core and an outer layer of covalently attached, well-defined uniform thickness poly(benzyl methacrylate) (Scheme 1). The silica cores are subsequently dissolved, resulting in hollow polymeric microspheres (Scheme 2). Living polymerization is a process used in solution-phase polymerization whereby termination reactions are virtually eliminated, thus lowering polydispersity and enabling control of molecular weight by adjusting the monomer concentration. In comparison to solution or bulk living polymerization, surface-initiated living radical polymerization has several advantages. The growing radicals generated on the surface are not easily terminated by bimolecular reactions due to limitations of the solid surface on which the polymer chains are chemically attached, the low free radical concentration, and the low mobility. By using a controlled living polymerization procedure to covalently attach polymer chains to microsphere surfaces, one can control the thickness and uniformity of the coated polymer film. Unwanted solution phase polymerization is also prevented using this method. An additional

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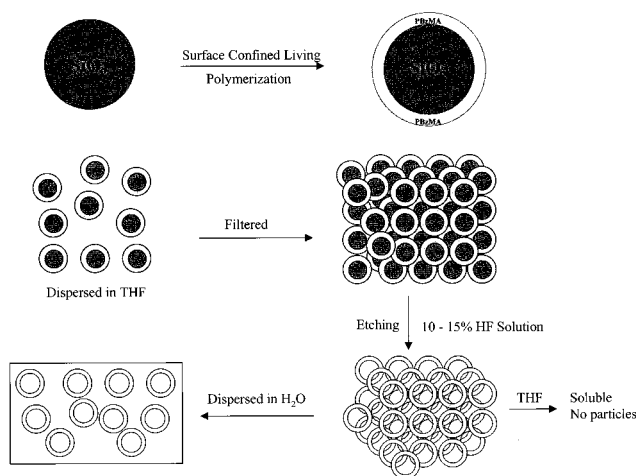
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Scheme 2



benefit is the ability to prepare block copolymers by the sequential activation of the dormant chain end in the presence of different monomers. Although there are many reports describing the grafting of polymers on flat^{31–34} and porous silica surfaces^{4,35,36} by using living radical polymerization, the procedure for making uniform hollow polymeric beads by using the living radical polymerization technique on a silica microsphere template is completely new.

Experimental Section

Reagents and Materials. Benzyl methacrylate, ethylene glycol dimethacrylate, 2,2'-dipyridyl (99%) and copper(I) chloride were purchased from Aldrich Chemical Co. (Milwaukee, WI). Luna porous silica beads ($\sim 3 \mu\text{m}$) were purchased from Phenomenex (Torrance, CA) and Bangs silica beads ($\sim 3.1 \mu\text{m}$) were from Bangs Laboratories, Inc. (Fishers, IN). ((Chloromethyl)phenylethyl)trimethoxysilane (CTMS) was obtained from Gelest, Inc (Tullytown, PA). HPLC grade solvents were used in both the reaction and washing steps. All the reagents were used without further purification.

Preparation of Poly(benzyl methacrylate)-Coated Silica Microspheres. The reactions for bead coating consisted of two steps, which are schematically summarized in Scheme 1. The silica particles were first cleaned with acetone several times to remove potential impurities. A benzyl chloride monolayer was prepared by silanization of silica microspheres. A mixture of 0.9 mL of acetone and 0.1 mL of CTMS was added to 6–7 mg of purified silica microspheres in a 1.5 mL polypropylene microcentrifuge tube. The bead suspension was shaken at room temperature for 2 h in dark. After silanization, the silica beads were separated from the suspension by centrifugation, washed with acetone to remove unreacted silane coupling agent, and then cured at room-temperature overnight in the dark.

