

Facile Synthesis of Functional Silica/Polymer Composite Materials and Hydrophilic Hollow Polymer Microspheres

Guangyu Liu,^{1,2} Han Zhang,¹ Xinlin Yang,¹ Yongmei Wang²

¹Key Laboratory of Functional Polymer Materials, Ministry of Education, Institute of Polymer Chemistry, Nankai University, Tianjin, China

²Department of Chemistry, Nankai University, Tianjin, China

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ABSTRACT: Monodisperse functional silica/polymer core-shell composite materials with silica as core and hydrophilic polymer with various functional groups, such as amide, carboxylic acid, hydroxyl, and pyridyl group, as shell were facilely prepared by a two-stage reaction, in which the silica core with diameter of 179 nm was synthesized in the first-stage reaction according to the Stöber method. The functional polymer shell was then encapsulated onto the silica core by distillation-precipitation copolymerization of *N,N'*-methylenebisacrylamide (MBAAm) as crosslinker and hydrophilic comonomers with different functional groups, including *N*-isopropylacrylamide, methacrylic acid, 2-hydroxyethyl methacrylate, and 4-vinylpyridine, in neat acetonitrile with 2,2'-azobisisobutyronitrile as initiator. The encapsulation of the functional polymer shell onto the silica core particles was driven by the hydrogen-bonding interaction between the hydroxyl group on the surface of silica core and the amide unit of MBAAm crosslinker as well as the functional groups

of the comonomers during the distillation-precipitation polymerization without modification of the silica surface in absence of any stabilizer or surfactant. The shell thickness of the composite can be controlled by MBAAm fraction in the monomer feed during the polymerization. Hydrophilic hollow polymer microspheres with various functional groups, including amide, carboxylic acid, hydroxyl, and pyridyl, were further developed after selective removal of silica core with hydrofluoric acid. The functional core-shell silica/polymer composites and the corresponding functional hollow microspheres were characterized with transmission electron microscopy, Fourier transform infrared spectra, and dynamic light scattering. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1964–1975, 2009

Key words: inorganic-organic composite; functional hydrophilic hollow microsphere; distillation-precipitation polymerization; hydrogen-bonding interaction

INTRODUCTION

Recently, the organic/inorganic hybrid and composite materials have attracted increasing attention from the researchers in academic as well as industrial area because of the combination of the thermally stable and robust inorganic component and the flexible organic component with various functional groups within a single material. These hybrid/composite materials can exhibit novel and excellent properties, such as mechanical, chemical, electrical, rheological, magnetic, optical, and catalytic, by varying the compositions, dimensions, and structures of the components, which have promised diverse applications as drug delivery system, diagnostics, coatings, and catalysis.^{1–7}

Silica/polymer composite/hybrid particles with various interesting morphologies such as silica core/organic shell,⁸ organic core/silica shell,⁹ raspberry-like,¹⁰ snowman-like,¹¹ daisy-shaped and multipod-like,¹² and raisinbun-like,¹³ have been prepared by different methods. The synthesis of silica/polymer hybrid/composite particles can be generally classified as two categories: the assembly of the resultant silica and polymer particles via physical or physicochemical interaction, and the direct polymerization of monomer on the surface of silica particles. Bourgeat-Lami and coworkers^{14–16} synthesized silica/organic hybrid particles with silica as seeds by dispersion polymerization, in which the vinyl group of silica core was introduced by 3-(trimethoxysilyl)propyl methacrylate. The hedgehog-like or raspberry-like hybrid particles were prepared by mini-emulsion polymerization,¹⁷ in which the silica nanoparticles acted as surfactants and fillers. Silica/poly(methyl methacrylate) nanocomposite particles were synthesized by emulsion polymerization with a cationic initiator 2,2'-azobis(isobutyramidine) dihydrochloride in the presence of a nonionic polyoxyethylenic surfactant (NVP30).¹⁸ However, the morphology

Correspondence to: X. Yang (xlyang88@nankai.edu.cn).

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of the resultant silica/polymer hybrid particles was hard to control, and the encapsulation efficiencies of the polymer on the silica core were much low for both dispersion polymerization and emulsion polymerization.^{14–18} Surface-initiated atom transfer radical polymerization (ATRP) has been widely used to prepare well-defined silica/polymer hybrids with the initiator-modified silica particles as macroinitiators,^{19–22} in which the synthesis was tedious with long reaction time and low conversion of monomer to polymer.

During the last decade, polymer hollow microspheres have been interesting for their various applications, such as encapsulation for controlled release of drugs and enzymes, fillers, pigments, catalysts, and adsorption materials for sound.^{23–26} A variety of physical and chemical techniques have been reported for the synthesis of hollow polymer microspheres. Polymer void particles were obtained by emulsion polymerization via encapsulation of a hydrocarbon nonsolvent, which was a complicated process controlled by a number of hydrocarbon nonsolvent, convoluted, thermodynamic, and kinetic factors.²⁷ Layer-by-layer assembly with electrostatic interaction as a driving force for the formation of hollow polymer particles was suitable only for polymer electrolytes.²⁸ Micelle formation of block copolymer afforded hollow polymer microspheres, which needed delicate design of block copolymer with UV-crosslinking of the shell layer and subsequent tedious ozonolysis of core.²⁹ Hollow polymer microspheres were prepared by surface-initiated ATRP of styrene with subsequent UV treatment for shell-crosslinking, which involved complex and tedious processes for synthesis.³⁰

Microspheres with various functional groups have many applications in different fields, such as solid carriers for the immobilization of biological substances including enzymes, antibodies, etc.³¹ To date, work has been reported on the utilization of microspheres as microscopic markers for antigens or antibodies on the surface of the cell.³² Hydrophilic polymer microspheres with uniform size are essential for drug delivery systems (DDS) because the distribution of the microspheres in the body and their interaction with biological cells are greatly affected by the particle size.³³ Additionally, if monodisperse microspheres are available, the drug release kinetics can be manipulated, therefore making it easier to formulate more sophisticated intelligent DDS. However, little attention has been paid to the synthesis of the hollow polymer microspheres with functional shell layer, which may be due to the difficulty in the selective modification of the structure of the shell layer in these hollow microspheres.

