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ARTICLE

Synthesis of Polymeric Yolk−Shell Microspheres by Seed Emulsion Polymerization

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ABSTRACT: The convenient synthesis of polymeric yolk−shell microspheres, which possess a hollow shell and an encapsulated spherical core, is both an interest and challenge in polymer chemistry. A method for the synthesis of polymeric yolk−shell microspheres by seed emulsion polymerization is proposed. The present synthesis includes a procedure for swelling the seed latex particles with the hydrophobic monomer mixture, polymerizing the adsorbed and entrapped monomer mixture, forming the coated microspheres, assembling the coated microspheres into sandwichlike ones through phase separation, and removing the seed by solvent etching. Followed this proposal, two kinds of yolk−shell microspheres, one of which contains an ∼200 nm hollow shell of cross-linked poly(styrene-*co*-acrylamide) and a spherical core of cross-linked polystyrene and the other containing a coordinative segment, are fabricated. The parameters affecting the synthesis of yolk−shell microspheres are investigated, and the phase separation within the seed particles is deemed to play the dominant role.

1. Introduction

Yolk−shell microspheres possess the unique structure of a hollow shell and an encapsulated single spherical core. A yolk−shell microsphere is different from a core−shell one, in which there exists an interstitial space between the shell and the core particle and therefore the core particle can move freely within the hollow shell. Over the past few years, yolk−shell microspheres have generated great interest because of their various applications in catalysis, batteries, and biomedical fields.[1−4] For example, the yolk−shell microsphere in which a single noble metal nanoparticle core is encapsulated within a hollow shell shows superiority of stability in catalysis because the trend for the confined noble metal nanoparticle core to sinter and grow into larger particles at high temperature is avoided.[5] It is also demonstrated that, ascribed to the novel structure, the Sn@carbon yolk−shell particles of Sn nanoparticles encapsulated within hollow carbon spheres exhibit a high capacity and good cycle performance when they are used as anode materials for lithium batteries.[1] Commonly, the methods for the synthesis of yolk−shell microspheres are specified by three methods: (1) the template-assisted approach, in which the sandwichlike structure (core/template/shell) is initially fabricated and then the sacrificial template is selectively removed by solvent etching or calcination to form voids;[6−10] (2) the Kirkendall effect[11−13] or the galvanic replacement process,[14,15] by which the shell of a core−shell particle is modified to obtain the yolk−shell structure; (3) selectively core-etching the core−-shell particles to form yolk−shell ones.[16] To date, various inorganic and inorganic/polymer hybrid yolk−shell microspheres have been synthesized.[17−22] The synthesis of polymeric yolk−shell microspheres is rarely reported,[23] possibly because it is not easy either to remove the template from the sandwichlike particles selectively or to etch the core layer of core−shell particles selectively. Very recently, Pan et al. have pioneered a method for the synthesis of polymeric yolk−shell microspheres by one-pot RAFT polymerization via polymerization-induced self-assembly and reorganization.[24,25] However, the feasible synthesis of polymeric yolk−shell microspheres is still a challenge in polymer chemistry.

Seed polymerization is a general method of synthesizing polymeric core−shell microspheres.[26−36] Following this method, polymerization of the shell-forming monomer is performed on the surface of the seed particles, therefore producing core−shell microspheres. Hollow microspheres can be further fabricated when the core of the resultant core−shell microspheres is selectively removed by solvent etching.[37−44] Herein, a convenient method of synthesizing polymeric yolk−shell microspheres by seed emulsion polymerization is proposed. This method is based on two concerns. First, it is assumed that some of the shell-forming monomers are entrapped within the seed particles and that the seed particles are swollen with the shell-forming monomers during seed polymerization if the seed particles and the shell-forming monomers are compatible. After polymerization, the resultant core−shell microspheres synthesized from seed polymerization contain a composite core, which is composed of the seed-forming polymer and the entrapped polymer resulting from the entrapped monomers. Second, phase separation between the seed-forming polymer and the entrapped polymer within the seed particles should occur, and the resultant core−shell microspheres can be assembled into sandwichlike microspheres such as the entrapped-polymer/core/shell microspheres or core/entrapped-polymer/shell ones. Thus, polymeric yolk−shell microspheres can be fabricated by selectively etching the core layer of the resultant sandwichlike microspheres.