In the second step, the living radical polymerization was performed. A 4 mL glass vial was charged with 6–7 mg of the silanized silica microspheres and 0.75 mL of dry *p*-xylene. Dry argon gas was bubbled through the mixture for 15 min to remove oxygen from the polymerization system. After the removal of oxygen, 0.0067 g (0.068 mmol) of CuCl, 0.0316 g

(0.21 mmol) of 2,2'-dipyridyl, and 0.75 mL of benzyl methacrylate were added to the same reaction mixture. The vial was then sealed with a high-temperature silicone rubber septum, and argon was bubbled through the mixture for another 20 min to ensure that oxygen was removed completely. The mixture was sonicated for 1 min to accelerate dissolution into xylene. The reaction was heated with constant stirring (with a magnetic stir bar) at 105–110 °C using a silicone oil bath. Polymerization time was varied from 1 to 14 h to produce polymer shells with different thicknesses. After polymerization, the coated microspheres were separated from the suspension by centrifugation and then washed several times by centrifuging/resuspending in THF and methanol. Cross-linked polymer shells were prepared by adding 10% ethylene glycol dimethacrylate (with respect to benzyl methacrylate monomer) into the above mixture. The rest of the procedures were the same as those for linear polymerization.

Procedure for Making Hollow Polymeric Microspheres. The synthesis of hollow polymeric microspheres is schematically represented in Scheme 2. Briefly, PBzMA coated silica particles were first suspended in THF. The bead suspension was filtered through a 0.5 μm pore size Fluopore membrane (Millipore Corp., Bedford, MA). A thin pellet of coated microspheres was formed on top of the membrane. The product was dried in an oven at 60 °C for 2 h. A 10% aqueous HF solution was prepared by diluting 50% HF with ultrapure water. **Caution: HF is extremely corrosive.** The membrane containing the pellet was placed in a small polystyrene Petri dish, and then 3.25 mL of 10% HF solution was added to immerse the pellet. The reaction was allowed to continue for 3 h at room temperature to etch the silica cores completely. The film was then withdrawn and dipped in ultrapure water that was replaced with fresh water four or five times to remove all the unreacted HF. Finally, the pellet was redispersed in water to obtain the individual hollow PBzMA microspheres.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR (Nicolet Magna-760, Nicolet Instrument Corp., Madison, WI) spectroscopy was used to identify the polymer on the bead surface and also to ensure that there was no silica present inside the hollow polymeric bead. Spectra were obtained at a resolution of 2 cm^{-1} , and averages of 64–100 spectra/scans (for enhanced signal) were obtained in the wavenumber range 400–4000 cm^{-1} . Spectra of the pure silica and polymer-coated silica were recorded from KBr pellets, prepared by mixing the microspheres with KBr in a 1:100(wt/wt) ratio. FTIR spectra for the pure PBzMA and the hollow polymer beads were obtained at room temperature by casting a THF solution on KBr pellets. FTIR spectra of the shell cross-linked hollow PBzMA microspheres were also measured from KBr pellets, prepared by the same procedure described above.

Scanning Electron Microscopy (SEM). SEM was performed using a JEOL SM 840 scanning electron microscope (JEOL, Peabody, MA) at an accelerating voltage of 25 kV. Samples were mounted on an aluminum stub and sputter-coated with gold to minimize charging. To obtain more information about the internal structure of the hollow microspheres, dry-etched polymer particles were sheared between two glass slides after freezing in liquid nitrogen to obtain cracked beads using a modification of an earlier reported procedure.¹⁰ This technique allows determination of the polymer shell thickness.

Atomic Force Microscopy. Surfaces of hollow polymer microspheres were imaged using a Digital Instruments Nanoscope IIIa scanning probe microscope. (Digital Instruments Inc., Santa Barbara, CA). Images were acquired in tapping mode with the *Z* range set at 4.0 μm . Scan size was 7.0 μm . The scan rate was 0.5 Hz. Images were acquired using a diamond-coated tapping mode tip ($L = 125 \mu\text{m}$, $F_s = 360 \text{ kHz}$). Samples of hollow polymer microspheres were allowed to dry from an aqueous suspension onto a glass microscope slide prior to AFM analysis. Surface roughness analysis was performed using Digital Instruments Nanoscope software (version 4.10).

