

# Hollow Polymer Particles with Nanoscale Pores and Reactive Groups on Their Rigid Shells: Preparation and Application as Nanoreactors

Jianping Deng, Yong Yu, Shuo Dun, and Wantai Yang\*

State Key Laboratory of Chemical Resource Engineering and College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

Received: September 22, 2009; Revised Manuscript Received: December 8, 2009

A novel type of hollow polymeric particles was prepared according to a strategy consisting of three major steps: the synthesis of template particles (PMV) based on maleic anhydride/vinyl acetate; the formation of core/shell particles by using maleic anhydride/divinylbenzene as comonomers, AIBN as initiator, and PMV as templates; and the removal of the core by dissolving it with an organic solvent. This route gave rise to core/shell and hollow particles in high yields, and the as-prepared particles possessed obvious advantages. The size of the core and the thickness of the shell were controllable by adjusting the reaction conditions. The shells were of high rigidity and strength as a result of the high cross-linking degree. The surface anhydride groups offered a platform for various postfunctionalization reactions of the particles. The nanoscale pores in the shells enabled an encapsulation of target compounds. The as-prepared hollow particles could be applied as “nanoreactors”. To attest to this concept, Ag-encapsulated composite particles were further prepared via redox reactions between  $\text{NaBH}_4$  and  $\text{AgNO}_3$  inside the hollow particles. A mechanism for the formation of core/shell particles and pores in the shells is proposed.

## Introduction

Hollow particles of nanometer dimensions are of particular interest due to their hollow core structure providing the ability to encapsulate significant quantities of guest molecules or large-sized compounds. Moreover, they have a potential in applications areas such as controlled delivery systems, artificial cells, lightweight fillers, and catalysis.<sup>1</sup> Hollow particles based on inorganic materials have been well studied,<sup>2</sup> and recently, inorganic/organic hybrid<sup>3</sup> and organic<sup>4</sup> hollow particles have begun to draw growing attention. Such hollow particles can be prepared via self-assembly,<sup>5</sup> emulsion/suspension polymerization,<sup>6</sup> dendrimer,<sup>7</sup> and template<sup>8</sup> approaches. However, the currently used methods to prepare hollow and core/shell-structured polymer particles always suffer from issues such as complex systems; tedious processes; difficulties in controlling the size of the particles; and particularly, the ease of collapse of the particles due to their insufficient rigidity and toughness. Furthermore, despite the great number of investigations on the preparation of hollow spheres, few studies have been devoted to the practical applications of the obtained particles.

Nanoscale reactors and their applications are a rapidly expanding area of research.<sup>9</sup> Reactions that are spatially confined in nanoreactors can provide nanomaterials with unusual crystal and morphological forms. Moreover, nanoreactors are advantageous in providing individual, randomly distributed nanoparticles without particle aggregates. Nanoscale spheres, micelles, vesicles, and capsules can all be employed as nanoreactors, and for this purpose, they should possess well-defined properties, including wall thickness and rigidity as well as permeability and affinity to the reactants involved. The nanoreactors currently used are mainly limited to emulsions, micellar systems, and polyelectrolyte capsules.<sup>10</sup> Even though they present significant efficiency and promise, each of the above-mentioned nanoscale

reactors has obvious disadvantages. Taking the most frequently used polyelectrolyte capsules as an example, nearly all of them suffer from complex and time-consuming fabrication and also present difficulties with regard to controlling the permeability of the shell, limitations concerning being applied to liquid systems, and instabilities against heat.<sup>11</sup> Accordingly, new types of reactors are still urgently desired in terms of an easy and straightforward preparation as well as the extensive applicability to emerging applications.

Recently, we developed a technique for preparing micro-/nanoparticles (denoted PMV) comprising alternating copolymers of maleic anhydride (MAH) and vinyl acetate.<sup>12</sup> The particles were easily prepared in *n*-butyl acetate (BA)/heptane (Hp) without the presence of a stabilizer and readily dissolved in various organic solvents due to their low molecular weight. In addition, particles consisting of highly cross-linked poly(divinyl benzene) were directly prepared in acetic acid. More importantly, the size of the particles was found to be controllable.<sup>13</sup>

The present article reports on a novel type of hollow polymeric particles prepared via precipitation polymerization by taking advantage of the above-mentioned PMV particles as template and referring to the method reported by Stöver<sup>14</sup> on preparation of microparticles based on polymers of MAH/divinylbenzene (DVB). These particles were fabricated on the basis of an effective and straightforward “polymerization/crosslinking → adsorption → crosslinking → growing” strategy; that is, the PMV particles were used as templates onto which MAH/DVB was polymerized and adsorbed to form the core/shell particles. After removing the template by a simple dissolution procedure, hollow particles were obtained.

The as-prepared polymeric hollow particles were characterized by techniques and were found to possess several obvious advantages: (1) The size of the core and the thickness of the shell were controllable by adjusting the preparation parameters. (2) The shells were rigid enough as a result of the high cross-linking degree due to the use of DVB, thus enabling the hollow

\* Corresponding author. Phone: 86-10-6442-2262. Fax: 86-10-6441-6338. E-mail: yangwt@mail.buct.edu.cn.

particles to maintain their initial shape, even under severe conditions. (3) The existence of carboxyl groups derived from anhydride groups on the shells could serve as an electrolyte, which is indispensable for subsequently selectively encapsulating target compounds inside the particles. The anhydride groups also offered a platform for numerous postfunctionalization reactions of the particles. (4) The pores in the shells provided channels for target compounds to pass through, allowing for an encapsulation of these compounds. Due to the existence of nanoscale pores in the shells, the prepared hollow spheres could be employed as ideal nanoreactors. To attest to this concept, silver (Ag) was synthesized inside the hollow particles, and polymer-encapsulated Ag composite particles could thus be prepared. Accordingly, a facile and efficient approach was developed for the fabrication of versatile hollow particles in mass production, which presented obvious advantages over their currently used counterparts.

## Experimental Section

**Materials.** Maleic anhydride was purchased from Beijing Chemical Reagents Company and used without further purification. Vinyl acetate (VAC) was purchased from Tianjin Chemical Reagents Company and purified by distillation at reduced pressure. Divinylbenzene (DVB-55, 55% mixture of isomers, technical grade) was purchased from Aldrich and used as received. Azo-bis-isobutyronitrile (AIBN, from Aldrich) was purified by recrystallization from methanol. All the other reagents were used without further purification.

**Preparation and Purification of the Template.** The details regarding the preparation of the template particles have been reported elsewhere.<sup>12</sup> The monomers MAH (24.5 g, 0.25 mol) and VAC (23 g, 0.25 mol), the initiator AIBN (0.48 g, 1 wt % of monomers), and the solvent *n*-butyl acetate (BA, 200 mL) were charged into a 250 mL, three-necked flask equipped with a gas supply, a thermometer and a condenser. After all the reagents were dissolved, the solution was subjected to N<sub>2</sub> purging for 30 min to obtain deoxygenation, after which the flask was placed in a water bath at 75 °C for 10 h. Subsequently, the particles were washed with BA three times and dried in vacuum at 70 °C for 24 h.