We have previously reported the distillation-precipitation polymerization as a novel and powerful technique for the synthesis of monodisperse polydi-

vinylbenzene (polyDVB),³⁴ poly(*N,N'*-methylenebisacrylamide) (polyMBAAm),³⁵ and other polymer microspheres with various functional groups.^{36–38} Recently, we utilized this technique to prepare the silica/polyMBAAm composite core-shell microspheres without modification of the silica surface in the absence of any stabilizer or surfactant, in which the driving force for the encapsulation was the hydrogen bonding interaction between the hydroxyl group on the surface of silica core and the amide unit of polyMBAAm.³⁹ Here, monodisperse functional silica/polymer core-shell composite materials with various groups on the shell layer, including amide, carboxylic acid, hydroxyl, and pyridyl, were readily prepared by distillation-precipitation copolymerization of MBAAm crosslinker and hydrophilic comonomers with silica as seeds and 2,2'-azobisisobutyronitrile (AIBN) as initiator in neat acetonitrile, in which the hydrophilic polymer shell was encapsulated onto the silica particles with the aid of hydrogen-bonding interaction between the hydroxyl group on the surface of silica core and the amide unit of MBAAm as well as the functional groups of the comonomers. Furthermore, the corresponding hollow hydrophilic polymer microspheres with different functional groups were developed after the selective removal of silica core by hydrofluoric acid (HF).

EXPERIMENTAL

Chemicals

Tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS) and *N*-isopropylacrylamide (NIPAAm) was purchased from Aldrich and used without any further purification. MBAAm (chemical grade, Tianjin Bodi Chemical Engineering, Tianjin, China) was recrystallized from acetone. Methacrylic acid (MAA) and 2-hydroxyethyl methacrylate (HEMA) were obtained from Tianjin Chemical Reagent II (Tianjin, China). 4-Vinylpyridine (VPy) was purchased from Alfa Aesar. The aforementioned functional comonomers were purified by vacuum distillation. AIBN was obtained from Chemical Factory of Nankai University and recrystallized from methanol. Acetonitrile (analytical grade, Tianjin Chemical Reagent II.) was dried over calcium hydride and purified by distillation before use. HF (containing 40% of HF) was available from Tianjin Chemical Reagent Institute (Tianjin, China). All the other reagents were analytical grade and used without any further purification.

Synthesis of silica core

Silica particles were prepared according to the classical Stöber method⁴⁰: 28 mL of TEOS was added to a

mixture of 500 mL of ethanol, 50 mL H₂O, and 12 mL of 25% ammonium aqueous solution with vigorous stirring at room temperature, and the reaction was continued further for 24 h with stirring. The resultant silica particles were then purified by three cycles of centrifugation, decantation, and resuspension in ethanol with ultrasonic bathing. The silica particles were dried in a vacuum oven at 50°C till constant weight.

Preparation of monodisperse silica/polymer composite microspheres with functional groups on the shell layer

A typical procedure for the distillation–precipitation copolymerization: In a dried 50-mL two-necked flask, 0.20 g silica particles were suspended in 40 mL of acetonitrile as a white suspension. The MBAAm crosslinker (0.10 g, 0.65 mmol), MAA comonomer (0.15 mL, 0.14 g, 1.40 mmol), and AIBN (0.005 g, 0.035 mmol, 2 wt % relative to the total comonomers) were dissolved in the suspension. The two-necked flask fitted with a fractionating column, Liebig condenser, and receiver was placed in a heating mantle. The reaction mixture was heated from ambient temperature till the boiling state within 15 min, and the reaction system was kept under refluxing state for further 10 min. The white color was deepened during the heating process, and 20 mL of the solvent was then distilled off from the reaction system within 70 min. After the polymerization, the resultant silica/poly(MBAAm-co-MAA) composite microspheres with carboxylic acid group on the shell layer were purified by repeating centrifugation, decantation, and resuspension in acetone with ultrasonic bathing for three times. The resultant composite particles were then dried in a vacuum oven at 50°C till constant weight.

The silica/poly(MBAAm-co-MAA) core-shell composite microspheres with different thickness of polymer shell and loading capacity of the carboxylic acid group were conveniently prepared via controlling the MBAAm/MAA ratio during the second-stage distillation–precipitation polymerization.

A series of parallel synthesis using different functional comonomers, including NIPAAm, HEMA, and VPy, together with MBAAm crosslinker were carried out by distillation–precipitation polymerization in the presence of silica as core to afford the silica/polymer core-shell composite microspheres with various functional groups on the shell-layer, while the ratio of MBAAm crosslinker fraction in the comonomer feed was maintained at 0.40 as mass ratio.

All the other distillation–precipitation copolymerizations were much similar to that of the typical procedure at 2 wt % relative to the total monomer. The

treatment of these composite particles was the same as that of the typical procedure.

The reproducibility of the distillation–precipitation copolymerization for the synthesis of silica/polymer functional core-shell composites was confirmed through several duplicate and triplicate experiments.

Synthesis of hydrophilic hollow polymer microspheres with various functional groups

The resultant silica/polymer core-shell composite particles with various functional groups on the shell layer were immersed in 40% HF solution for 2 h (caution: HF is very corrosive and should be handled carefully!). The hydrophilic hollow polymer microspheres with different functional groups, such as carboxylic acid, amide, hydroxyl, and pyridyl, were obtained by several centrifugation/washing cycles in water till pH of 7 for expelling the excess HF and the formed SiF₄. The final hydrophilic hollow polymer microspheres with different functional groups were dried in a vacuum oven at 50°C till constant weight.

Characterization

The morphology, size, and size distribution of silica core, silica/polymer functional core-shell composite microspheres, and the corresponding hydrophilic hollow polymer microspheres with various functional groups were characterized by transmission electron microscopy (TEM, Technai G2 20 S-TWIN). All the size and size distribution reflect the averages about 100 particles each, which are calculated according to the following formula:

$$U = D_w/D_n, \quad D_n = \frac{\sum_{i=1}^k n_i D_i}{\sum_{i=1}^k n_i},$$

$$D_w = \frac{\sum_{i=1}^k n_i D_i^4}{\sum_{i=1}^k n_i D_i^3}$$

where U is the polydispersity index, D_n is the number-average diameter, D_w is the weight-average diameter, N is the total number of the measured particles, and D_i is the particle diameters of the determined microparticles.

Fourier transform infrared spectra (FTIR) were scanned over the range of 400–4000 cm⁻¹ with potassium bromide plate on a Bio-Rad FTS 135 FTIR spectrometer.

Hydrodynamic diameters of the samples were measured by dynamic light scattering (DLS) on a laser light scattering spectrometer (BI-200 SM) equipped with a Brookhaven BI-9000 AT digital correlator and a He-Ne laser at 659 nm. All the samples were measured at 25°C.

