Preparation of Organic/Inorganic Hybrid Hollow Particles Based on Gelation of Polymer Vesicles

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ABSTRACT: In a previous communication, we have reported the study of novel organic/inorganic hollow particles based on a reactive amphiphilic diblock copolymer, poly(ethylene oxide)-*block*-poly[3-(trimethoxy-silyl)propyl methacrylate] (PEO-*b*-PTMSPMA). The preparation of these novel particles involved the preformed vesicles of the block copolymers in a methanol/water solvent mixture, followed by a gelation process to fix the vesicular morphology. In this paper, the detailed conditions for the preparations of the hybrid vesicles, including water contents in the binary solvent, initial copolymer concentration (C_{ini}) in methanol, compositions of the diblock copolymers, and gelation catalyst, have been explored in great detail. The results demonstrated that the robust vesicles could be prepared under a variety of conditions, such as over a broader range of the water content (from ca. 34 to 98.4 wt %) at the C_{ini} of 5.0 mg/mL for PEO$_{45}$-*b*-PTMSPMA$_{59}$. Furthermore, exclusive vesicles were formed under the C_{ini} ranging from 0.5 to 20 mg/mL of PEO$_{45}$-*b*-PTMSPMA$_{59}$ in methanol while the water content was kept constant at 55.8 wt %, whereas the average size of vesicles and the size distribution increased correspondingly. Before the exclusive vesicles appeared, spheres, short rods, and lamellae were observed as the coexisted morphologies when the water content increased gradually. For the block copolymers with a constant PEO length and different PTMSPMA lengths, i.e., PEO$_{45}$-*b*-PTMSPMA$_x$ (x = 29, 42, and 180), only vesicles were produced under the conditions applied with the longer PTMSPMA blocks resulting in a thicker vesicle wall. The gelation catalyst plays a critical role in the morphological fixation. We have found that triethylamine (TEA) was the best gelation catalyst under the conditions used in this study, while the acid catalysts destroyed the vesicles. In addition, because of the inorganic components, the nanocapsule was very stable, and its morphology remained even after calcination at 450 °C.

1. Introduction

Self-assembly of block copolymers has attracted an increasing interest for applications as nanomaterials and for nanofabrications.[1] It is known that amphiphilic diblock copolymers can form micelles by self-assembling in selective solvents, such as polar solvents for hydrophilic blocks.[1−3] The commonly observed morphologies of the micelles include spheres, wormlike rods or tubules, and vesicles. The morphologies depended on various factors, such as the composition of the block copolymers, the chain architectures, and the conditions of the aggregation.[2−16] Among these versatile micelles, the vesicles that enclose a hollow cavity by a bilayer membrane are of particular interest due to their potential applications in encapsulation and release.[8,15c] In addition, it needs to lay emphasis on applying water as the medium of self-organizing block copolymers since water is required for biomedical applications and is also environment friendly. The state of the art of the polymer vesicles has been summarized in some recent reviews.[9,10] It is of note that the compositions and the structures of the block copolymers are very important for the preparations of polymer vesicles as seen in the limited successful examples. The highly asymmetric coil−coil block copolymers with a long core-forming block were the main precursors to produce the vesicles reported in the literature;[10b] a few coil−rod[11,12] and coil−dendron[16] block copolymers were reported to form vesicles as well in some recent publications. However,

these vesicles were the aggregates of many polymer chains and were destroyed easily when the environment changed. If some repeat units in one of block copolymer segments bear reactive groups, the resulted vesicles can be fixed by chemical cross-linking. Such hollow nanoparticles are shape-persistent against environmental change. There are a few examples in recent years to fix the polymer vesicles by chemical cross-linking.[12−15] One typical example from Liu et al. involved the self-assembly of the polyisoprene-*block*-poly(2-cinnamoyl-ethyl methacrylate) diblock copolymer in hexane/THF.[15] By exposure of the vesicles in solution to UV light, the domains containing cinnamoyl groups were cross-linked by photodimerization, and the stable vesicles were obtained. However, those nanocapsules had purely organic structures originating from their precursor copolymers.