Gel Permeation Chromatography. Molecular weights and molecular distributions were obtained on a Waters 2690 Separation Module (Waters Corp., Milford, MA) connected to

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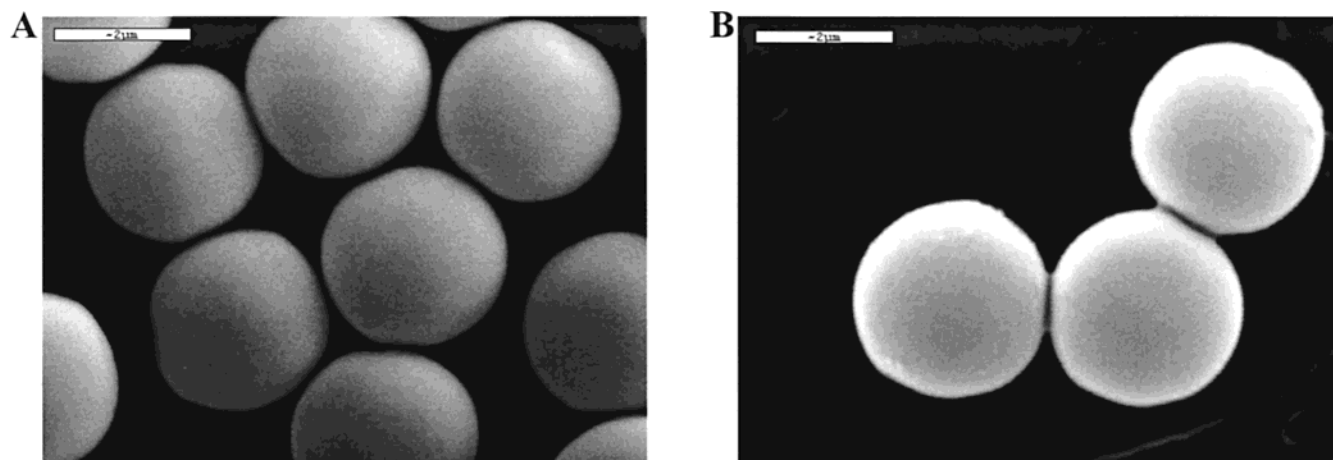


Figure 1. Scanning electron micrographs of (A) silanized silica microspheres and (B) the same microspheres as in 1A after coating with poly(benzyl methacrylate) by controlled/living radical polymerization for 14 h.