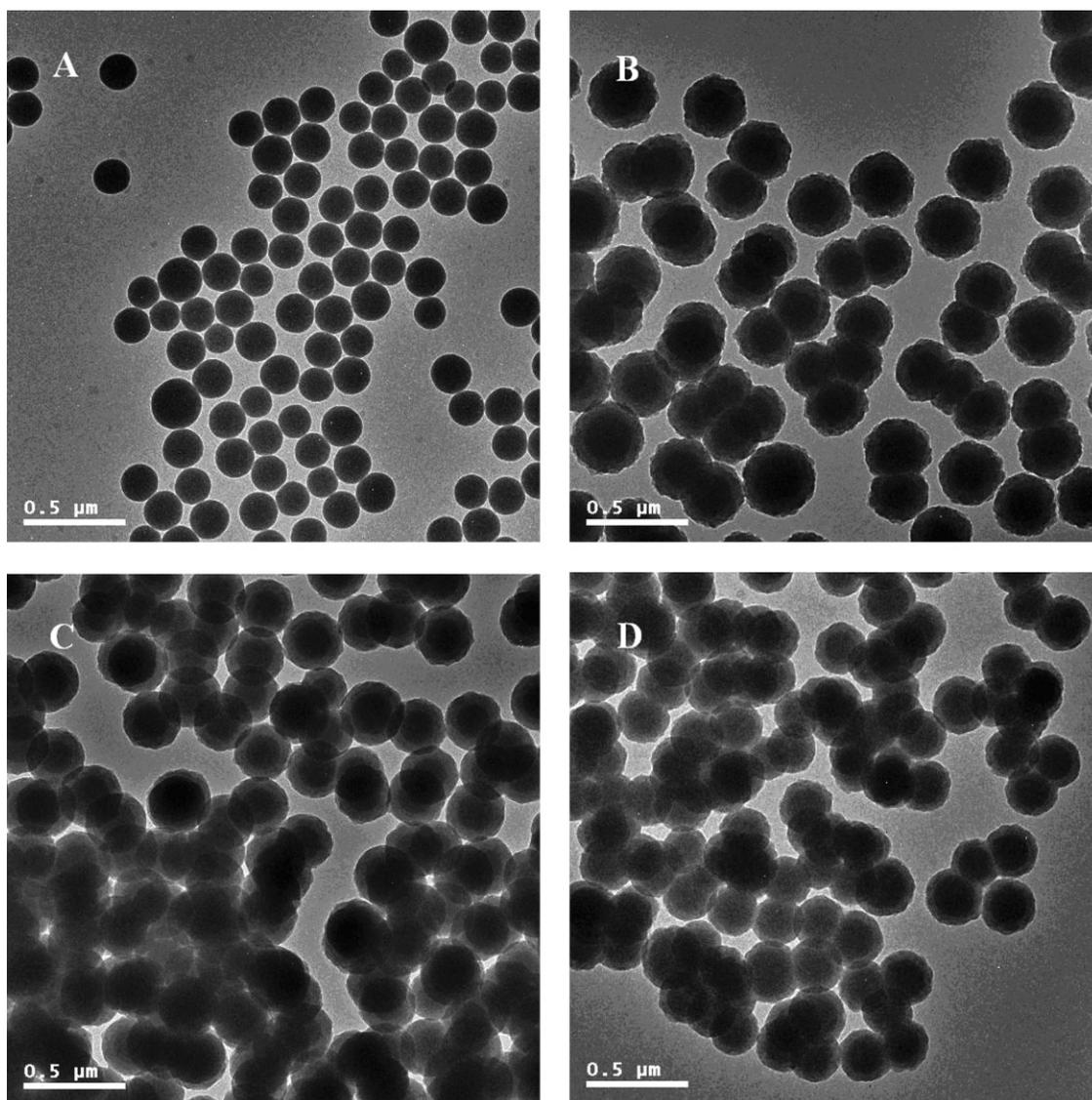


Figure 1 TEM micrographs of (A) silica core; (B, C) silica/poly(MBAAm-*co*-MAA) core-shell composite microspheres with different MAA fraction in the comonomer feed as mass ratio: (B) 0.20; (C) 0.80; (D) poly(DVB-*co*-MAA) particles formed in the presence of silica particle as seed. Reaction conditions: 40 mL of acetonitrile with 0.20 g silica core, 0.25 g comonomer, and AIBN initiator 2 wt % of the total comonomer.

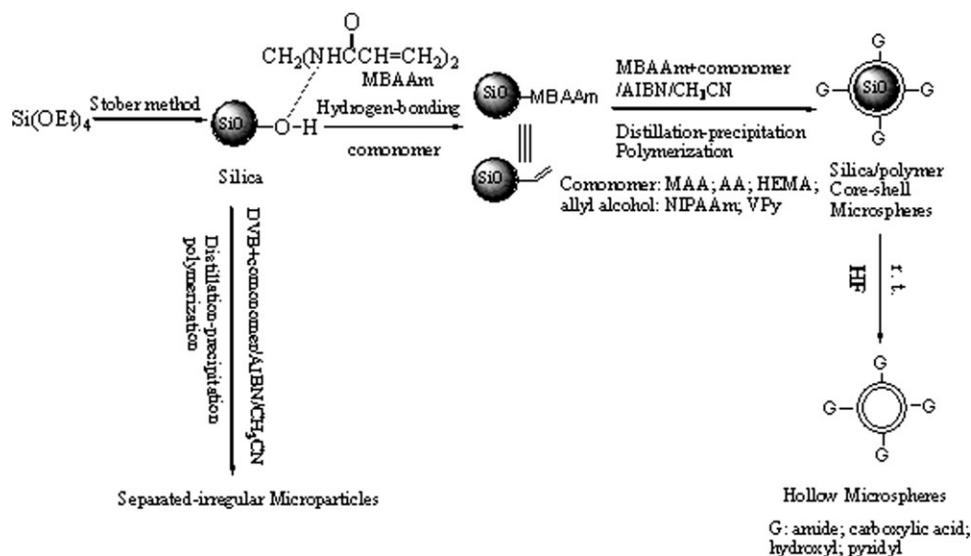
Loading capacity of the carboxylic acid group on the surface of silica/poly(MBAAm-*co*-MAA) composites was determined by acid–base titration.

RESULTS AND DISCUSSION

The TEM micrograph of silica particles from a sol gel process according to Stöber technique as shown in Figure 1(A) indicated that the silica microspheres had a spherical shape with an average size of 179 nm and monodispersity index (U) of 1.026.