**Preparation of Core/Shell Particles.** The template prepared above (3.0 g) was dispersed in BA (56 mL) in a 100 mL, three-neck flask by ultrasonication for 40 min, then heptane (24 mL), MAH (1.60 g, 16.4 mmol), DVB-55 (1.44 g 17.2 mmol in vinyl groups), and the initiator AIBN (0.060 g, 2 wt. % of monomers) were added to the system. The flask was placed in a water bath at 25 °C. After purging with N<sub>2</sub> for 30 min, the temperature of the water bath was raised to 75 °C within 30 min. The polymerization was carried out for 10 h at 75 °C with stirring at a speed of 150 rpm. To determine the monomer conversion by a gravimetric method, the pure particles were obtained subsequently by centrifugation and filtration and then by washing with acetone to exclude the residual MAH.

**Preparation of Hollow Spheres.** After polymerization, the product (about 6 g) was separated from the solvent by centrifugation and placed in a 100-mL beaker with 20 mL of acetone. The beaker was then ultrasonicated for 2 h. The template was extracted during this process, and the micrometer-sized hollow spheres of a MAH/DVB copolymer were obtained.

**Preparation of Spheres with Encapsulated Ag.** The hollow spheres were first dispersed in a AgNO<sub>3</sub> aqueous solution for 2 h to make AgNO<sub>3</sub> enter the cavity of the spheres via sonication. The AgNO<sub>3</sub> on the outer surface of the spheres was removed by rinsing the particles with water, after which they

were dispersed in a NaBH<sub>4</sub> aqueous solution. When NaBH<sub>4</sub> entered the spheres, a redox reaction took place, and thereby, Ag was yielded. Inversely, Ag could be generated by first encapsulating NaBH<sub>4</sub> inside the spheres and then dispersing the spheres in the AgNO<sub>3</sub> aqueous solution.

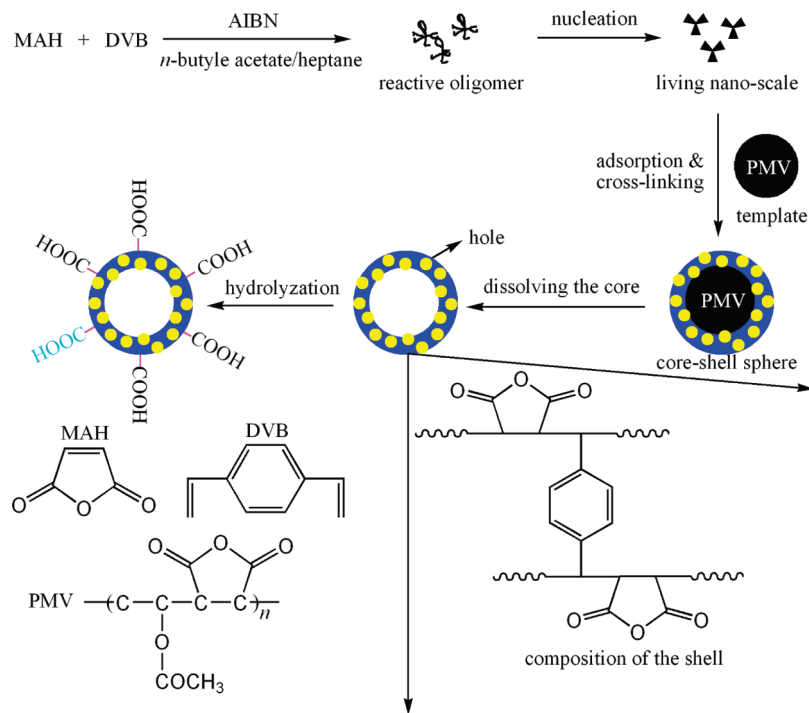
**Characterization.** The morphology of the produced particles was observed on a Hitachi S-4700 field emission scanning electron microscope (FEG-SEM) as well as on a Hitachi H-800 transmission electron microscope (TEM). The particle size and shell thickness were measured by the IBAS 1/2 image analysis system.<sup>12</sup> This method was based on the micrographs obtained from TEM, and for each sample, at least 100 objects were measured. The surface pore diameter of the particles was determined by a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry analyzer.

## Results and Discussion

**Overall Preparation Strategy.** The strategy for preparing the hollow spheres is schematically presented in Figure 1. This strategy consists of three major steps: the synthesis of the template; the formation of the core/shell particles; and the removal of the core. In the first step, PMV particles were prepared according to an earlier report.<sup>12</sup> Next, the preprepared PMV template particles of varying size were placed in a BA/Hp solution with MAH/DVB/AIBN. When heated, copolymerization and cross-linking of MAH/DVB took place, forming oligomers carrying propagating species. These oligomers coagulated to some degree, yielding scales (more details will be presented later) that were adsorbed by the template. The propagating species further underwent coupling reactions or initiated monomers to polymerize successively. Finally, core/shell particles were generated. After dissolution of the core, hollow particles were formed. The described approach featured the following advantages: a facile synthesis process, a high uniformity in composition of the hollow particles, and a significant similarity between the template (core) and the shell in composition, which facilitated the adsorption of the oligomers onto the core.

**Formation of the Core/Shell Particles.** MAH is an ideal monomer due to its highly reactive and flexible anhydride group as well as its ability to undergo alternating copolymerization with a series of monomers. In view of the specific molecular structure of PMV particles, the use of MAH/DVB as comonomers affords a high similarity between the core and the shell in the resultant core/shell particles, including the involved copolymerization mechanism and the structure of the copolymers. The high similarity in structure signified a considerable affinity of the oligomers to the template, which constitutes one of the key steps when forming core/shell particles. In other words, it enables the adsorption of the oligomers to the template to proceed smoothly. On the other hand, in the case of precipitation copolymerization of MAH and DVB, Stöver's group has performed numerous ground-breaking investigations.<sup>14</sup> By controlling the composition of the solvent mixture made up of methyl ethyl ketone and heptane, they were able to prepare microspheres and microgels, respectively. The microspheres were obtained according to the following: oligomer formation → particle nucleation by coagulation of oligomers → particle growth → microsphere formation mechanism; whereas the preparation of microgels included these: oligomer formation → microgel growth by intermolecular oligoradical reactions → colloiddally stable microgel mechanism.