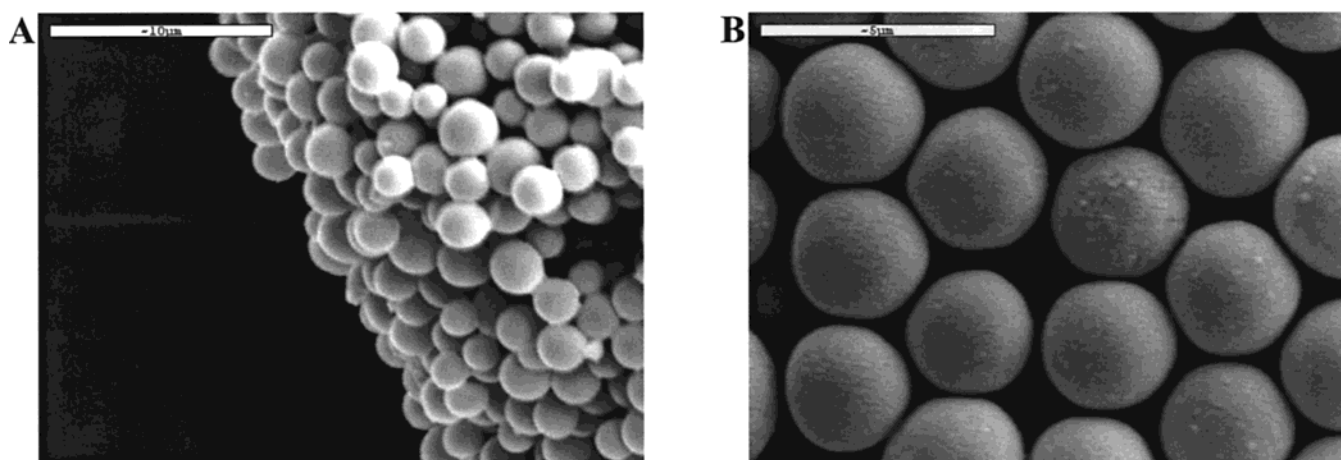


Figure 2. (A) Scanning electron micrograph of the polymer microspheres after etching with HF. (B) Scanning electron micrograph of the same microspheres as in 2A dispersed in water showing individual particles.

a Waters 410 differential refractometer with THF as the carrier solvent. Molecular weights were calibrated using polystyrene standards.

Results and Discussion

Spherical silica particles with an average diameter of 3 μm were used as a template for the synthesis of uniform hollow poly(benzyl methacrylate) microspheres. The ((chloromethyl)phenylethyl)trimethoxysilane (CTMS) initiator was attached to the silica surface by treating the silica with CTMS in acetone. Upon curing, a covalently linked benzyl chloride monolayer is formed on the silica microsphere surface. Elemental analysis results showed that the initial silica microparticles contained <0.02% chlorine and that the CTMS-attached microparticles contained 3.15% chlorine (Galbraith Laboratories, Inc., Knoxville, TN). This difference is equivalent to an average of 0.88 mmol of initiator/g of silica. The grafting density of the monolayer of benzyl chloride was 2.3 $\mu\text{mol}/\text{m}^2$, calculated on the basis of average surface area (400 m^2/g , data supplied by Phenomenex) of the pure silica particles. The resulting surface-modified silica particles could be redispersed in organic solvents. Scanning electron micrographs of the CTMS-modified silica microparticles showed that they remain unaggregated (Figure 1A) and were similar to the original silica microparticles, exhibiting no charac-

Table 1. Shell Thicknesses and Molecular Weights of the Hollow Poly(benzyl methacrylate) Microspheres Prepared by Varying Polymerization Time

polymerization time (h)	shell thickness (nm)	molecular weight (M_n)	PDI (M_w/M_n)
3.5	175–225	9150	1.56
6.5	350–400	13450	1.37
14.0	550–600	26500	1.26

^a Conditions: 6–7 mg of CTMS-modified silica microparticles (0.88 mmol of initiator); $[\text{CuCl}] = 90.6 \text{ mM}$, $[\text{bipy}] = 280 \text{ mM}$, $[\text{benzyl methacrylate}] = 7.57 \text{ M}$; and *p*-xylene solvent at 105–110 $^\circ\text{C}$.

teristic features. Although, the benzyl chloride ($-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$) of CTMS is not an efficient initiating group for atom transfer radical polymerization compared to 1-phenylethyl chloride or bromide, it performs acceptably in this case. Benzyl chloride has also been used previously for grafting polymers to solid surfaces or preparing polymers in solution.^{4,28,32} It may be possible to coat the silica microspheres with higher molecular weight PBzMA by using more efficient initiators.

The surface-modified microparticles were then used as macroinitiators for benzyl methacrylate atom transfer radical polymerization. Polymer growth was confined, as expected, to the surface of initiator-modified silica microspheres. The polymer-coated silica microspheres could be dispersed easily in good solvents for poly(benzyl methacrylate) (PBzMA). The FTIR spectra