Residual vinyl groups on the polyDVB core were essential to afford monodisperse core-shell functional polymer microspheres by two-stage distillation–precipitation polymerization,³⁷ in which the newly formed oligomers were captured by the reac-

tive vinyl groups in the absence of any second-initiated particles during the second-stage polymerization. In our previous article, the hydrogen-bonding interaction has played an active role during the distillation–precipitation polymerization in neat acetonitrile while involving the hydrophilic comonomers, such as acrylic acid,³⁶ methacrylic acid,³⁶ MBAAm, and NIPAAm.³⁵ Monodisperse silica/poly-MBAAm particles were prepared by distillation–precipitation polymerization of MBAAm in the presence of silica particles as seeds driven by the hydrogen-bonding interaction between the hydroxyl group on the surface of silica core and the amide unit of polyMBAAm during the second-stage polymerization without modification of the silica surface in the absence of any stabilizer or surfactant.³⁹ In



Scheme 1 Preparation of silica/polymer core-shell composites and the corresponding hydrophilic hollow polymer microspheres with different functional groups.

this work, we utilized the distillation–precipitation copolymerization technique for the preparation of monodisperse functional silica/polymer composite microspheres with MBAAm as crosslinker together with the functional comonomers, including MAA, NIPAAm, HEMA, and VPy, in which the hydrogen-bonding interaction between the active hydroxyl group on the surface of silica core and the amide unit of MBAAm crosslinker as well as the functional groups of the comonomers would promote the encapsulation of polymer shell layer having the different functional groups onto the silica particles. Monodisperse functional silica/polymer core-shell composite microspheres were prepared by the second-stage distillation–precipitation copolymerization of MBAAm crosslinker and functional comonomers in neat acetonitrile with AIBN as initiator as illustrated in Scheme 1, in which the silica particles with active hydroxyl groups were used as seeds for the growth of shell layer having different functional groups. The previous results indicated that acetonitrile met the solvency conditions required for the formation of monodisperse polyMBAAm and the corresponding functional microspheres with regular shape by distillation–precipitation polymerization, that is, it dissolved MBAAm and the functional comonomer, but precipitated the resultant polyMBAAm and their functional copolymer network.³⁵

Preparation of silica/poly(MBAAm-co-MAA) core-shell composites with carboxylic acid group

A series of experiments were initially carried out for the synthesis of silica/poly(MBAAm-co-MAA) core-shell composite microspheres by varying the ratio of MBAAm to MAA functional comonomer, while the

amount of solvent and silica core, the whole weight of MBAAm and MAA comonomer as well as the reaction time were maintained constant for the copolymerizations. The TEM micrographs of the silica/poly(MBAAm-co-MAA) microspheres with different MAA fractions in the comonomer feed of 0.20 and 0.80 (as mass ratio in the total comonomer) are illustrated in Figure 1(B,C). It can be observed that MAA fraction in the comonomer feed had much effect on the morphology of the resultant silica/poly(MBAAm-co-MAA) core-shell microspheres. It has been a major area of interest for particles in the nanomicro size range to control size, size distribution, and morphology of the polymer microspheres and the hybrid/composite particles. All the silica/poly(MBAAm-co-MAA) core-shell composites had spherical shape and the surface became smoother with increasing the MAA fraction in the comonomer feed. The silica/poly(MBAAm-co-MAA) core-shell particles with rough surface and high yield in the case of low MAA fraction in the comonomer feed as shown in Figure 1(B) after the second-seeded copolymerization may originate from the structure and the high reactivity of the MBAAm crosslinker, which has been discussed in detail for the synthesis of silica/polyMBAAm composite particles in our previous work.³⁹ With increasing fraction of MAA in the comonomer feed, the oligomers can be dissolved better in the solvent to retard the precipitation copolymer network over the silica core from the reaction system. In such case, the capability of the active hydroxyl groups and the functional groups on the silica/poly(MBAAm-co-MAA) composite surface was enough to efficiently capture all the newly formed oligomers from the reaction system during the copolymerization driven by the

TABLE I
Size, Size Distribution, Yield, Shell Thickness, Fraction of Polymer Component, and Loading Capacity of the Accessible Carboxylic Acid Group on the Surface of Silica/Poly(MBAAm-co-MAA) Composites with Different MAA Fraction in the Comonomer Feed

Entry	SiO ₂ (g)	MBAAm (g)	MAA (mL)	D_n (nm)	D_w (nm)	U	Shell thickness (nm) ^a	Loading of carboxylic acid groups ^b (mmol/g)	Fraction (%) ^c	Yield (%) ^d
A ^e	0.2	0	0	179	184	1.026	0	0	0	0
B	0.2	0.2	0.05	293	300	1.023	57	0.12	57	98
C	0.2	0.15	0.1	289	292	1.011	55	0.22	52	74
D	0.2	0.1	0.15	258	262	1.015	40	0.36	41	53
E	0.2	0.05	0.2	256	260	1.018	39	0.55	28	30

^a Shell thickness = $(D_{\text{core-shell}} - D_{\text{silica}})/2$.

^b Determined by acid–base titration.

^c Fraction = $M_{\text{hollow}}/M_{\text{core-shell}} \times 100\%$.

^d Yield = $(M_{\text{core-shell}} - M_{\text{silica}})/M_{\text{monomer}} \times 100\%$.

^e Silica core.

strong hydrogen-bonding interaction between the hydroxyl group and the amide group of MBAAm as well as the carboxylic acid unit of MAA. The mechanism for the formation of monodisperse polyMAA microspheres induced by hydrogen-bonding interaction between the carboxylic acid groups has been reported in detail in our previous paper in absence of any crosslinker.⁴¹

The experimental conditions for the distillation–precipitation copolymerizations of MBAAm and MAA in the presence of silica particles as seeds, yield, size, size distribution, and loading capacity of the accessible carboxylic acid group on the surface of the resultant silica/poly(MBAAm-co-MAA) core-shell composites are summarized in Table I. The diameter of the composite particles decreased considerably from 293 to 256 nm with increasing the MAA fraction from 0.20 to 0.80 in the comonomer feed, while the monodispersity index (U) was kept in the range of 1.011–1.023. The yield of silica/poly(MBAAm-co-MAA) composite microspheres decreased significantly from 98% to 30% with enhancing MAA fraction from 0.20 to 0.80 (mass ratio) in the comonomer feed, whereas the loading capacity of the accessible carboxylic acid group on the surface of silica/poly(MBAAm-co-MAA) core-shell composites was increased considerably from 0.12 to 0.55 mmol/g determined by acid–base titration. The silica/polymer composite microspheres with various loading capacity of the accessible functional groups may have applications, such as DDS, polymer composites, supports for the immobilization of biological substances, and catalysis.