It is known that the inorganic structures are more stable compared to the organic ones. The hollow silica or polyorganosiloxane nanoparticles were prepared mainly by template approaches in the literature. Schacht et al. have prepared the hollow silica spheres in the oil/water emulsions, which resulted from an interfacial reaction.[17] Pinnavaia et al. introduced the silica into the interlayer regions of the multilamellar vesicles to form nearly spherical particles with stable lamellar mesostructures.[18] The ultrastable mesostructured silica vesicles were also reported by the same group using the neutral gemini surfactants as the structure-directing agents.[19] An organic/inorganic hybrid vesicle was prepared by the gelation in the vesicles given by a lipid-bearing alkoxysilyl head, and a hierarchical vesicle

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Scheme 1. Schematic of Preparation of Hybrid Vesicles by Self-Assembly of Reactive Block Copolymers[a]
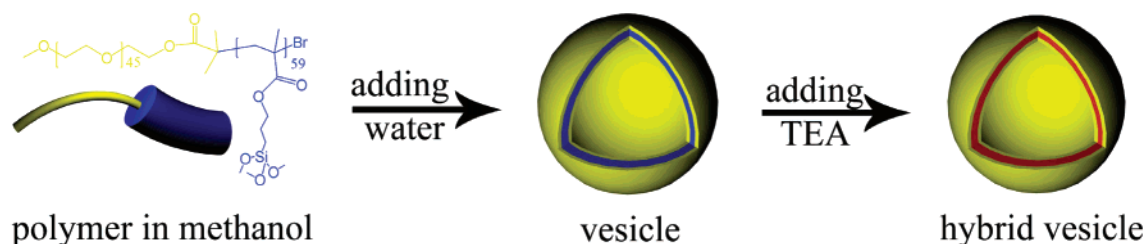

[a] The yellow part stands for the PEO, the blue part for the PTMSPMA, and the red part for the polyorganosiloxane from the gelation process.

assembly was made through a layer-by-layer approach.[20] The colloids have been used as the templates for forming the inorganic shells. The linear polysiloxane colloids as the templates formed in situ in an emulsion polymerization were further coated with a cross-linked polysilsesquioxane shell by the gelation of trimethoxymethylsilane, and the hollow particles were formed through extracting the soluble core by a solvent.[21a,b] Functional molecules such as dyes were encapsulated in the siloxane network and the cavity of the hollow particles.[21c] In a very recent report, the hybrid core−shell particles were prepared by coating the surfaces of monodisperse polystyrene beads with uniform silica shells.[22] Hollow silica spheres could be obtained by removing the polymer cores via calcination or by wet etching with toluene. The surfaces of block copolymer micelles have also been coated with a silica layer by reacting with an active silicate, making use of few trimethoxysilane groups born on the corona-forming blocks of the micelles.[23]

Our research focuses on the preparation of soluble nanocapsules with an organic polymer/polyorganosiloxane hybrid structure through self-assembly of block copolymers. Recently, we have reported the preliminary results on preparing such hollow nanoparticles using a novel reactive diblock copolymer, poly(ethylene oxide)-*block*-poly[3-(trimethoxysilyl)propyl methacrylate] (PEO-*b*-PTMSPMA), which was synthesized by atom-transfer radical polymerization (ATRP).[24] The approach for preparing this nanocapsule and its structure are illustrated in Scheme 1. It is known that PEO is a hydrophilic polymer while the PTMSPMA with many −Si(OCH$_3$)$_3$ groups is hydrophobic and readily form cross-linked polysiloxane by the gelation process. PEO$_{45}$-*b*-PTMSPMA$_{59}$ diblock copolymers form polymer vesicles in a binary solvent mixture of methanol and water with the PEO blocks as the corona and the PTMSPMA blocks as the wall, as confirmed by ^{1}H NMR analysis.[24] After the addition of a gelation catalyst, triethylamine (TEA), which only plays a role to fix the vesicular morphology, the shape-persistent hybrid vesicles with a cross-linked polysilsesquioxane wall were obtained. A typical scanning electron microscope (SEM) of the hybrid vesicles is shown in Figure 1, which gives a clear three-dimensional vesicular morphology. The formation of these unique vesicles by this block copolymer was rather remarkable. In this paper, we had studied how the preparation conditions and the copolymer compositions influenced the formation of these novel hybrid vesicles.