On the basis of these two concerns, the typical polymeric yolk−shell microspheres of PS@PS-*co*-PAM, which contain a spherical core of polystyrene (PS) and a hollow shell of poly(styrene-*co*-acrylamide) (PS-*co*-PAM), are initially synthesized

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by seed emulsion polymerization employing the polystyrene-*co*-poly(methylacrylic acid) (PS-*co*-PMAA) core−shell microspheres as seed. Subsequently, this methodology is further extended to fabricate polymeric yolk−shell microspheres containing a coordinative segment of poly[2-(acetoacetoxy)ethyl methacrylate] (PAEMA). It is found, as ascribed to the phase separation between the entrapped polymer and the seed-forming polymer within the seed particles, that polymeric yolk−shell microspheres can be fabricated. Compared to the general seed emulsion polymerization used to produce core−shell microspheres or hollow microspheres, the procedure of swelling the seed particles with the shell-forming monomer and phase separation within the seed particles is needed.[27−44] Compared with the synthesis of polymeric yolk−shell microspheres either by one-pot RAFT polymerization via polymerization-induced self-assembly and reorganization or by multistage seed polymerization,[23−25] the proposed synthesis of yolk−shell microspheres has the advantage that only one-stage seed emulsion polymerization is needed.

2. Experimental Section

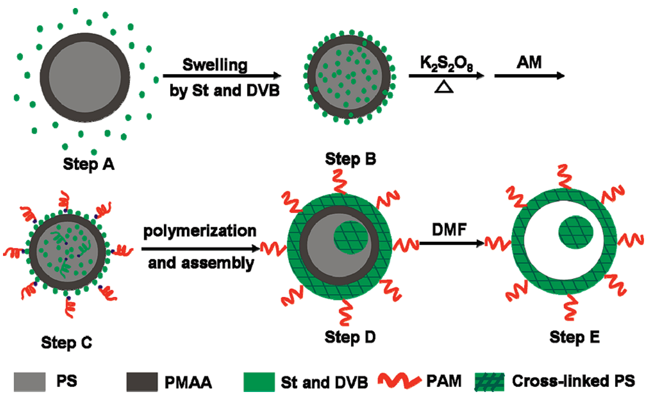
2.1. Materials. Styrene (St, >98%) and methylacrylic acid (MAA, >99%) were purchased from Tianjin Chemical Company and distilled under vacuum before being used. Acrylamide (AM, >99%, Tianjin Chemical Company) was recrystallized from acetone before being used. The divinylbenzene cross linker (DVB, >80%, Alfa Aesar) was washed with 5% NaOH aqueous solution and water, followed by drying with $MgSO_4$. The 2-(acetoacetoxy)ethyl methacrylate monomer (AEMA, >95%, Aldrich) and the $K_2S_2O_8$ initiator (>99.5%, Tianjin Chemical Company) were used as received. The seed particles of the PS-*co*-PMAA core−shell microspheres, which contain a 84 wt % PS core and a 16 wt % PMAA shell and have an average size of 220 nm, were synthesized by one-stage soap-free emulsion polymerization, as discussed elsewhere.[45] Other chemical reagents were analytical grade and used as received.