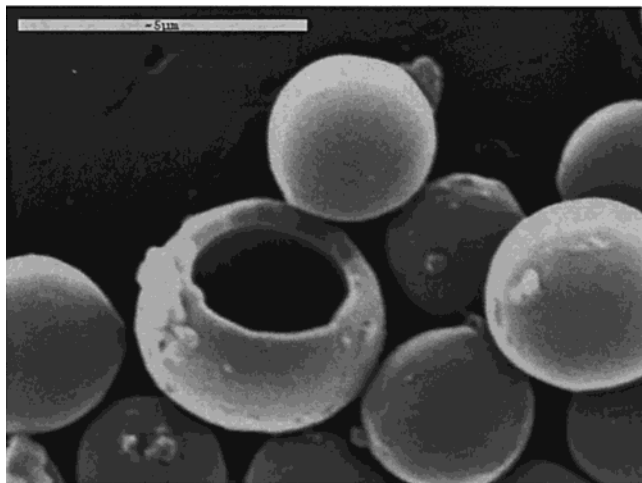


Figure 3. Scanning electron micrograph of the hollow polymeric microspheres obtained by crushing the hollow spheres by applying physical pressure after freezing in liquid nitrogen. Both broken and intact polymer spheres are seen.

of the resulting composite particles showed bands corresponding to both poly(benzyl methacrylate) and silica. The FTIR spectra will be discussed in more detail later in this section. We confirmed that the polymer chains were not physically adsorbed but chemically anchored onto the silica surface by repeatedly rinsing the coated microspheres with THF, with the expectation

that physically adsorbed polymer would be rinsed off. A SEM micrograph of the polymer-coated silica microspheres shows that the polymer is uniformly coated over the silica surface (Figure 1B). Tapping mode atomic force microscopy was used to obtain more detailed information about the surface topography. The AFM image of the surface of hollow polymer microspheres shows that the surface is very smooth. The root mean-square roughness (R_q) value is 8–10 nm. This value compares well with R_q values for silanized nonporous silica microspheres. Atom transfer radical polymerization forms primarily monodisperse polymer chains, with a uniform surface coating. The thickness of the grafted polymer layer increases with increasing polymerization time at fixed monomer concentrations. It was reported that when polymer chains are densely grafted to a surface, steric crowding forces the chains to stretch away from the surface.³⁷ On the other hand, the curvature of the silica particles may help to reduce steric crowding. Overall, the thickness of the polymer layer should be larger than the radius of gyration for the equivalent free polymer in solution.

Polymer/silica particle composites were converted to hollow polymeric microspheres by immersing a pellet of the composite particles (supported by a Fluopore membrane) in an aqueous solution of HF. Silica dissolution presumably occurs via transport of etchant through the polymer shell to the core. Figure 2A shows

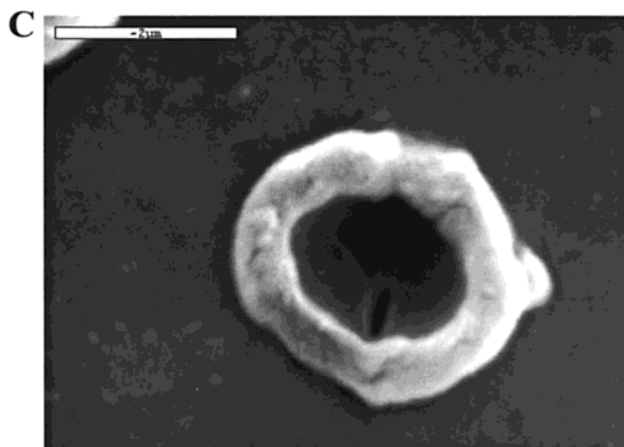
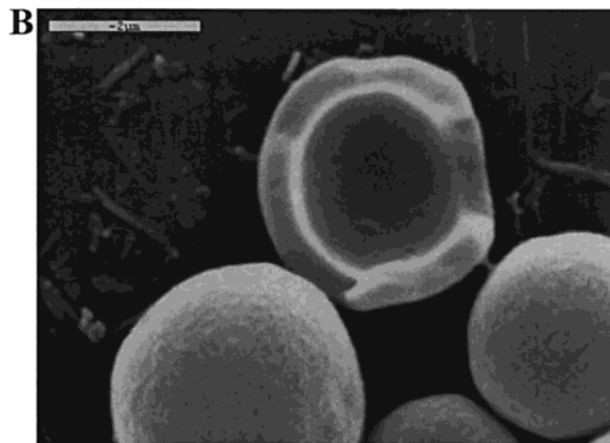
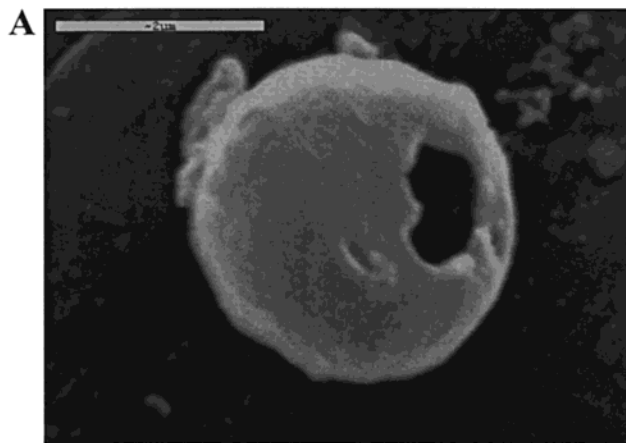