In this work, the diameters of the resultant silica/poly(MBAAm-co-MAA) composite particles decreased considerably with increasing the fraction of the monovinyl group MAA comonomer for the copolymerization with MBAAm crosslinker. The size of the final composite particles was determined by

the conversion of the comonomers and the number of nuclei formed during the copolymerization. Here, the number of nuclei formed may maintain constant as determined by the number of silica seeds used for the copolymerizations, as there were not any second-initiated small particles observed after the second-stage copolymerization. The yield of the resultant silica/poly(MBAAm-co-MAA) core-shell composites decreased considerably with increasing MAA fraction in the comonomer feed, which led to the decrease in size of the final core-shell composite particles.

The crosslinker MBAAm was essential and necessary in the series of experiments for the synthesis of silica/polymer core-shell composites, especially at the initial stage of polymerization. When MBAAm crosslinker was substituted by the other crosslinker, such as DVB, no polymer shell layer was encapsulated over the silica core, while the other reaction conditions were unchanged. Figure 1(D) showed the formation of separated irregular microparticles in the presence of silica particles as seeds for the distillation–precipitation copolymerization of DVB and MAA with MAA fraction of 0.60, in which the silica particles were as smooth as the original silica core with the same diameter as shown in Figure 1(A). This result indicated that poly(DVB-co-MAA) nucleated itself during the polymerization without encapsulation onto the silica particles, which may be due to the hydrophobic nature of polyDVB lacking the hydrogen-bonding interaction with the silica particles. In other words, the crosslinked poly(DVB-co-MAA) network cannot efficiently encapsulate over the silica particles in the absence of MBAAm crosslinker, although the carboxylic acid group of polyMAA segment can form hydrogen-bonding interaction with the active hydroxyl group of silica particles. The formation mechanism of silica/polyMBAAm core-shell composite driven by

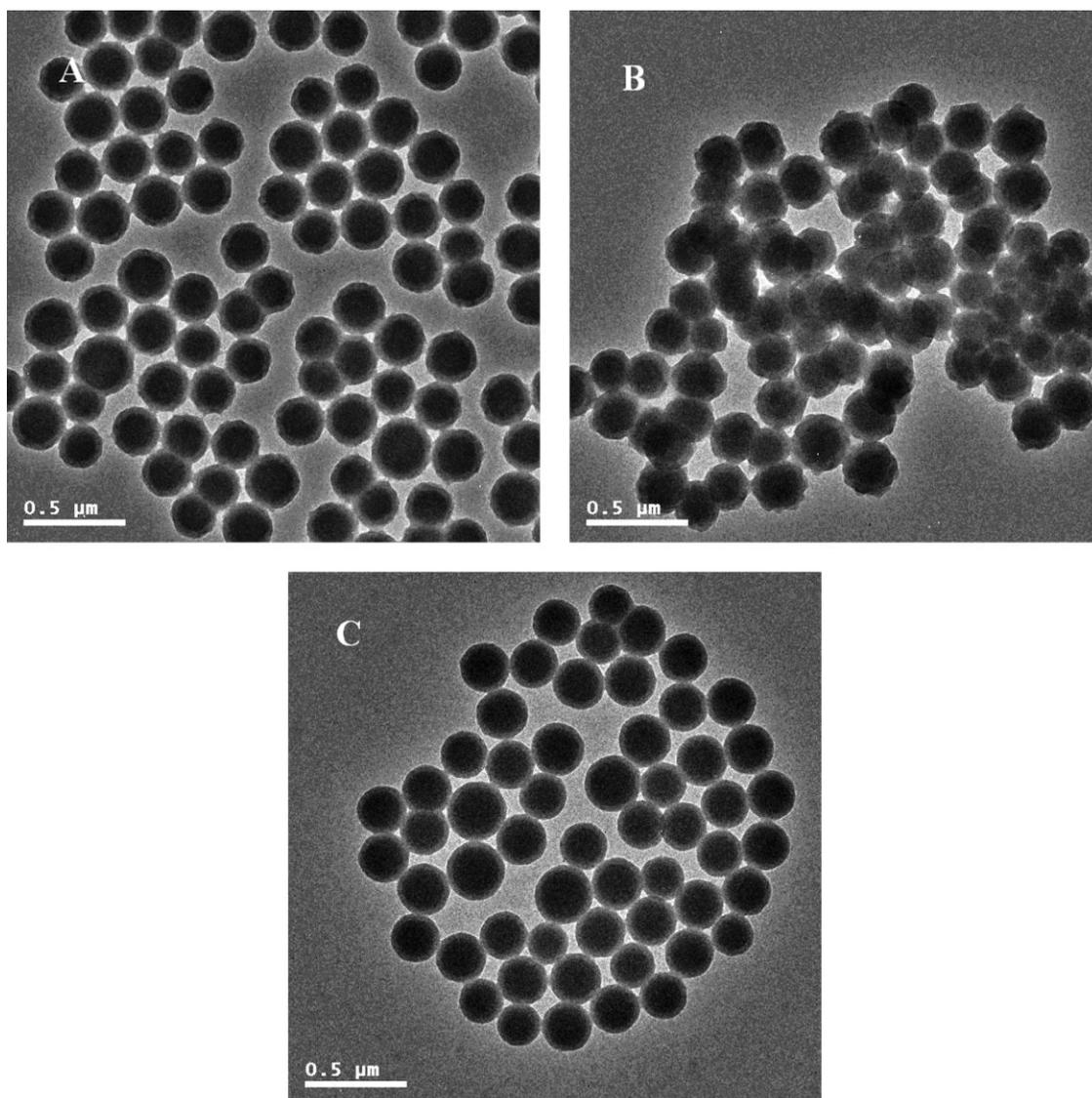


Figure 2 TEM micrographs of silica/polymer core-shell functional composites: (A) silica/poly(MBAAm-co-NIPAAm); (B) silica/poly(MBAAm-co-HEMA); (C) silica/poly(MBAAm-co-VPy).

hydrogen-bonding interaction between the hydroxyl groups on the surface of silica seeds and the amide unit of polyMBAAm was investigated in detail in our previous paper.³⁹ In this work, the formation of monodisperse silica/poly(MBAAm-co-MAA) core-shell composites with efficient encapsulation of poly(MBAAm-co-MAA) shell layer onto the silica cores even in the case of low crosslinking degree of 0.20 (Entry E in Table I) indicated that the hydrogen-bonding interaction between the carboxylic acid-functional groups played an active role during the polymerization. The synthesis of monodisperse functional polymer microspheres driven by the hydrogen-bonding interaction in the case of crosslinking degree as low as 0.05^{36,42} as well as in the absence of any crosslinker³⁹ have been investigated in detail in our previous paper.