2.2. Synthesis of the PS@PS-*co*-PAM Yolk−Shell Microspheres. In a typical synthesis, a given weight of the monomer mixture of St and 5 wt % DVB was added to 20 mL of the aqueous dispersion containing 1.85 g of the PS-*co*-PMAA core−shell microspheres. The mixture was initially kept at room temperature with magnetic stirring for 1 h and then degassed under nitrogen purging for 30 min with vigorous stirring, and then a certain amount of $K_2S_2O_8$ (the molar ratio of $K_2S_2O_8$ to the total feed monomers including St, AM, and DVB is set at 2.0%) was added. Subsequently, the mixture was held at 80 °C for 5 min and then 5 mL of the AM aqueous solution containing 0.14 g of AM was added dropwise. Polymerization was performed under a nitrogen atmosphere with vigorous stirring for 24 h at 80 °C. After the completion of polymerization, the resultant coated microspheres were washed with water (3×20 mL) and collected by centrifugation. The collected coated microspheres were dried under vacuum at 40 °C, and then the coated microspheres were dispersed in 50 mL of dimethylformamide (DMF) at room temperature for about 12 h to remove the seed-forming polymer. The resultant yolk−shell microspheres were washed initially with DMF (20 mL × 3) and then with water (20 mL × 2), collected by centrifugation, and finally dried under vacuum at 40 °C.

2.3. Synthesis of the Yolk−Shell Microspheres Containing the Coordinative PAEMA Segment. The yolk−shell microspheres of PS/PAEMA@PS/PAEMA-*co*-PAM, which contain the coordinative PAEMA segment,[46,47] were synthesized similarly to those of the PS@PS-*co*-PAM yolk−shell microspheres, except that 1.0 g of the hydrophobic monomer mixture of St, AEMA, and DVB (75:20:5 by weight) was used.

2.4. Characterization. Transmission electron microscopy (TEM) observation was performed using a Philips T20ST electron microscope at an acceleration of 200 kV, whereby a small drop of the aqueous dispersion of the synthesized microspheres was deposited onto a piece of copper grid and then dried at room temperature under vacuum. The Fourier transform infrared spectroscopy (FTIR) measurement was performed on a Bio-Rad FTS-6000 IR spectrometer. The X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos Axis Ultra DLD spectrometer employing a monochromated Al Kα X-ray source (1486.6 eV) and a delay line detector (DLD).

Scheme 1. Schematic Synthesis of the PS@PS-*co*-PAM Yolk−Shell Microspheres



3. Results and Discussion

3.1. Synthesis and Characterization of the PS@PS-*co*-PAM Yolk−Shell Microspheres. Scheme 1 schematically shows the synthesis of the PS@PS-*co*-PAM yolk−shell microspheres. In the synthesis, the PS-*co*-PMAA core−shell microspheres, which are fabricated by one-stage soap-free emulsion polymerization as described in our recent paper,[45] are employed as the seed particles. Initially, the hydrophobic monomer mixture of St and DVB is added to the aqueous dispersion of the seed particles (step A). After 1 h of vigorous stirring, the seeds are swollen with the monomer mixture. Meanwhile, the droplets of the hydrophobic monomer mixture dispersed in the aqueous phase are adsorbed onto the surfaces of the seed particles (step B). For the sake of succinctness, the monomer mixtures adsorbed onto the surfaces of the seed particles and those swollen within the seed particles are called the adsorbed monomer mixture and the entrapped monomer mixture in the next discussion, respectively. Then, a hydrophilic initiator of $K_2S_2O_8$ and a hydrophilic monomer of AM are added, and the polymerization of the hydrophilic monomer and the adsorbed monomer mixture is initiated instantaneously. As polymerization proceeds, the number of chains of the resultant oligo(AM) increases and they gradually coagulate onto the surface of the seed particles, which will further initiate the polymerization of the entrapped monomer mixture (step C). With the polymerization going forward, the coated polymer layer, which results from the hydrophilic monomer of AM and the hydrophobic adsorbed monomer mixture, is produced. Inside the seed particles, the polymerization of the entrapped monomer mixture produces the entrapped polymer of cross-linked polystyrene, which is briefly called entrapped polymer in the next discussion. The resultant entrapped polymer becomes incompatible with the seed-forming polymer of linear polystyrene; therefore, phase separation within the seed occurs and the coated microspheres assemble into sandwichlike ones as shown in Scheme 1 (step D). Finally, the resultant sandwichlike microspheres are dispersed in DMF to remove the seed-forming polymer; therefore, the PS@PS-*co*-PAM yolk−shell microspheres are formed (step E).