In the present investigation, the formed oligomers of MAH and DVB should not dissolve in the solvent, but rather,



**Figure 1.** A schematic representation of the strategy employed in the preparation of hollow spheres.

**TABLE 1: Effects of the Solvent Mixture on the Morphology of the Core/Shell Particles after Removing the Core<sup>a,b</sup>**

BA (vol %)	diam hollow particles (nm)	shell thickness (nm)	appearance
40	370	35	hollow particles
50	382	41	hollow particles
60	384	42	hollow particles
70	408	54	hollow particles
80			gel
90			gel

<sup>a</sup> The average size of the template was  $\sim 300$  nm. <sup>b</sup> Other polymerization conditions: PMV, 3 g; MAH, 1.6 g; DVB, 1.44 g; AIBN, 0.06 g; 75 °C.

precipitate and even undergo particle nucleation by coagulation. To form core/shell particles in the presence of templates, the oligomers and premature particles should not coagulate to a large degree. In other words, the particles should not grow large enough, but should be adsorbed by the templates. To this end, the solvent composition and nature play crucial roles. Therefore, the effects of solvent composition were first investigated on the formation of core/shell particles. Considering that BA/Hp is a favorable solvent mixture for the preparation of PMV template particles since it cannot dissolve and swell the particles,<sup>12</sup> BA/Hp was employed for the copolymerization of MAH and DVB. The effects of the mixed solvent on the formation of core/shell particles are presented in Table 1 and Figure 2.

Table 1 shows that an increase in BA content up to 70% led to an increase in both the diameter and the thickness of the shell of the core/hollow particles. This can be explained by the effects caused by the solvent mixtures as a result of the different solubility parameters [BA,  $\delta = 8.3$  (cal/cm<sup>3</sup>)<sup>1/2</sup>; Hp,  $\delta = 7.4$  (cal/cm<sup>3</sup>)<sup>1/2</sup>]. Increasing the content of BA, a relatively good solvent for the resultant oligomers, allowed the oligomers to swell to a certain degree in the solvent. This, in turn, would lead to two simultaneous situations: a decrease in the cross-linking degree of the shells and an increase in the coagulation of the particles. In addition, when Hp, a relatively poor solvent

for the oligomers, is increased in the solvent mixture, the adsorption of the oligomers by the template is facilitated, resulting in a closer packing of the oligomers and, consequently, thinner shells. Apart from the BA/Hp solvent mixture, BA/hexane systems gave similar results (data not shown here).

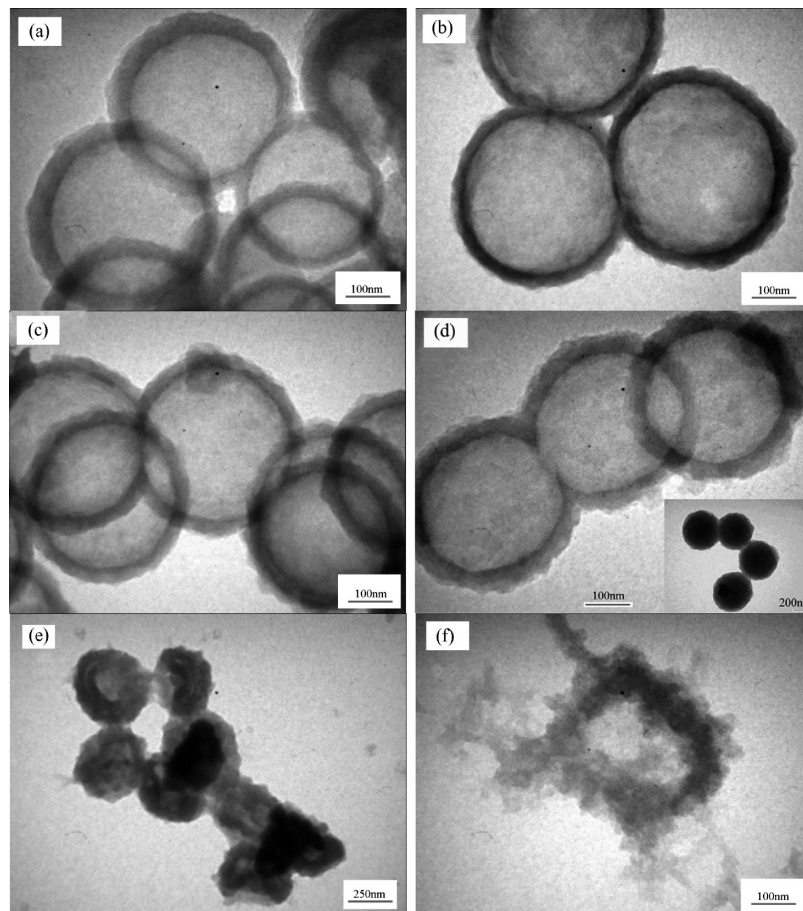
It is clear from Figure 2 that a low content of BA ( $\leq 70$  vol %) is suitable for preparing hollow particles (parts a–d in Figure 2). In these cases, round, hollow particles of uniform thickness could be formed. However, a further increase in the content of BA resulted in irregularly shaped hollow particles, and a conglutination among the particles became pronounced (Figure 2e). A system with 90% of BA provided a structured microgel coagulation. Hence, the results in both Table 1 and Figure 2 indicate that an appropriate composition of the solvent mixture was crucial for the formation of anticipated core/shell and the subsequent hollow particles. On the basis of these results, the following experiments were carried out with a solvent mixture of BA/Hp at 70/30 (vol %).

**Morphology of the Core/Shell Particles.** Following the strategy depicted in Figure 1, core/shell particles were prepared by using PMV particles as the template, MAH/DVB as the comonomers, and BA/Hp (70/30, V/V) as the solvent mixture. The morphology of the prepared core/shell particles is presented in Figure 3. The TEM of the PMV template particles are presented in Figure S1 of the Supporting Information for a comparison.

According to Figure 3, the particles became gradually larger with the prolongation of the polymerization time (from approximately 350 nm for 1 h to 600 nm for 20 h). This phenomenon was the result of a continuous adsorption of MAH/DVB oligomers on the template as well as of the successive propagation of growing polymer chains and the cross-linking from the coupling reactions between propagating polymer chains. The propagation of the polymer chains could be confirmed by monomer conversion percentage, as illustrated in Figure 4.

As can be seen in Figure 4, the systems with 90, 70, and 50 vol % of BA were systemically investigated, and all polymer-





**Figure 2.** TEM micrographs of the hollow particles prepared in a solvent mixture with varying BA/Hp ratios: (a) 40/60, (b) 50/50, (c) 60/40, (d) 70/30, (e) 80/20, and (f) 90/10 (in vol %). The inset in panel d shows the TEM for core/shell particles for a comparison. Other polymerization conditions: PMV, 3 g; MAH, 1.6 g; DVB, 1.44 g; AIBN, 0.06 g; and 75 °C.

izations of these three systems were found to occur quickly within the first 5 h. Monomer conversions reached 90% and above at a polymerization time of 10 h and approached 100% after 20 h. When comparing the three systems, the one with 90% of BA displayed the highest polymerization rate, most likely due to the higher solubility of MAH in BA as opposed to in Hp. The results demonstrated that the monomer conversion in the examined system was high, allowing a facile preparation of the core/shell particles.

In addition to the particles growing gradually larger with the polymerization time, the shells of the particles became uniform and the surfaces of the particles became progressively smoother during the course of polymerization, as clearly seen in Figure 3. The prepared core/shell particles were found to be composed of scale-like building blocks. These “scales” were approximately 10 nm in size (Figure S2 in the Supporting Information) and were formed by the appropriate coagulation of the oligomers from MAH/DVB. Subsequently, the scales were adsorbed onto the template while the propagating species and the residual double bonds led to further intra- or intermolecular cross-linking reactions. The cross-linking reaction resulted in shrinkage and phase separation, which in turn gave rise to the formation of pores in the shells. This is clearly portrayed in Figure 3g and Figure 8a, which will be involved later.