Figure 4. Scanning electron micrographs of the broken microspheres isolated after different polymerization times: (A) 3.5 h, (B) 6.5 h, (C) 14 h.

the SEM micrograph of the aggregated intact hollow PBzMA microspheres after etching the silica core. Aggregated hollow polymer particles could be redispersed as individual particles by sonicating a portion of the pellet in water (Figure 2B). When the composite particles are prepared by 1 h polymerization, no hollow microspheres are obtained after HF etching. This result indicates that the polymer shell thickness was not sufficient to maintain the initial spherical structure of the silica microsphere upon core removal. The hollow microspheres are soluble in THF and other organic solvents because the polymer chains are no longer grafted to the solid silica surface. This result proves that the silica cores are completely etched by the HF solution. Shell cross-linked hollow polymer microspheres, however, are not soluble in most organic solvents. For this reason they may be useful for drug delivery or encapsulating drugs/dyes in nonaqueous solvents. A SEM image of such shell cross-linked hollow polymer microspheres is shown in the Supporting Information.

After etching the silica core, the spheres were dissolved in THF, and the molecular weight of the dissolved polymer was determined by GPC. The molecular weights of three samples of cleaved surface initiated PBzMA, prepared with different polymerization times, are given in Table 1. The molecular weight (M_n) of the grafted polymer, as determined by GPC, increased with polymerization time. The molecular weight distribution (M_w/M_n) remained narrow after the initial stage of polymerization. The polydispersity indices are consistent with that expected from living polymerization ($PDI < 1.5$)²⁶ for the 6.5 and 14 h cleaved samples, although the polydispersity of the 3.5 h sample is somewhat higher than 1.5.

To confirm that the microspheres were hollow, they were frozen in liquid nitrogen and then crushed between two glass plates. Figure 3 shows a SEM image of intact and broken polymer microspheres. Broken hollow PBzMA microspheres produced by varying the polymerization time are shown in Figure 4. The shell thicknesses were measured from the SEM micrograph of the broken hollow PBzMA particles, which are given in Table 1. The data reveal that shell thickness increases with increasing polymerization time; however, the measured shell thicknesses of the samples prepared with different polymerization times were much higher than expected on the basis of the calculated values for the fully extended chains from their respective molecular weights. Higher shell thickness values may be due to a number of possibilities: First, shell thickness was measured using SEM after the hollow polymer microspheres were freeze-fractured. It is possible that measured shell thickness is artificially high due to distortion of the polymer, since the microspheres were frozen and compressed between glass plates prior to fracturing. A second possibility is the formation of polymer inside the pores of the silica templates. Polymer chain attachment and growth at different distances from the template center contributes to the observed shell thickness after etching. The silica core dissolution process may also affect the shell thicknesses. For example, when HF diffuses through the polymer shell and reaches the core, it reacts with silica