Synthesis of silica/polymer core-shell composites with various functional groups on the shell layer

To investigate whether other functional groups can be incorporated into the shell layer of the silica/polymer composites via altering the type of the functional comonomer together with MBAAm as crosslinker, the hydrophilic comonomers, including NIPAAm, HEMA, and VPy, were copolymerized with MBAAm crosslinker (0.60 of comonomer fraction in the monomer feed) in the presence of silica particles as seeds while keeping the other reaction conditions the same as the typical one. The TEM micrographs of the resultant silica/polymer core-shell composites with different functional groups on the shell layer are shown in Figure 2. The results indicated that all the silica/polymer core shell

TABLE II
Size, Size Distribution, Yield, and Shell Thickness of Silica/Polymer Composite Particles with Different Functional Groups

Entry	SiO ₂ (g)	MBAAm (g)	Water-soluble monomer	D_n (nm)	D_w (nm)	U	Shell thickness (nm) ^a	Fraction (%) ^b	Yield (%) ^c
A ^d	0.2	0	0	179	184	1.026	0	0	0
B	0.2	0.1	NIPAM 0.15 g	239/286 ^e /499 ^f	243	1.017/1.029 ^e /1.317 ^f	30	43	57
C	0.2	0.1	MAA 0.15 mL	258/335 ^e /375 ^f	262	1.015/1.125 ^e /1.066 ^f	40	41	53
D	0.2	0.1	AA 0.15 mL	251	258	1.030	36	49	68
E	0.2	0.1	HEMA 0.15 mL	239	242	1.012	30	31	36
F	0.2	0.1	Allyl alcohol 0.15 mL	213	215	1.010	17	29	34
G	0.2	0.1	VPy 0.15 mL	227	234	1.028	24	28	32

^a Shell thickness = $(D_{\text{core-shell}} - D_{\text{silica}})/2$.

^b Fraction = $M_{\text{hollow}}/M_{\text{core-shell}} \times 100\%$.

^c Yield = $(M_{\text{core-shell}} - M_{\text{silica}})/M_{\text{monomer}} \times 100\%$.

^d Silica core.

^e Hydrodynamic diameter and polydispersity index of the core-shell composites from DLS.

^f Hydrodynamic diameter and polydispersity index of the hollow polymer microspheres from DLS.

composites with different functional groups, such as amide [Fig. 2(A)], hydroxyl [Fig. 2(B)], and pyridyl [Fig. 2(C)], had spherical shape with smooth surface.

The experimental conditions for the distillation-precipitation copolymerizations of hydrophilic comonomers, including NIPAAm, HEMA, and VPy, together with MBAAm as crosslinker and silica particles as seeds, size, size distribution, and yield of the resultant functional silica/polymer core-shell composites are summarized in Table II, in which the fraction of the hydrophilic functional comonomer fraction in the monomer feed was maintained at 0.60 in mass ratio. Sizes of the core-shell functional silica/polymer composite materials were varied between 227 and 258 nm, which depended on the type of the functional comonomer used for the copolymerizations. The maximum diameter of 258 nm and the minimum diameter of 227 nm were obtained with silica/poly(MBAAm-co-MAA) and silica/poly(MBAAm-co-VPy) core-shell composites, respectively. All the diameters of the resultant silica/polymer functional composites were much larger than that of silica seeds (179 nm), which indicated the successful formation of the core-shell structure silica/polymer composites without any second-initiated particles. The polydispersity indexes of the silica/polymer core-shell composites with various functional groups were kept between 1.012 and 1.028, indicating that the composite microspheres were monodispersed. The yield of the final silica/polymer core-shell composites were in the range of 32 and 57% depending on the functional comonomers used, which were much higher than the encapsulation efficiencies of the dispersion polymerization¹⁴⁻¹⁶ and emulsion polymerization.^{17,18}

The successful incorporation of various functional groups, including carboxylic acid, amide, hydroxyl, and pyridyl, into the shell layer of the silica/poly-

mer core-shell composite microspheres was confirmed further by FTIR spectra as shown in Figure 3. The FTIR spectrum of the silica particles in Figure 3(Curve a) had a strong peak at 1104 cm⁻¹, a middle peak at 802 cm⁻¹ and 947 cm⁻¹ corresponding to the symmetrical and asymmetrical vibration of the Si—O—Si bond and stretching vibration of the hydroxyl group. All the FTIR spectra of the silica/polymer core-shell composite functional microspheres in Figure 3(Curves b–e) had a peak at 3304 cm⁻¹ and a strong peak at 1658 cm⁻¹ attributed to the stretching vibration of N—H and carbonyl vibration of the amide unit of polyMBAAm segment, together with a strong peak at 1104 cm⁻¹ of the asymmetrical vibration of Si—O—Si bond of silica core. The characteristic peak at 1626 cm⁻¹ assigning to the vibration of vinyl group in Figure 3(Curves

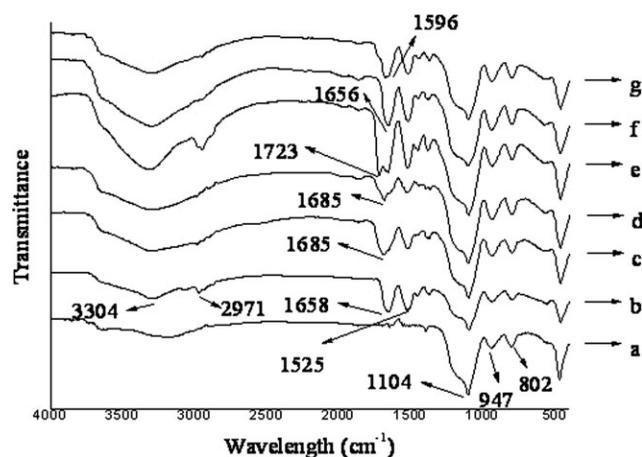


Figure 3 FTIR spectra of the silica and silica/polymer composites with different functional groups on the shell layer: (a) silica; (b) silica/poly(MBAAm-co-NIPAAm); (c) silica/poly(MBAAm-co-MAA); (d) silica/poly(MBAAm-co-HEMA); (e) silica/poly(MBAAm-co-VPy).