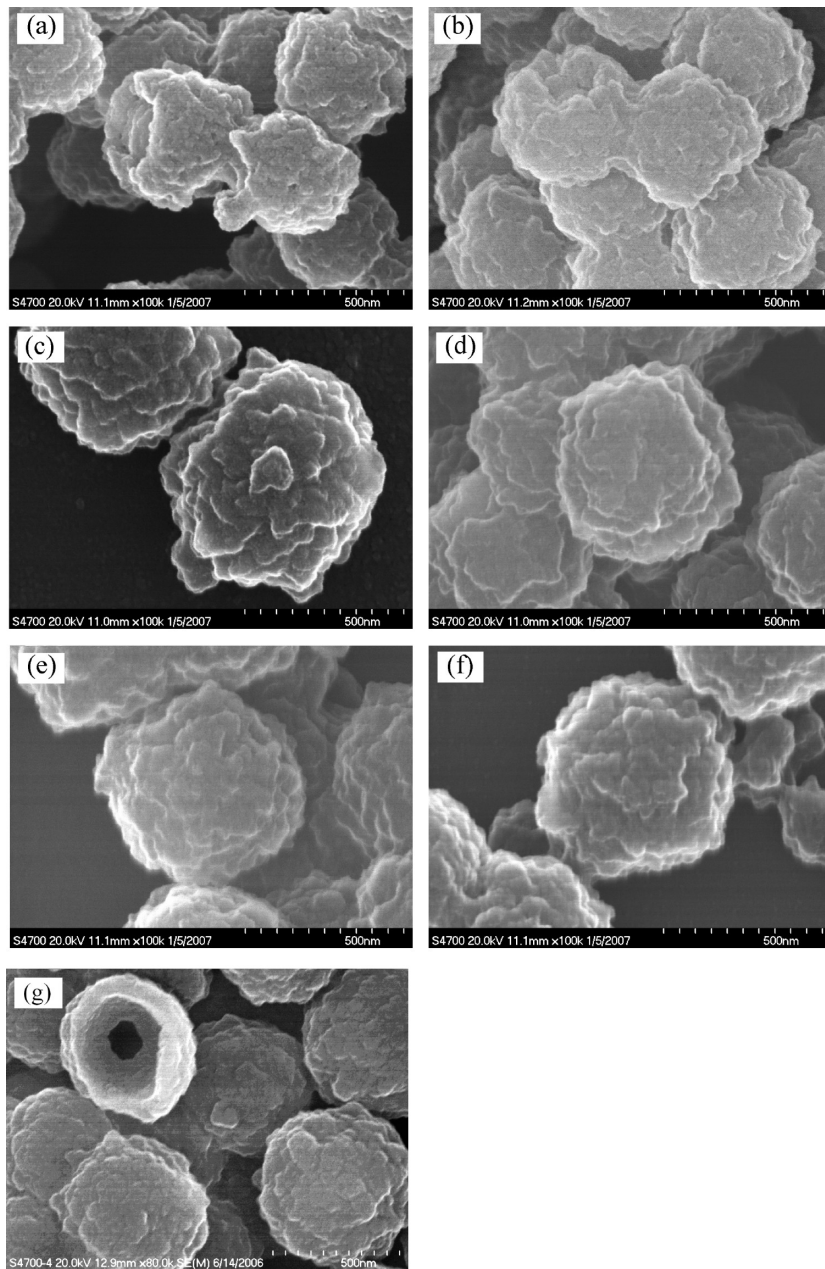
Han et al.<sup>15</sup> have already reported on the preparation of hollow polymeric spheres of 3.5  $\mu\text{m}$  in size with holes of 0.7–2.0  $\mu\text{m}$  in their surfaces. Regarding the core/shell particles prepared in the present study, the pore size was experimentally determined, and the results are presented in Figure 5.

The diameters of the pores were found to be 2 nm and above (Figure 5), and the BJH average diameter was about 17.1 nm. For this reason, despite the spheres’ shells being highly cross-linked, small particles as well as macromolecules were able to diffuse through the shell, offering the possibility of removing the core to prepare hollow particles to be employed as nanoreactors (see below).

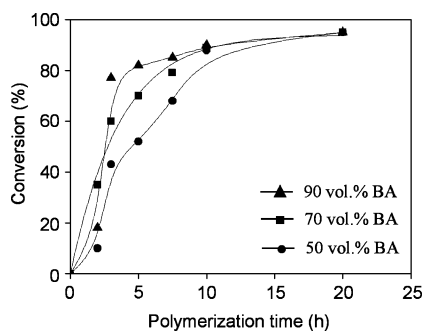
A possible mechanism for the formation of core/shell particles and nanoscales described above is illustrated in Figure 6. The driving forces for the adsorption of nanoscales of oligomers to the PMV template include both physical (high similarity between the molecular structures of the scales and templates) and chemical effects (propagation and cross-linking due to the existing free radicals and C=C bonds).

**Hollow Particles.** As mentioned above, the template particles in the present investigation are constituted of MAH/VAC copolymers without cross-linking. In addition, there are holes on the shells of the core/shell particles. Therefore, the templates (i.e., the cores of the obtained core/shell particles) could be readily extracted through these holes with a suitable solvent (e.g., acetone), giving rise to hollow microspheres for which typical micrographs are shown in Figure 2. These images in Figures 2 and 3 display a good comparison between the core/shells (Figure 3) and the hollow particles (Figure 2).

When comparing Figure 2d with its inset and Figure 3, one can observe that the templates were almost completely extracted from the microspheres. The diameters of the spheres changed very little after extraction of the core; moreover, the hollow particles could retain their round-sphere morphology, and the

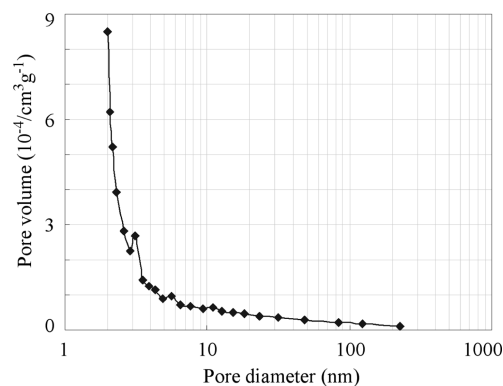


**Figure 3.** SEM micrographs of the core/shell spheres for various polymerization times: (a) 1, (b) 3, (c) 5, (d) 7, (e) 10, and (f) 20 h; and (g) an FEG-SEM image of the hollow spheres. PMV, 3 g; MAH, 1.6 g; DVB, 1.44 g; template, 3 g; AIBN, 0.06 g; BA, 56 mL; Hp, 24 mL; 75 °C.