2. Results and Discussion

Depending upon the interfacial curvature between the core and the corona of the micelles, spheres, rods, and vesicles could be formed as a result of the balance of all
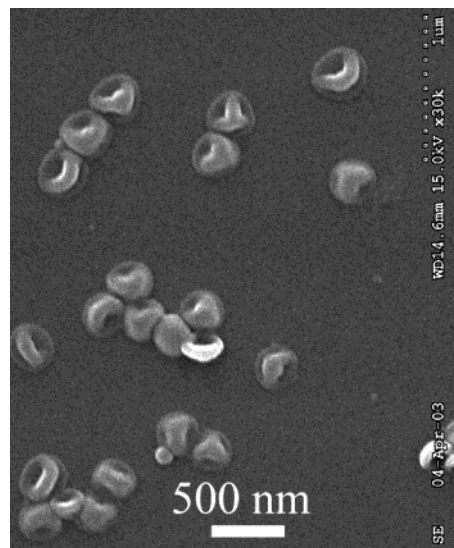

Figure 1. SEM image of the vesicles from PEO$_{45}$-*b*-PTMSPMA$_{59}$. Conditions: initial copolymer concentration in methanol is 10 mg/mL, water content is 91.0 wt %, and the TEA concentration is 0.04 wt %.

Table 1. Characteristics of PEO-*b*-PTMSPMA Diblock Copolymers Used for Preparation of Hybrid Vesicles

composition[a]	M_n[b]	M_w/M_n[b]
45/29	8 200	1.25
45/42	11 600	1.34
45/59	13 800	1.28
45/180	45 000	1.10

[a] The number of repeat unit of EO/TMSPMA, obtained from ^{1}H NMR in CDCl$_3$. [b] Obtained from SEC.

factors to the free energy of aggregation.[9,10] Many factors, such as preparation condition, common solvent, and copolymer composition, may influence the curvature of the hydrophobic−hydrophilic interfaces of the self-assembly from the block copolymers with a given structure. In this work, four diblock copolymers were used: PEO$_{45}$-*b*-PTMSPMA$_x$, x = 29, 42, 59, and 180 (the composition was determined by ^{1}H NMR in CDCl$_3$, which is a good solvent for both segments) as shown in Table 1. The solutions of the vesicles based on PEO-*b*-PTMSPMA were made by adding water into a block copolymer solution of methanol. The gelation catalyst, TEA, was added 5 h after the vesicles formed. The following factors for the vesicle formation were explored: (1) the solvent composition in the binary solvent mixture of water and methanol; (2) the initial copolymer concentration (C_{ini}) in methanol; (3) the PTMSPMA length of the block copolymers; (4) the effect of catalyst and gelation time. Finally, the mechanism of vesicle formation and the structure of vesicles were discussed briefly.
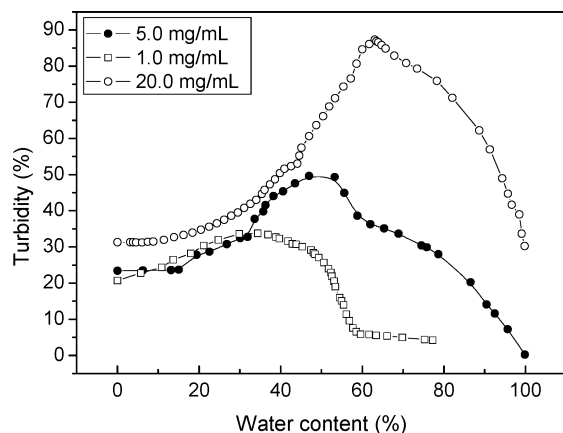
Figure 2. Plot of the turbidity of PEO_{45}-b-$PTMSPMA_{59}$ in methanol against the water contents. The initial copolymer concentrations in methanol are 1.0, 5.0, and 20.0 mg/mL.