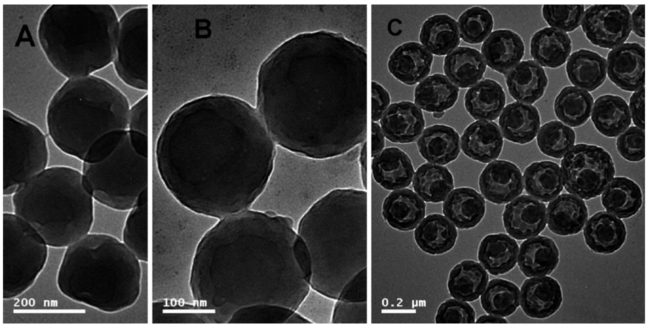


Figure 1. TEM images of the seed particles of PS-*co*-PMAA core−shell microspheres (A), the coated microspheres of PS-*co*-PMAA/PS-*co*-PAM (B), and the PS@PS-*co*-PAM yolk−shell microspheres (C).

In the proposed synthesis of yolk−shell microspheres, the hydrophilic monomer of AM is used becauase the resultant hydrophilic polyacrylamide (PAM) segment in the shell layer of the yolk−shell microspheres is useful in stabilizing the synthesized microspheres in water, which avoids using additional surfactant in the seed emulsion polymerization. As to the seed particles of the PS-*co*-PMAA core−shell microspheres,[45] their convenient synthesis through one-stage soap-free emulsion polymerization and easily being swollen with the hydrophobic monomer mixture of St and DVB prove them to be a suitable candidate.

To testify to the proposal, seed emulsion polymerization under a 59% weight ratio of the hydrophobic monomer mixture of St and DVB to the seed particles is tracked by TEM observation, in which the DVB weight percent in the hydrophobic monomer mixture remains constant at 5 wt %. Figures 1A and S1 (Supporting Information) show the TEM images of the seed particles of the PS-*co*-PMAA core−shell microspheres, which have been synthesized through one-stage soap-free emulsion polymerization as discussed elsewhere.[45] The seed particles, the average size of which is 220 nm, have a core−shell structure and a uniform size distribution. After seed emulsion polymerization, the coated microspheres (Figures 1B and S2) are fabricated. Similar to the seed microspheres, the resultant coated microspheres have a uniform size distribution, and the average size, 230 nm, is slightly larger than those of the seed microspheres. After the seed-forming polymer is removed by DMF etching, it is found that about 60 wt % of the polymer is removed by dissolving in DMF and the yolk−shell microspheres (Figure 1C) are produced. The average diameter of the hollow shell, the core size, and the shell thickness of the yolk−shell microspheres are 214, 97, and 37 nm, respectively. The size of the yolk−shell microspheres is slightly smaller than that of the coated microspheres (214 vs 230 nm), suggesting shrinkage of the yolk−shell microspheres during solvent etching.

The synthesized yolk−shell microspheres are composed of two parts: (1) One part is the hollow shell of cross-linked PS-*co*-PAM. It is expected that the hydrophilic PAM segment is located mainly on the outer periphery of the shell layer because of its hydrophilic character, which will be further discussed later. (2) The other part is the spherical core of the cross-linked PS. To confirm the structure and study the composition of the PS@PS-*co*-PAM yolk−shell microspheres, the following explorations are made.