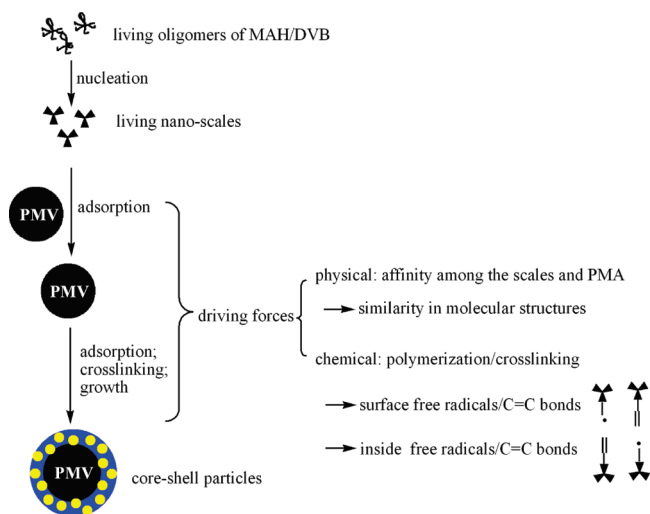
**Figure 4.** The monomer conversion as a function of the polymerization time. MAH, 1.6 g; DVB, 1.44 g; AIBN, 0.06 g; 75 °C.

thickness of the shells was found to be rather uniform. This observation provides partial evidence for the conclusion that the shells of the hollow particles possessed a high rigidity. Another pronounced advantage of the present hollow particles



**Figure 5.** The surface pore size distribution of the core/shell particles.

was the ease with which the shell thickness could be controlled. This was done by adjusting the ratio of monomer to template,



**Figure 6.** A schematic illustration of the formation of core/shell particles and the proposed driving forces (physical and chemical) for the adsorption of the “scales” on the template.

the monomer composition, the cross-linking degree of the shells, the composition of the mixed solvent, the content of the initiator, or a combination thereof. Next follows a detailed description of relevant results.

By maintaining a constant template content and varying the concentration of monomers, the shell thickness of the hollow particles could be effectively controlled. The TEM images of the hollow particles thus acquired are presented in Figure 7. For a fixed template content, increasing the concentration of monomer gave rise to an increase in shell thickness. It is important to note that when the ratio of monomer to template was too low, the resulting hollow particles were not sufficiently rigid, and considerable deformation was observed. This is demonstrated in Figure 7a, in which the shell thickness of the hollow particles was also rather thin. By appropriately increasing the monomer content, this problem could be successfully overcome, as shown in Figure 7b–e. Figure 7f plots the change in the thickness of the hollow particle shells as a function of the monomer/template ratio. The thickness of the hollow particles was found to increase nonlinearly with the increase in monomer concentration and could be tuned from 15 to 90 nm.

Similarly, the shell thickness of the hollow particles could also be readily and effectively controlled by adjusting the content of DVB, the comonomer, and cross-linking agent. To change the cross-linking degree of the shells, part of the amount of DVB was replaced by styrene (St), and this strategy resulted in the possibility of tuning the thickness of the shells. Relevant images are illustrated in Figure S3 in the Supporting Information. For the particles displayed in that figure, the total content of DVB + St was maintained constant; however, the ratio between them was purposely varied. This change in DVB/St ratio led to different thicknesses in the shells of the particles. For a DVB content higher than 50 mol %, changing the content further caused little variation in the thickness of the shell. However, when the content of DVB was lower than 50 mol %, a further decrease of it led to a reduction in shell thickness. A too low content of DVB (lower than 33%) gave rise to highly deformed hollow particles, thus demonstrating that a too low cross-linking degree did not favor the hollow particles’ retaining their spherical shape.

In the present research, DVB was simultaneously used as a comonomer and a cross-linking agent. The high cross-linking degree was believed to be crucial for the particles to be provided

with shells that were strong enough, an important requirement in order for the hollow particles to keep their original shape under dry condition and in vacuum environments. This assumption was strongly supported by Figure 8, where the morphology of the hollow particles is shown before and after hydrolysis.

Prior to hydrolysis, the hydrophilicity of the hollow particles was rather low, and the particles could not be uniformly dispersed in water. After hydrolysis, the anhydride groups were transformed to hydrophilic carboxyl groups, which led to a large increase in the hydrophilicity, thus permitting the hollow particles to be dispersed in an aqueous medium where they formed a homogeneous phase on the macro scale. Furthermore, SEM micrographs demonstrate that the particles exhibited little change in morphology before (Figure 8a) and after hydrolysis (Figure 8b). This observation was attributed to the high cross-linking degree in the shells of the hollow particles.

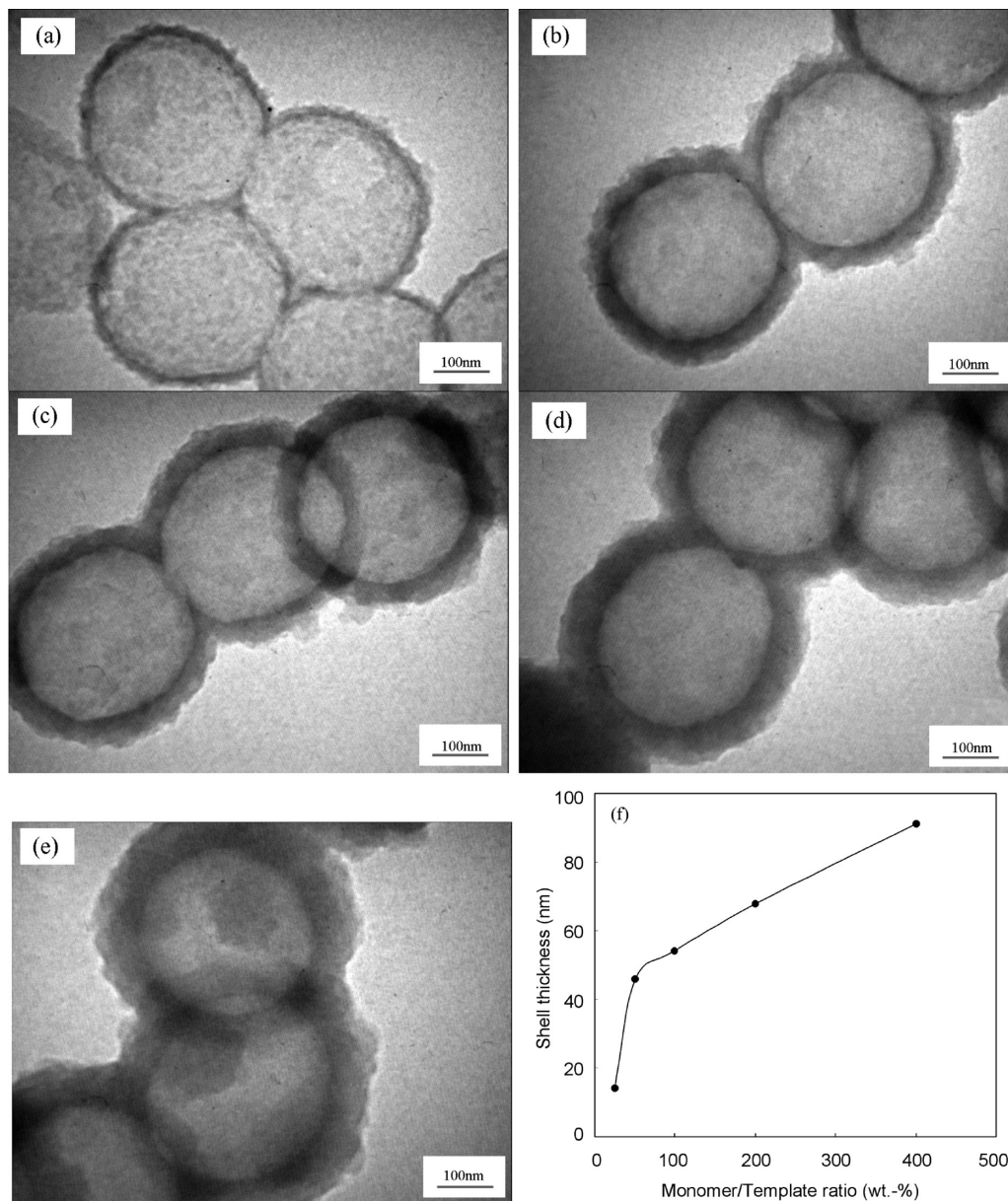
A high cross-linking degree of the shells was also helpful for the formation and maintenance of pores in the shells, as already discussed above. In particular, these pores remained intact even after hydrolysis (Figure 8a). On the other hand, it can be anticipated that soft shells would undergo a large deformation or even lose pores under severe conditions, which would be undesirable from the viewpoint of practical applications. Accordingly, this desirable feature of a high cross-linking degree constitutes an obvious advantage for the present hollow particles, as opposed to the common hollow polymeric particles that frequently lose their original shape under loading or severe conditions. The robust shells of the present hollow particles are thus favorable for further practical applications.