2.1. Vesicle Formation upon Preparative Conditions. 2.1.1. Effect of Water Content.

The composition of binary solvents has been shown to have a great influence on the morphology of the crew-cut micelles as reported in the literature.[3,10] In this section, such an effect was explored for the vesicle formation of PEO-b-PTMSPMA.

Turbidity studies were performed to explore the possible transition of different morphologies during self-assembling with increasing of water content based on PEO_{45}-b-$PTMSPMA_{59}$. We performed this measurement without adding TEA at three different C_{ini}'s in methanol: 1.0, 5.0, and 20.0 mg/mL. Figure 2 shows the turbidity against the weight fractions of water at ambient temperature. All the three curves show a similar evolution trend, i.e., having a maximal turbidity value and some inflections as the water content increases. As indicated by the appearance of turbidity in the solution, the aggregations of the block copolymers generally occurred at ca. 20 wt % water content. Further addition of water into methanol led to the turbidity increasing gradually, implying the transformation of the micelle structure or the size increase of the micelles. Then the turbidity declined after reaching the maximum as the water content reached some level, possibly due to the decrease of the micelle concentrations or the sizes.

For the curve at 5.0 mg/mL of C_{ini}, there are two obvious jumps at ca. 16 and 32 wt % water, respectively. The latter step corresponded to the vesicle formation as indicated by transmission electron microscopy (TEM) analysis shown below. At 1.0 mg/mL of C_{ini}, it was a relatively smooth curve over the entire range of water contents. The turbidity increased gradually as the water content increased then declined at ca. 35 wt %. For 20.0 mg/mL of C_{ini}, only one slight jump appeared at 44 wt % water. The maximum appeared at ~65 wt % water, which was higher than the other two cases.