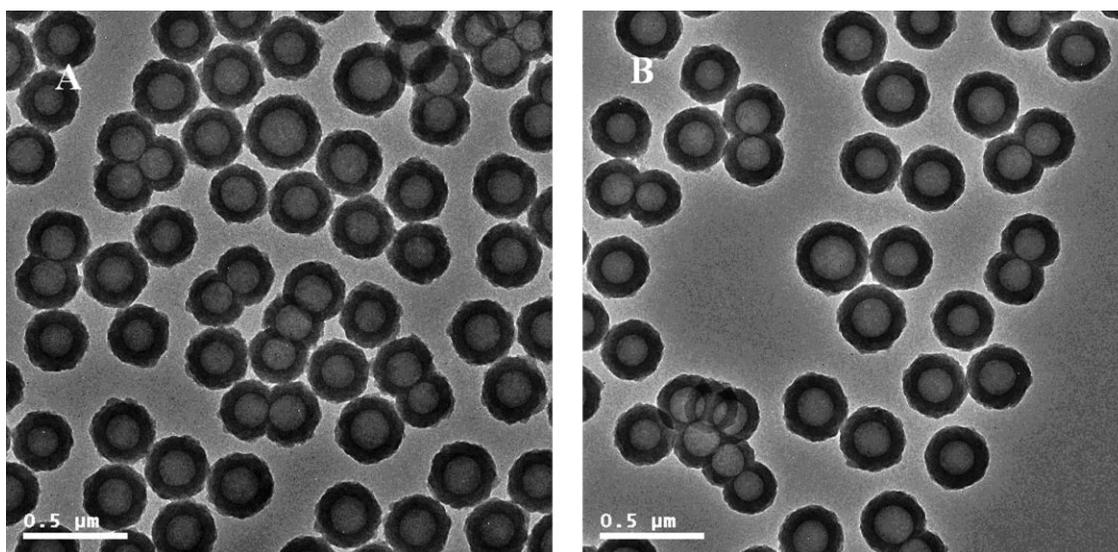


Figure 4 TEM micrographs of hollow poly(MBAAm-*co*-MAA) microspheres with different thickness of shell layer and loading capacity of carboxylic acid group obtained from various MAA fractions in the comonomer feed: (A) 0.20; (B) 0.80.

b–e) disappeared completely in these silica/polymer core-shell composites proving the high reactivity of the double-vinyl groups of polyMBAAm species as discussed earlier. A peak at 2970 cm^{-1} in Figure 3(Curve b) was corresponded to C–H vibration of the methyl group in polyNIPAAm segment. A strong peak at 1685 cm^{-1} in Figure 3(Curve c) due to the typical stretching vibration of the carbonyl unit of the carboxylic acid group demonstrated that polyMAA segments were incorporated into the shell layer of silica/poly(MBAAm-*co*-MAA) core-shell composites. A strong peak at 1723 cm^{-1} in Figure 3(Curve d) was attributed to the stretching vibration of carbonyl unit of ester group of polyHEMA, confirming the formation of silica/(polyMBAAm-*co*-HEMA) core-shell composites. The presence of a strong shoulder peak at 1596 cm^{-1} in Figure 3(Curve e) was assigned to the typical vibration of the polyVPy segment. All these results indicated the successful synthesis of silica/polymer core-shell composite microspheres with various functional groups on the shell layer by the distillation-precipitation copolymerizations.

Synthesis of monodisperse hydrophilic hollow polymer microspheres with various functional groups

In our previous work, the crosslinked polyDVB core in the core-shell functional polymer microspheres³⁷ cannot be selectively removed for the preparation of the corresponding hollow functional polymer microspheres. Silica cores of the silica/polymer core-shell functional composites were selectively removed by etching in HF to afford the corresponding hydrophilic hollow polymer microspheres with various

functional groups. The driving force for such removal was originated from the formation of SiF_4 gas, which was given off from the microspheres during the etching of the silica core to result in hollow polymer microspheres. The fraction of polymer component in the core-shell composites was obtained from mass difference between the silica/polymer core-shell composites and the corresponding hydrophilic hollow functional polymer microspheres after the selective removal of silica core.

The TEM micrographs of poly(MBAAm-*co*-MAA) hollow microspheres having carboxylic acid group with different shell thickness are shown in Figure 4, which were developed from the corresponding silica/poly(MBAAm-*co*-MAA) core-shell microspheres in Figure 1. When the MAA fraction in the comonomer feed was as high as 0.80, the results in Figure 4(B) indicated that the shell layer with 39 nm was not thick enough to support the cavities formed during the removal of silica cores, in which partially collapsed particles were observed with irregular shape. The hollow microspheres with carboxylic acid groups were obtained with MAA fraction in the comonomer feed between 0.20 and 0.60 for the formation of the functional shell layer. In the TEM images as shown in Figure 4(A), which corresponded the silica/poly(MBAAm-*co*-MAA) core-shell microspheres in Figure 1(B), convincing hollow-sphere structures were afforded. The size of the shell layer for the resultant poly(MBAAm-*co*-MAA) functional hollow microspheres was estimated by increasing the shell thickness from 39 to 57 nm as tabulated in Table I when MAA fraction in the comonomer feed was decreased from 0.80 to 0.20. These results implied that the poly(MBAAm-*co*-