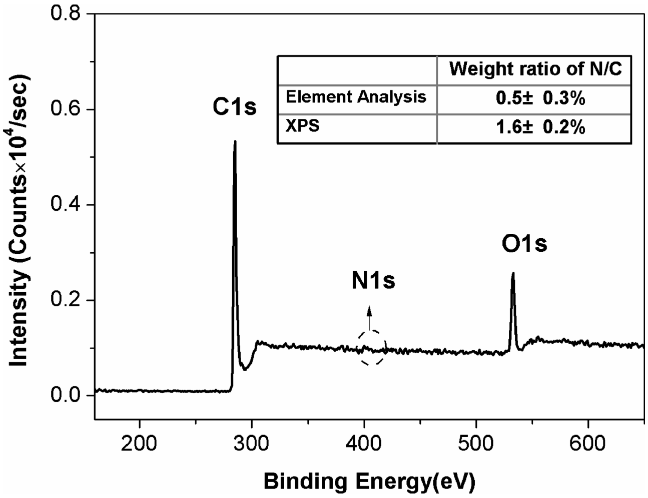


Figure 2. XPS spectra of the PS@PS-*co*-PAM yolk−shell microspheres.

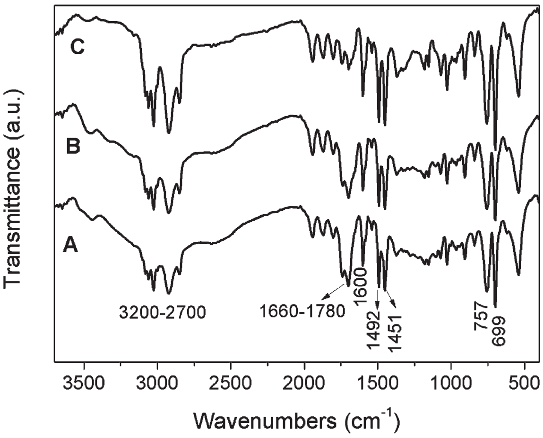


Figure 3. FTIR spectra of the seed particles of the PS-*co*-PMAA microspheres (A), the coated microspheres of PS-*co*-PMAA/PS-*co*-PAM (B), and the PS@PS-*co*-PAM yolk−shell microspheres (C).

First, the PS@PS-*co*-PAM yolk−shell microspheres are dispersed in water, and milky colloidal dispersion can be optically observed. The colloidal dispersion is stable at room temperature and can remain suspended in water for more than 2 months. The stability of the colloidal dispersion in water is partially ascribed to the hydrophilic PAM segment on the outer periphery of the yolk−shell microspheres. Besides, it is expected that the interstitial space or vacancy between the shell and the core particle is also helpful in suspending the yolk−shell microspheres in water.

Second, XPS analysis and elemental analysis of the yolk−shell microspheres are performed. Figures 2 and S3 (Supporting Information) show the XPS spectra of the yolk−shell microspheres. The peaks corresponding to C 1s (282.4 eV), N 1s (397.7 eV), and O 1s (530.8 eV) are observed in which N is originates from the PAM segment and C comes from both the PS and PAM segments. On the basis of the relative intensities of N 1s and C 1s, the weight ratio of the surface N/C can be calculated. It is found that the weight ratio of N/C calculated by XPS, 1.6 ± 0.2%, is much larger than that measured by elemental analysis, 0.5 ± 0.3%. Thus, it is concluded that most of the PAM segment is located in the outer surface of the shell and the cross-linked PS constructs the core of the yolk−shell microspheres as shown in Scheme 1.

Third, the synthesis of the yolk−shell microspheres is further tracked by FTIR analysis (Figure 3). Figure 3A is the FTIR spectra of the seed particles of the PS-*co*-PMAA microspheres, wherein the characteristic absorptions at