TEM studies based on two diblock copolymers, PEO_{45}-b-$PTMSPMA_{59}$ and PEO_{45}-b-$PTMSPMA_{42}$, were performed to examine the effect of water contents on the morphological development. Water was added dropwise into the polymer solution of 5.0 mg/mL in methanol with vigorous stirring. TEA (0.4 wt %) was added 5 h later to fix the shape by the gelation. The morphology of the hybrid particles was examined by TEM several days later.
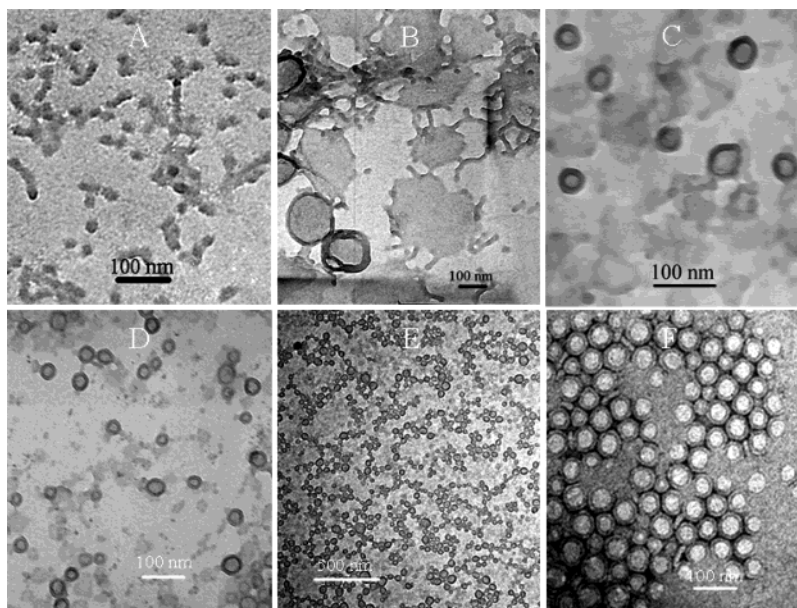
Illustrated in Figure 3 were the TEM images of the gelated aggregates prepared at different water contents
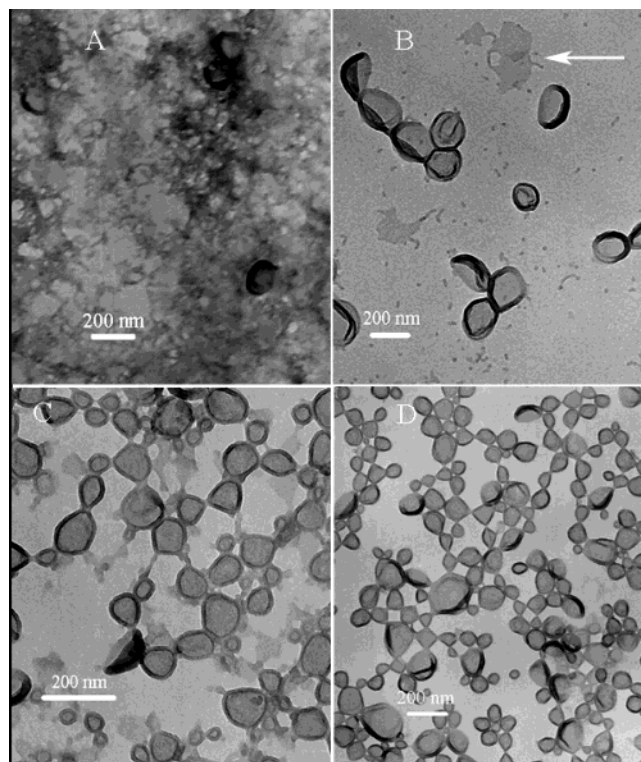
Figure 3. TEM images of the gelated polymer micelles from PEO_{45}-b-$PTMSPMA_{59}$ at different water contents in the solvent mixture. The initial copolymer concentration in methanol is 5.0 mg/mL. (A) irregular objects and few vesicles, 31.3 wt %; (B) vesicles, coexisted with spheres and lamellae with some protruding rods, 33.6 wt %; (C) vesicles, 38.7 wt %; (D) vesicles, 48.7 wt %. TEM images of vesicles at higher water contents are not presented.

for PEO_{45}-b-$PTMSPMA_{59}$ diblock copolymer. The morphological transition points agreed with the turbidity study. Exclusive vesicles were observed from ca. 40 to 98.4 wt % water content. A few vesicles that coexisted with spheres, rods, and lamellae were found at 33.6 wt % water content. It was of note that it was difficult to find recognizable particles in the TEM window when the water content was less than 30 wt %.

Figure 4A–E shows the aggregates after gelation at different water contents when PEO_{45}-b-$PTMSPMA_{42}$ diblock copolymer was used as the precursor. A more obvious effect of the water content on the morphological change was observed compared with that of PEO_{45}-b-$PTMSPMA_{59}$. As shown in Figure 4A, spheres coexisted with some short rods at 31.3 wt % water. The diameter of the spheres was 19 ± 1 nm, the same as the rod diameter. When slightly increasing water to 33.6 wt %, the lamellae appeared and coexisted with some protruding rods and separated rods, as shown in Figure 4B. At this point, the vesicles emerged. One may notice the diameter of rod is the same as the wall thickness of vesicle (20 ± 2 nm), slightly thicker than the wall thickness (~16 nm) of vesicles that formed at higher water content. Apparently, this figure had captured the transition intermediate, i.e., from the rods, the lamellae, to the vesicles. The content of vesicles became more at 38.7 wt % water; however, the lamellae could still be found (Figure 4C). From 48.7 wt % water content, exclusive vesicles were obtained, as demonstrated in Figure 4D,E. Up to 98.4 wt % water, the vesicles were still obtained exclusively (TEM images not shown). Compared with PEO_{45}-b-$PTMSPMA_{59}$, it appeared that