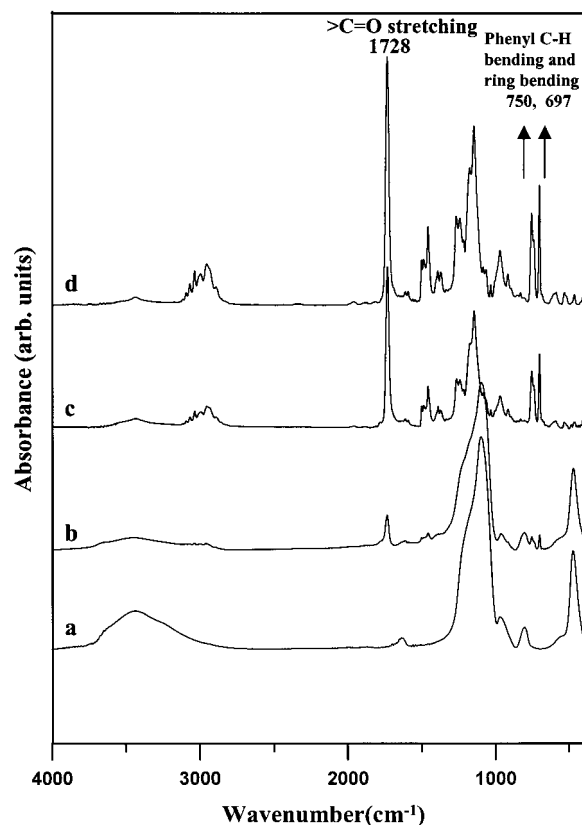


Figure 5. FTIR spectra of (a) pure silica particles, (b) hybrid poly(benzyl methacrylate)/silica particles, (c) hollow PBzMA microspheres after silica core etching, and (d) pure poly(benzyl methacrylate).

to form silicon tetrafluoride gas, and the polymer chains detach from the surface at their point of attachment. The resulting gas from the interior may produce microvoids inside the polymer shell and result in an increased shell thickness. The detached polymer chains have no solid support, and may also aid in the void generation.

For further confirmation that the polymer microspheres contains no silica inside the core, FTIR characterization was performed on etched hollow PBzMA particles and was compared with that of pure poly(benzyl methacrylate) and neat silica. Figure 5 shows the FTIR spectra of pure silica, PBzMA-coated silica particles, and PBzMA particles after etching of the silica core. Spectra for polymer-coated silica particles (Figure 5b) reveal bands at 750 and 697 cm^{-1} , corresponding to phenyl C–H out-of-plane bending and benzene ring out-of-plane ring bending, respectively, and the 1728 cm^{-1} carbonyl stretching vibrations characteristic of PBzMA. In addition to the PBzMA signals, a broad intense signal in the 1350–1000 cm^{-1} region corresponds to the solid-state vibration of the Si–O–Si bond in silica. The FTIR spectrum of the hollow PBzMA particles (Figure 5c) and cross-linked hollow particles (shown in Supporting Information) is similar to the spectrum of neat PBzMA (Figure 5d) and shows no spectral characteristics of silica, confirming that the silica cores were etched completely.

We have demonstrated a procedure for making uniform hollow microspheres using surface-initiated controlled/living radical polymerization on silica templates followed by core removal by etching. This method is flexible and enables control over the shell thickness and

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composition by adjusting polymerization time and monomer concentration. This approach may allow for the fabrication of different shapes of hollow polymeric materials produced from a variety of templates. Finally, it might be possible to produce hollow microspheres containing different polymer layers by the sequential activation of the dormant chain in the presence of different monomers during polymerization.

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Supporting Information Available: Atomic force micrograph of the hollow PBzMA microspheres surface, SEM micrograph of shell cross-linked hollow PBzMA microspheres, and FTIR spectra of cross-linked hollow PBzMA microspheres after silica etching with HF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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