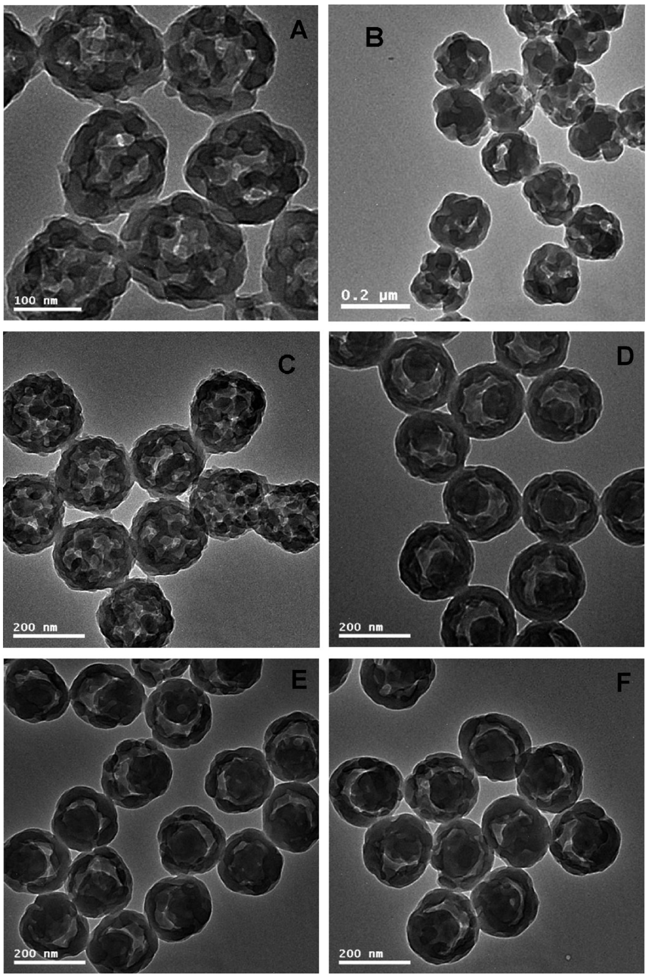


Figure 4. TEM images of the porous microspheres and yolk−shell microspheres under the M/S weight ratio of the hydrophobic monomer mixture to the seed particles at 30 (A), 44 (B), 52 (C), 59 (D), 67 (E), and 74% (F) with a constant DVB weight percentage of 5 in the hydrophobic monomer mixture.

1600, 1492, 1451, 757, and 699 cm^{-1} are ascribed to the PS segment and two broad absorptions at 3200−2700 and 1660−1780 cm^{-1} are ascribed to the PMAA segment. Figure 3B is the spectra of the coated microspheres of PS-*co*-PMAA/PS-*co*-PAM, wherein the broad absorption at 1660−1780 cm^{-1} is ascribed to the carbonyl group in the PAM segment and the carboxyl group in the PMAA segment. Figure 3C is the spectra of the yolk−shell microspheres, wherein the weakening absorption in 1660−1780 cm^{-1} confirms the elimination of the PS-*co*-PMAA seed microspheres and the formation of the PS@PS-*co*-PAM yolk−shell microspheres.