Figure 4. TEM images of the gelated polymer micelles from PEO_{45}-b-$PTMSPMA_{42}$ at different water contents. The initial copolymer concentration in methanol is 5.0 mg/mL. (A) spheres, coexisted with few rods, 31.3 wt %; (B) lamellae with protruding rods and a few vesicles, 33.6 wt %; (C) vesicles and lamellae, 38.7 wt %; (D) vesicles, 48.7 wt %; (E) vesicles, 55.8 wt %; (F) vesicles in (E) stained with uranyl acetate for 8 min. TEM images of vesicles at higher water contents are not presented.
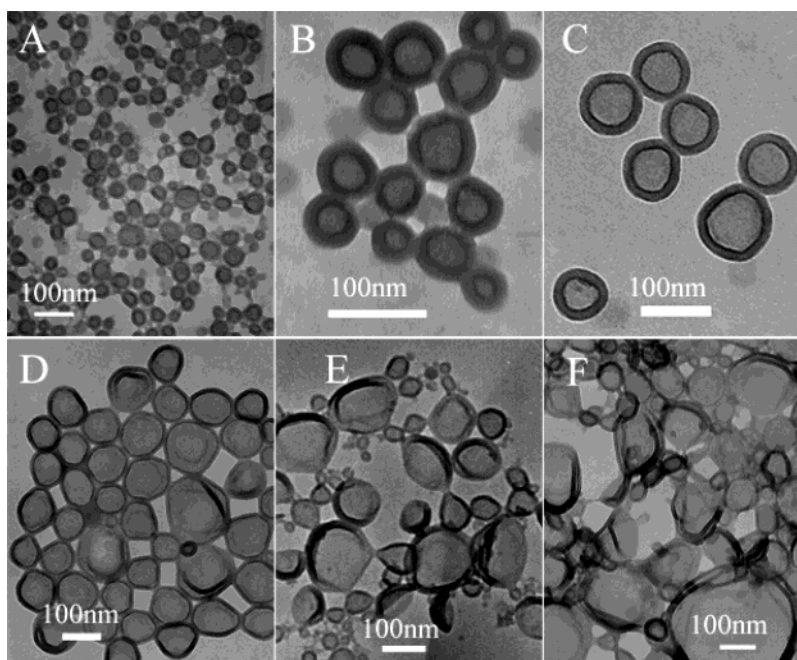
Figure 5. TEM images of the gelated vesicles prepared from PEO_{45}-b-$PTMSPMA_{59}$ at different initial copolymer concentrations in methanol (the water content is 55.8 wt %). (A–F) 0.1, 0.5, 1.0, 2.0, 5.0, and 10.0 mg/mL in methanol. TEM image of vesicles from C_{ini} = 20 mg/mL are not presented.

longer PTMSPMA was favorable for the vesicle formation. The diameters of vesicles from PEO_{45}-b-$PTMSPMA_{42}$ decreased gradually from 52 ± 8 to 38 ± 9 nm when the water content increased from 43.1 to 98.4 wt % (Figure S1 in the Supporting Information). The wall thickness is ca. 12 nm and remains constant for the vesicles under all conditions.

One vesicle sample (Figure 4E) was further stained with saturated uranyl acetate ethanol solution, as illustrated in Figure 4F. The boundary between the outer dark loop and the wall was very clear, so was the boundary between the inner void and the wall. The thickness of the wall was 15.7 ± 1.1 nm, ~4.0 nm thicker than that of the unstained ones. This result was

expected because the cross-linked walls were covered by the PEO layer as well as some free −SiOH groups, which have been stained by uranyl acetate.