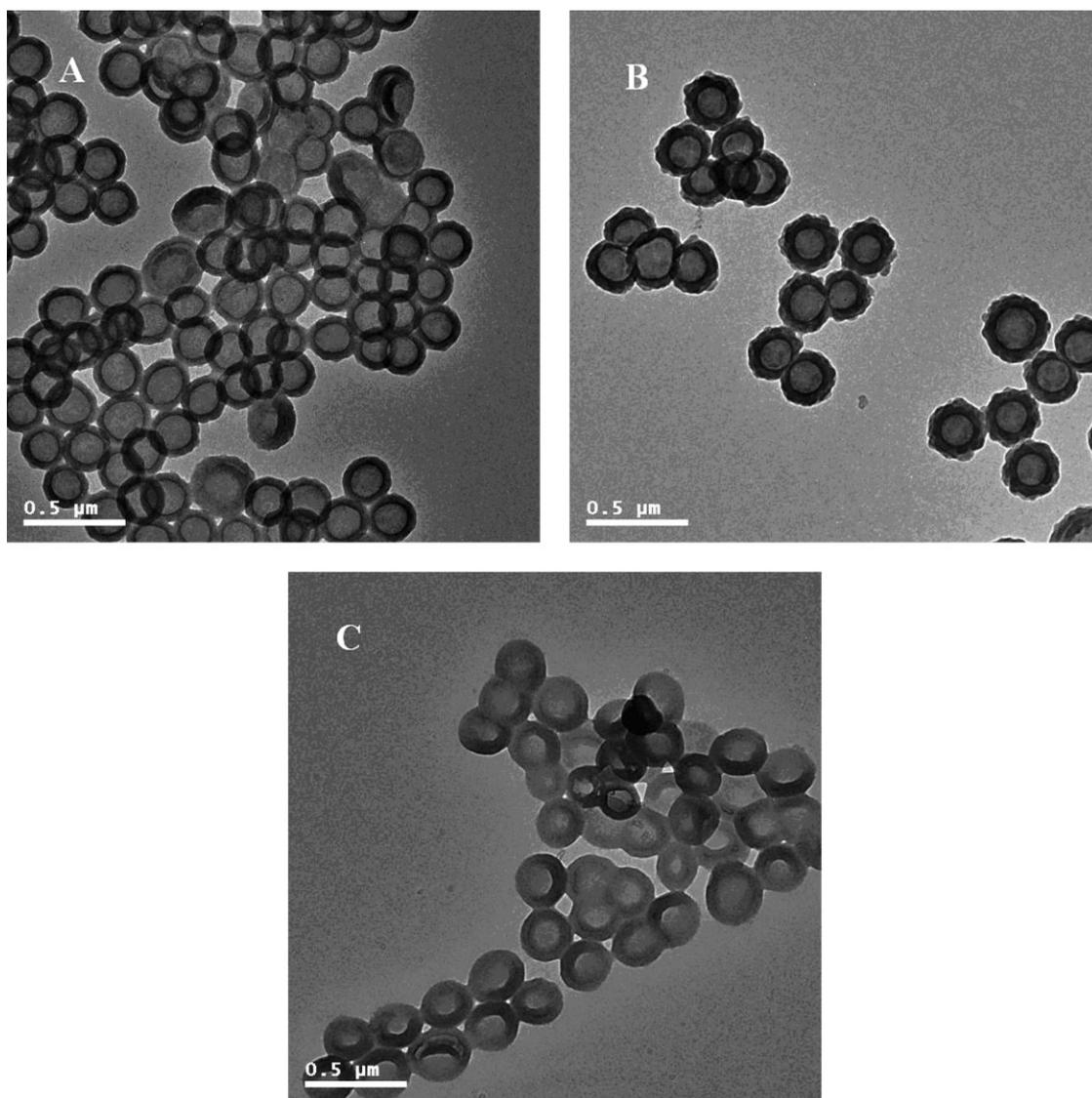


Figure 5 TEM micrographs of hydrophilic polymer microspheres with different functional groups: (A) poly(MBAAm-co-NIPAAm); (B) poly(MBAAm-co-HEMA); (C) poly(MBAAm-co-VPy).

MAA) hollow microspheres with different thickness and loading capacity of the functional carboxylic acid group could be facily controlled via varying the amount of MAA feed used for the synthesis of the polymer shell layer.

TEM micrographs of other hydrophilic hollow polymer microspheres with different functional groups, such as amide, hydroxyl, and pyridyl, are shown in Figure 5, which were obtained by the selective removal of silica from the corresponding silica/polymer core-shell functional composites as illustrated in Figure 2. The monodisperse hollow polymer microspheres with different functional groups, including amide, hydroxyl, and pyridyl, as shown in Figure 5(A–C), were obtained when the functional polymer shell layer were thick enough to get the convincing hollow-sphere structures.

Hydrodynamic sizes and size distributions of the resultant silica/polymer core-shell functional microspheres and the corresponding hydrophilic hollow polymer microspheres with different functional groups were determined by DLS in water for comparison of the results from TEM characterization (only with four samples for comparison in the present work) as summarized in Table II. Hydrodynamic diameters of silica/poly(MBAAm-co-NIPAAm) core-shell composite (NIPAAm fraction of 0.60 in the comonomer feed) and the corresponding poly(MBAAm-co-NIPAAm) hollow functional microsphere were 286 and 499 nm with monodispersity index of 1.029 and polydispersity index of 1.317, respectively, which were a little larger than the diameter from TEM of 239 nm with monodispersity index of 1.017. The hydrodynamic diameter of

silica/poly(MBAAm-*co*-MAA) (MAA fraction of 0.60 in the comonomer feed), core-shell microspheres, and the corresponding poly(MBAAm-*co*-MAA) hollow functional microspheres were 355 and 375 nm with narrow dispersity index of 1.125 and monodispersity index of 1.066, respectively, which were slightly larger than the size obtained from TEM of 258 nm with PDI of 1.015. The larger hydrodynamic diameters from DLS in water than those from TEM observation proved the hydrophilic property of the resultant silica/polymer core-shell microspheres and the corresponding hollow polymer microspheres with various functional groups, as the former ones were determined as in a swollen state. On the other hand, the considerably larger hydrodynamic diameter of the hollow functional microspheres than that of the corresponding silica/polymer microspheres indicated that the former was in a swollen state with a higher degree after removal of the silica core. All these results confirmed the hydrophilic property of the resultant silica/polymer core-shell microspheres and the hollow polymer microspheres having different functional groups, such as amide, carboxylic acid, hydroxyl, and pyridyl group. The studies on the scope of such silica/polymer core-shell functional composites and the functional hollow microspheres including the applications of such hydrophilic particles in DDS, polymer nanocomposites, and bioseparation are in systematical progress in our group.

CONCLUSIONS

Monodisperse silica/polymer core-shell composites having various functional groups on the polymer shell layer, such as carboxylic acid, amide, hydroxyl, and pyridyl, with regular shape were prepared by distillation-precipitation copolymerizations of MBAAm crosslinker together with functional comonomers, including MAA, NIPAAm, HEMA, and VPy, in the presence of silica particle as seed and AIBN as initiator in the absence of any stabilizer. The hydrogen-bonding interaction between the active hydroxyl group on the surface of silica core and the amide group of MBAAm as well as the functional group of the hydrophilic comonomer played a key role for the efficient encapsulation of functional polymer shell layer onto the silica core. The thickness of the poly(MBAAm-*co*-MAA) shell layer and the morphology of the resultant silica/poly(MBAAm-*co*-MAA) core-shell composites were conveniently controlled by the MAA fraction in the comonomer feed during the copolymerization, in which the various loading capacity of the accessible carboxylic acid group on the shell later was obtained. The corresponding hydrophilic hollow polymer microspheres with different functional groups, such as carboxylic acid, amide, hydroxyl,

and pyridyl, were further developed by selective etching of the silica core in HF solution from the silica/polymer core-shell composites. The much difference between the hydrodynamic diameter from DLS in water and the diameter from TEM characterization confirmed the hydrophilicity of the silica/polymer core-shell composites and the corresponding hollow polymer microspheres with different functional groups.

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