Clearly, compared to the general seed emulsion polymerization used to synthesize hollow microspheres,[40−43] the present synthesis of yolk−shell microspheres includes a procedure to swell the seed particles with the hydrophobic monomer mixture of St and DVB for about 1 h. It is believed that two roles constitute the dominant effect on the synthesis of the PS@PS-*co*-PAM yolk−shell microspheres. The first one is to entrap the hydrophobic monomer mixture within the seed particles of the PS-*co*-PMAA core−shell microspheres. To understand the swollen effect, seed emulsion polymerization under different weight ratios of the hydrophobic monomer mixture to the seed particles are used in which a constant DVB weight percent of 5 in the hydrophobic monomer mixture is maintained. In the next discussion, the weight ratio of the hydrophobic monomer mixture to the seed particles is named M/S. Figure 4 shows the TEM images of the resultant microspheres synthesized under an M/S weight ratio ranging from 30 to 74%. It is found that porous microspheres containing several linked nanoparticles within the cavity (Figure 4A−C) are formed when the M/S weight ratio is below 52%. When the M/S weight ratio increases above 59%, a single spherical core inside the hollow shell is formed and yolk−shell microspheres are fabricated (Figure 4D−F). Furthermore, the sequential increase in the M/S weight ratio leads to the increase in the size of the spherical core of the PS@PS-*co*-PAM yolk−shell microspheres. For example, when the M/S weight ratio increases from 59 to 67 and further to 74%, the core size increases from 97 (Figure 4D) to 110 (Figure 4E) and further to 119 nm (Figure 4F). The reason for the formation of porous microspheres under a low M/S weight ratio and the formation of yolk−shell microspheres under a high M/S weight ratio is discussed. Under a low M/S weight ratio, less of the hydrophobic monomer mixture is entrapped within the seed particles of the PS-*co*-PMAA core−shell microspheres and therefore less entrapped polymer of cross-linked polystyrene results. This less entrapped cross-linked polystyrene is expected to exist as an isolated phase within the seed particles because the cross-linked polystyrene becomes incompatible with the seed-forming polymer of linear polystyrene. Therefore, when the seed-forming polymer is removed by solvent etching, porous microspheres are fabricated under a low M/S weight ratio. When more hydrophobic monomer mixture is added to an aqueous dispersion of the seed particles under a high M/S weight ratio, more of the hydrophobic monomer mixture is entrapped within the seed particles and more entrapped polymer of cross-linked polystyrene results. Different from those under a low M/S weight ratio, this high amount of the entrapped polymer of cross-linked polystyrene, which also induces phase separation within the seed particle, extends to the assembly into a single sphere to form three-layered sandwichlike structure. This assembled sandwichlike structure is finally converted into yolk−shell microspheres as shown in Figure 4 by solvent etching.

The second role to affect the synthesis of yolk−shell microspheres is the phase separation between the entrapped polymer of cross-linked polystyrene and the seed-forming polymer of linear polystyrene within the seed particles. Clearly, the phase separation is caused by the entrapped DVB cross linker, and it is deduced that high cross linking of the entrapped polymer induces more serious phase separation within the seed particle. To test the phase separation effect due to the DVB cross linker on the synthesis of yolk−shell microspheres, seed emulsion polymerization at a 62% M/S weight ratio with a high DVB weight percent of 11 wt % under similar conditions such as the synthesis of yolk−shell microspheres shown in Figure 4 is explored. It is found that porous microspheres as shown in Figure 5 are fabricated. The present porous microspheres are similar to those shown in Figure 4 synthesized under a low M/S weight ratio (below 52%) with 5 wt % DVB in the monomer mixture, except that the encapsulated nanoparticles are slightly larger. This result suggests that the increased cross linking of the entrapped polymer causes more serious phase separation within the seed particles and therefore leads to the formation of porous microspheres.

3.2. Synthesis of the PS/PAEMA@PS/PAEMA-*co*-PAM Yolk−Shell Microspheres. The proposed method is further extended to produce the PS/PAEMA@PS/PAEMA-*co*-PAM yolk−shell microspheres. Figure 6 shows the TEM image of the PS/PAEMA@PS/PAEMA-*co*-PAM yolk−shell microspheres,

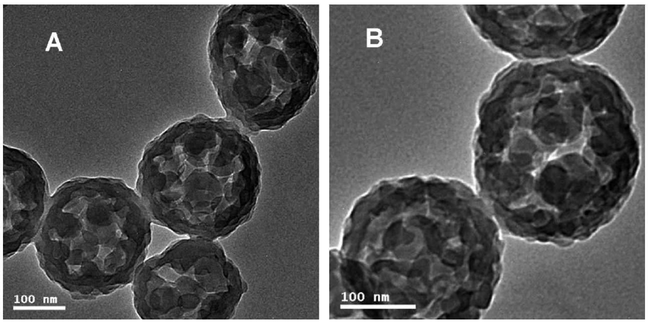


Figure 5. Low- (A) and high-magnification (B) TEM images of the porous microspheres synthesized under a 62% M/S weight ratio of the hydrophobic monomer mixture to the seed particles with 11 wt % DVB in the hydrophobic monomer mixture.