It should be pointed out that there are various other alternatives for realizing an effective control of the thickness of the shell: for example, by adjusting the concentration of initiator and the composition of the solvent mixture. For the MAH/DVB system, BA and Hp were selected to constitute the mixed solvent. The former substance is a good solvent for the monomers, whereas the latter is a poor one. Therefore, a solvent mixture with varying BA/Hp ratios would provide different results in the preparation of hollow particles, as seen in Table 1 and Figure 2, and as already discussed above.

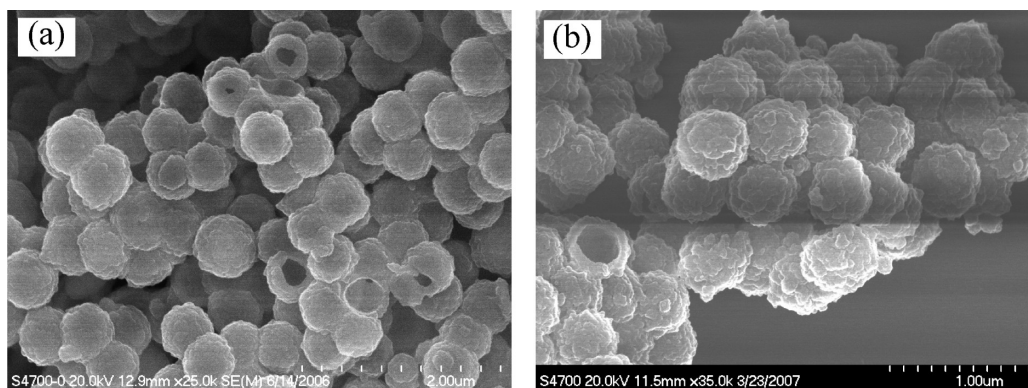
**Attesting to the Applicability of the Hollow Particles As Nanoreactors.** The as-prepared hollow particles can be utilized for a number of potential applications, thanks to the rigidity of the shells and their nanopores. In particular, the anhydride groups (or the carboxyl groups after hydrolysis) in the shells render this class of particles highly versatile and full of promise. Postfunctionalization according to practical situation can be readily achieved taking advantage of the reactive anhydride groups. The hollow particles with carboxyl groups can serve as an electrolyte and perform switch functions under certain conditions. It is thus believed that these hollow particles will provide an important and promising platform for a series of subsequent investigations, on the basis of which various practical applications will be developed further.

In the current research, the prepared hollow particles were applied as nanoreactors so as to attest to their values in practical applications. Spatially confined reactions were realized on the basis of prepared hollow polymeric spheres, making use of the holes in their walls. Typically, spheres encapsulating Ag could be readily prepared by two different approaches (cf. Figure 9). In the first, the hollow particles were filled with AgNO<sub>3</sub> by placing them in a AgNO<sub>3</sub>/ethanol solution. AgNO<sub>3</sub> thus penetrated inside the hollow particles through the pores. Subsequently, the particles encapsulating AgNO<sub>3</sub> were placed in a NaBH<sub>4</sub>/ethanol solution, where, in a similar way, NaBH<sub>4</sub>





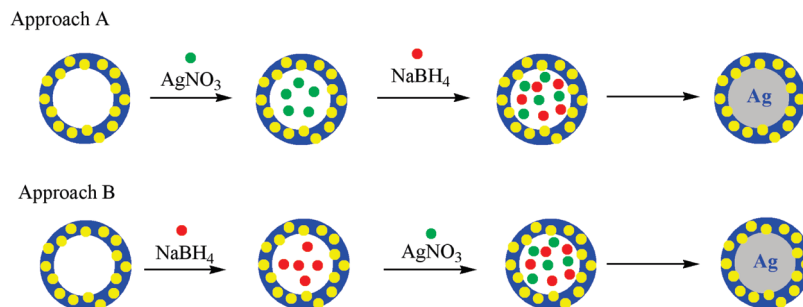
**Figure 7.** TEM micrographs of the hollow particles prepared in various monomer/template ratios: (a) 1/4; (b) 1/2; (c) 1/1; (d) 2/1; (e) 4/1 (wt %). The amount of monomer was fixed at MAH, 1.6 g; DVB, 1.44 g. Other conditions: AIBN, 0.06 g; BA, 56 mL; Hp, 24 mL; 75 °C. (f) The relationship between the shell thickness and the monomer/template ratio based on the TEM images (a–e).



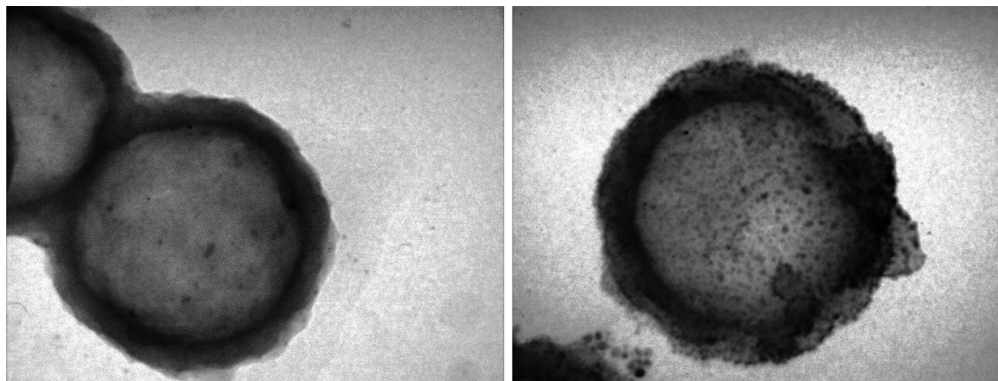
**Figure 8.** FEG-SEM micrographs of the hollow particles (a) before and (b) after hydrolysis.

penetrated into the hollow core of the particles, there giving rise to a reduction of  $\text{AgNO}_3$  and the subsequent formation of Ag. Inversely, the second strategy involved first filling the particles with  $\text{NaBH}_4$  and then placing the particles in the

$\text{AgNO}_3$  solution. This way,  $\text{NaBH}_4$  and  $\text{AgNO}_3$  underwent the same reaction inside the particles, once again leading to the generation of Ag there. These two strategies are schematically presented in Figure 9. The Ag particles thus prepared and



**Figure 9.** The schematic process for preparing polymer-encapsulated Ag spheres.



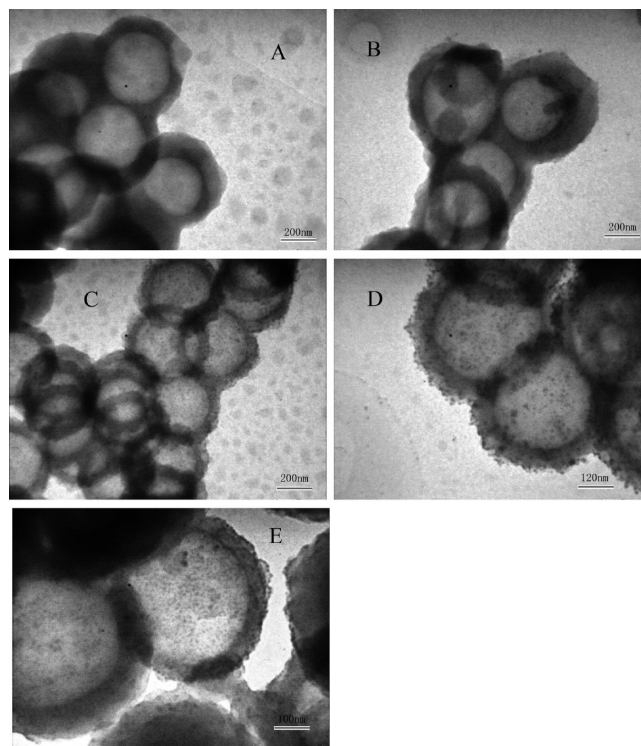
**Figure 10.** SEM micrographs of the spheres encapsulating Ag. These particles were obtained by filling the hollow spheres with (a)  $\text{AgNO}_3$  which was then reduced with  $\text{NaBH}_4$ ; (b)  $\text{NaBH}_4$  which was then reacted with  $\text{AgNO}_3$ . Both procedures were carried out at room temperature.

contained within the hollow polymer spheres were observed by TEM, and the micrographs are presented in Figure 10.

The images in Figure 10 demonstrate that with either of the two routes, Ag was successfully encapsulated inside the spheres. The size of the obtained Ag crystals was 5–10 nm, and the amount of Ag contained within the spheres could be quantitatively governed by controlling the reaction time. Figure 11 displays TEM micrographs of the Ag-encapsulating particles at varying reaction times. The elongation of the reaction time gave rise to an increase in the amount of generated Ag: for reaction times of 4.5 and 12 h, the difference was not obvious, indicating that the reaction could be completed within 4.5 h. Controlling the content of Ag encapsulated in the hollow particles could be realized not only by adjusting the reaction time, but also by tuning the concentration of  $\text{NaBH}_4$ ,  $\text{AgNO}_3$ , or both. All these observations attest to that Ag-encapsulating particles could be readily prepared with the technique developed in the present article, and the amount of encapsulated Ag could be highly controlled.

It would be possible to obtain Ag particles by removing the polymeric shells.<sup>16</sup> Reportedly, Ag composite nanoparticles or nanoshells exhibit antibacterial effects<sup>17</sup> as well as unique optical properties.<sup>18</sup> Undoubtedly, other compounds in addition to Ag can be prepared in a similar way, suggesting that the nanoreactor developed in the present work is extensively applicable for the preparation of various compounds of interest, including organic, inorganic, metallic, and bioactive compounds as well as conjugates. The technique might also be useful for the fabrication of a series of metallic (inorganic)/polymer composite particles and even polymeric particles encapsulating drugs and catalysts. Such experiments are currently ongoing.

The preparation of Ag inside the hollow particles is just one example of applications of the developed nanoreactors. These robust hollow particles demonstrate considerable advantages as nanoreactors,<sup>19,20</sup> especially for reactions sensitive to light or other factors and for reactions with noxious or irritant reactants,



**Figure 11.** SEM micrographs of the obtained Ag-encapsulating particles reacted for (A) 5 min; (B) 30 min; (C) 1.5 h; (D) 4.5 h; and (E) 12 h. Here, the Ag encapsulation was performed at room temperature by approach a according to Figure 9. Saturated solutions of  $\text{NaBH}_4$ /ethanol and  $\text{AgNO}_3$ /ethanol were used.

since the hollow spheres provide safe reaction sites. Meanwhile, the polymeric sphere walls do not affect the reactions. It is particularly important that the particles encapsulating targeted compounds (e.g., either  $\text{AgNO}_3$ ,  $\text{NaBH}_4$  or Ag in the current research) could be easily isolated by merely performing



centrifugation. Moreover, the encapsulated compounds were found to be safely entrapped, and no leaking occurred outside the particles during the subsequent procedures. This distinctive advantage was especially desirable when the hollow particles were to be used as micro-/nanoreactors. It is also noteworthy that the reactive anhydride groups in the particles' shells can be further tailored according to specific end uses. Consequently, this novel approach toward the preparation of hollow particles is expected to find numerous applications in the preparation of highly advanced materials.

## Conclusions

Micrometer-sized hollow spheres based on an MAH/DVB copolymer were readily prepared with MAH/VAC copolymers as the template particles. The high cross-linking degree of the shells provided the particles with a high strength and rigidity. Due to the existence of holes in the shells of the spheres, the macromolecular templates could be removed with a suitable solvent. Furthermore, by making use of these holes,  $\text{Ag}^+$  and a reductant could be irreversibly diffused into the interior cavity across the particle shells, where redox reactions could take place, yielding Ag. The presented technique thus offers a novel route for the preparation of "nanoreactors" because confined reactions may be realized inside the hollow particles. The technique to prepare such core/shell spheres and hollow spheres possesses some obvious advantages. The shell thickness of the hollow spheres and the volume of their hollow core could be controlled simply by varying the size of the template, the monomer concentration, and the ratio of monomer to template. Moreover, the reactive anhydride groups and nanopores on the shells provide a versatile platform for the further development of numerous promising applications.