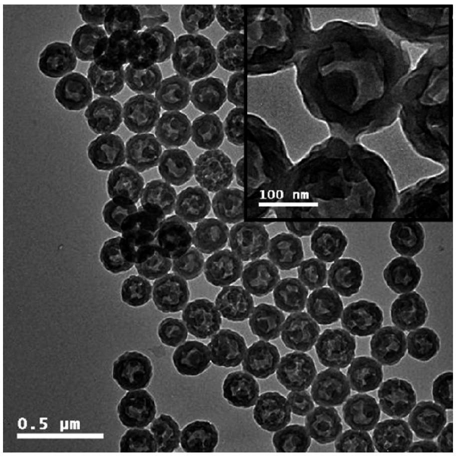


Figure 6. TEM image of the PS/PAEMA@PS/PAEMA-*co*-PAM yolk−shell microspheres.

and it indicates that the average diameter of the hollow shell, the core size, and the shell thickness of the yolk−shell microspheres are 220, 80, and 40 nm, respectively. The PS/PAEMA@PS/PAEMA-*co*-PAM yolk−shell microspheres are expected to have a PS/PAEMA core and a PS/PAEMA-*co*-PAM hollow shell. The core particle encapsulated within the PS/PAEMA@PS/PAEMA-*co*-PAM yolk−shell microspheres seems to be partially molten, possibly because the PAEMA segment has a relatively low glass-transition temperature (~3 °C).[46,47] Compared with the PS@PS-*co*-PAM yolk−shell microspheres, the present yolk−shell microspheres contain the chelating ligand of β-diketone in the PAEMA segment, thus these yolk−shell microspheres can be used to immobilize noble metal nanoparticles and can be employed in catalysis as the general polymeric hollow microspheres.[40−42]

4. Conclusions

Convenient synthesis of the polymeric yolk−shell microspheres containing a hollow shell and a spherical core is proposed. The synthesis includes the procedure of swelling the seed particles of the PS-*co*-PMAA core−shell microspheres with the hydrophobic monomer mixture including the DVB cross linker, polymerization of the hydrophobic monomer mixture both adsorbed on the surface of the seed particles and entrapped within the seed particles, formation of coated microspheres and assembly of the resultant coated microspheres to sandwichlike ones through phase separation between the entrapped polymer and the core-forming polymer within the seed particles, and removal of the seed-forming polymer by solvent etching to fabricate yolk−shell microspheres. The phase separation between the entrapped polymer and the core-forming polymer within the seed particles in forming sandwichlike microspheres is deemed to be the key to synthesizing yolk−shell microspheres, and the parameters affecting the synthesis of yolk−shell microspheres are explored. It is found that the weight ratio of the hydrophobic monomer mixture to the seed particles and the weight percent of the DVB cross linker in the hydrophobic monomer mixture affect the synthesis of yolk−shell microspheres. That is, the synthesis of yolk−shell microspheres can be achieved under a suitable weight ratio of the hydrophobic monomer mixture to the seed particles and with a moderate value of the DVB cross linker in the hydrophobic monomer mixture. Otherwise, the formation of porous microspheres encapsulating several linked nanoparticles within the cavity takes place. Following the proposed method, the PS@PS-*co*-PAM yolk−shell microspheres containing a 200 nm hollow shell of PS-*co*-PAM and a spherical PS core with size ranging from 97 to 119 nm and the PS/PAEMA@PS/PAEMA-*co*-PAM yolk−shell microspheres containing the coordinative PAEMA segment are fabricated.

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Supporting Information Available: TEM images of the seed particles of the PS-*co*-PMAA core−shell microspheres and the coated microspheres and XPS spectra of the PS@PS-*co*-PAM yolk−shell microspheres. This material is available free of charge via the Internet at http://pubs.acs.org.

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