**Acknowledgment.** The Program for New Century Excellent Talents in University (NCET-06-0096)), Special Research Fund for the Doctoral Program of Higher Education (20060010001), National Science Foundation of China (20574004, 20974007), and Major Project for Polymer Chemistry and Physics Subject Construction from Beijing Municipal Education Commission (BMEC) (XK 100100540, XK 100100640) are gratefully acknowledged for financial support of this work.

**Supporting Information Available:** The TEM images of the template particles and the TEM images of the hollow particles prepared by varying DVB/St ratio. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) (a) Shi, X.; Shen, M.; Möhwald, H. *Prog. Polym. Sci.* **2004**, 29, 987. (b) Meier, W. *Chem. Soc. Rev.* **2000**, 29, 295. (c) Hu, Y.; Jiang, X.; Ding, Y.; Chen, Q.; Yang, C. *Adv. Mater.* **2004**, 16, 933. (d) Caruso, F. *Chem.—Eur. J.* **2000**, 6, 413.
- (2) (a) Chen, D.; Ye, J. *Adv. Funct. Mater.* **2008**, 18, 1922. (b) Ras, R. H. A.; Kemell, M.; de Wit, J.; Ritala, M.; ten Brinke, G. *Adv. Mater.* **2007**, 19, 102. (c) Yu, J.; Guo, H.; Davis, S. A.; Mann, S. *Adv. Funct. Mater.* **2006**, 16, 2035. (d) Zhong, Z.; Yin, Y.; Gates, B.; Xia, Y. *Adv. Mater.* **2000**, 12, 206. (e) Jackson, J. B.; Halas, N. *J. Phys. Chem. B* **2001**, 105, 2743.
- (3) (a) Chen, T.; Colver, P. J.; Bon, S. A. F. *Adv. Mater.* **2007**, 19, 2286. (b) Tan, B.; Vyas, S. M.; Lehmler, H. J.; Knutson, B. L.; Rankin, S. E. *Adv. Funct. Mater.* **2007**, 17, 2500. (c) Cong, H. P.; Yu, S. H. *Adv. Funct. Mater.* **2007**, 17, 1814. (d) Fleming, M. S.; Mandal, T. K.; Walt, D. R. *Chem. Mater.* **2001**, 13, 2210.
- (4) (a) Cohen, I.; Li, H.; Houghland, L.; Mrksich, M.; Nagel, S. R. *Science* **2001**, 292, 265. (b) Kamata, K.; Lu, Y.; Xia, Y. *J. Am. Chem. Soc.* **2003**, 125, 2384.
- (5) (a) Chen, D.; Jiang, M. *Acc. Chem. Res.* **2005**, 38, 494. (b) Zhang, Y.; Jiang, M.; Zhao, J.; Zhou, J.; Chen, D. *Macromolecules* **2004**, 37, 1537. (c) Khopade, A. J.; Caruso, F. *Biomacromolecules* **2002**, 3, 1154.
- (6) (a) Emmerich Hugenberg, N.; Schmidt, M.; Sheiko, S. S.; Baumann, F.; Deubzer, B.; Weis, J.; Ebenhoch, J. *Adv. Mater.* **1999**, 11, 1299. (b) Okubo, M.; Konishi, Y.; Minami, H. *Colloid Polym. Sci.* **1998**, 276, 638.
- (7) (a) Sunder, A.; Krämer, M.; Hanselmann, R.; Mühlhaupt, R.; Frey, H. *Angew. Chem., Int. Ed.* **1999**, 38, 3552. (b) Wendland, M. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1999**, 121, 1389.
- (8) (a) Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, 282, 1111. (b) Zhong, Z.; Yin, Y.; Gates, B.; Xia, Y. *Adv. Mater.* **2000**, 12, 206. (c) Marinakos, S. M.; Novak, J. P.; Brousseau, L. C., III; House, A. B.; Edeki, E. M.; Feldhaus, J. C.; Feldheim, D. L. *J. Am. Chem. Soc.* **1999**, 121, 8518. (d) Wang, D.; Song, C.; Hu, Z.; Fu, X. *J. Phys. Chem. B* **2005**, 109, 1125. (e) Nelson, K.; Deng, Y. *Macromol. Chem. Phys.* **2007**, 292, 1158.
- (9) (a) Shi, X.; Shen, M.; Möhwald, H. *Prog. Polym. Sci.* **2004**, 29, 987. (b) Yang, Z.; Yang, L.; Zhang, Z.; Wu, N.; Xie, J.; Cao, W. *Colloid Surf., A* **2008**, 312, 113.
- (10) (a) Shchukin, D.; Sukhorukov, G. B. *Adv. Mater.* **2004**, 16, 671. (b) Sood, A.; Panchagnula, R. *Chem. Rev.* **2001**, 101, 3275.
- (11) (a) Ibarz, G.; Dahne, L.; Donath, E.; Möhwald, H. *Chem. Mater.* **2002**, 14, 4059. (b) Petrov, A. I.; Gavryushkin, A. V.; Sukhorukov, G. B. *J. Phys. Chem. B* **2003**, 107, 868.
- (12) (a) Xing, C. M.; Yang, W. T. *Macromol. Rapid Commun.* **2004**, 25, 1568. (b) Xing, C. M.; Yang, W. T. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, 43, 3760. (c) Xing, C. M.; Yu, Y.; Yang, W. T. *Macromol. Chem. Phys.* **2006**, 207, 621.
- (13) Yan, Q.; Bai, Y.; Meng, Z.; Yang, W. T. *J. Phys. Chem. B* **2008**, 112, 6914.
- (14) (a) Frank, R. S.; Downey, J. S.; Yu, K.; Stöver, H. D. H. *Macromolecules* **2002**, 35, 2728. (b) Li, W. H.; Stöver, H. D. H. *Macromolecules* **2000**, 33, 4354. (c) Frank, R. S.; Downey, J. S.; Stöver, H. D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, 36, 2223.
- (15) Han, J.; Song, G.; Guo, R. *Chem. Mater.* **2007**, 19, 973.
- (16) Yang, Z.; Yang, L.; Zhang, Z.; Wu, N.; Xie, J.; Cao, W. *Colloids Surf., A* **2008**, 312, 113.
- (17) Wang, J. X.; Wen, L. X.; Wang, Z. H.; Chen, J. F. *Mater. Chem. Phys.* **2006**, 96, 90.
- (18) Jackson, J. B.; Halas, N. J. *J. Phys. Chem. B* **2001**, 105, 2743.
- (19) (a) Han, W.; Fan, S.; Li, Q.; Hu, Y. *Science* **1997**, 277, 1287. (b) Dal, H.; Wong, E. W.; Lu, Y. Z.; Fan, S.; Lieber, C. M. *Nature* **1995**, 375, 769.
- (20) Sivaguru, J.; Natarajan, A.; Kaanumalle, L. S.; Shailaja, J.; Uppili, S.; Joy, A.; Ramamurthi, V. *Acc. Chem. Res.* **2003**, 36, 509.

JP909115P