2.1.2. Effect of the C_{ini}. The effects of C_{ini} on the vesicle formation were explored by varying the C_{ini} over a broad range, while the water content was kept constant at 55.8 wt % and the TEA concentration for gelation was 0.4 wt %. Illustrated in Figure 5 were the TEM images of the vesicles prepared from PEO_{45}-b-$PTMSPMA_{59}$ at the C_{ini} = 0.1, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 mg/mL in methanol after adding TEA. Exclusive vesicles were produced at all the C_{ini}'s used. The size of the vesicles at low C_{ini} was relative smaller, and the size distribution was narrower. The quality of the

vesicle walls in the TEM images was better when the C_{ini} was higher than 0.5 mg/mL. For example, as shown in Figure 5C, the high-quality vesicles with a narrow size distribution were obtained at 1.0 mg/mL of C_{ini}, and their diameters were ~90 nm. The average vesicle sizes increased with the C_{ini}, whereas the polydispersities were broadened correspondingly. The contour became irregular for the larger vesicles due to the collapse of the vesicles out of solution during TEM analysis. The larger the vesicles were, the more likely they collapsed. However, the wall thickness was uniform (around 16 nm), as a character of the bilayer polymer vesicles through self-assembly. Figure S2 (in the Supporting Information) shows the dependence of the mean size and the wall thickness of the vesicles on the C_{ini}.

2.1.3. Effect of PTMSPMA Block Length. In general, the highly asymmetric composition is a precondition for a coil−coil block copolymer to form the vesicles in selective solvents for the short block.[9,10] So far, we have demonstrated that PEO$_{45}$-*b*-PTMSPMA$_{42}$ and PEO$_{45}$-*b*-PTMSPMA$_{59}$ could form vesicles under a variety of conditions. In this part, the degree of polymerization of TMSPMA other than 42 and 59, i.e., 29 and 180, were examined whereas the PEO blocks remained the same. To prepare micelles, the C_{ini} in methanol was 2.0 mg/mL for PEO$_{45}$-*b*-PTMSPMA$_{29}$, and the C_{ini} was 1.0 mg/mL for PEO$_{45}$-*b*-PTMSPMA$_{180}$. The water content was 55.8 wt %, and TEA concentration for gelation was 0.4 wt %.

TEM analyses have shown that exclusive vesicles were obtained for the block copolymers with the short and the long TMSPMA blocks under the conditions applied. In comparison with the results of PEO$_{45}$-*b*-PTMSPMA$_{42}$ and PEO$_{45}$-*b*-PTMSPMA$_{59}$, the wall thickness of the vesicles increased from 11.4 to 12.2, 16.9, and 21.7 nm as the degrees of polymerization of TMSPMA increased from 29 to 42, 59, and 180. This observation is consistent with the bilayer structure of vesicles. Therefore, to adjust the length of PTMSPMA block is an efficient way to control the wall thickness of vesicles. The vesicle diameters from four samples were 45 ± 3, 49 ± 13, 127 ± 34, and 62 ± 8 nm.

2.1.4. Effect of Gelation Conditions. The vesicles of PEO-*b*-PTMSPMA formed spontaneously once water was added. However, the vesicles in this stage were soft due to the low glass transition temperature of PTMSPMA, and it was difficult to keep their shapes in dryness.[24] Once the gelation catalyst was added, a stable hollow structure with high quality was obtained. It is known that the gelation of −Si(OCH$_3$)$_3$ groups may occur even without the catalyst. Therefore, the reactive groups in the vesicle walls should be hydrolyzed progressively in a methanol/water mixture. Hence, there is a possibility that the polarity of the hydrolyzed blocks switches from the hydrophobic to the hydrophilic. If this process happened, the vesicles would have been disappeared. It is necessary to examine the time interval after the vesicle formation but before the addition of the catalyst. Since the acid is also a catalyst of gelation, we have also tried to fix the vesicles using some acids as catalysts. The diblock copolymer used was PEO$_{45}$-*b*-PTMSPMA$_{59}$, unless specified otherwise. The C_{ini} in methanol was 5 mg/mL, and the water content was at 55.8 wt %.

The TEM results demonstrated that the time to add TEA after vesicle formation showed no difference within the initial 5 h. However, the mean diameter and the wall thickness were all increased slightly if the time was over 1 day (Figure S3 in the Supporting Information). It can be explained by the partial hydrolysis of −Si(OCH$_3$)$_3$ groups in the aqueous media. The hybrid vesicles were formed after 1 month even without catalyst, unlike the soft vesicles newly formed without the addition of TEA. In an extreme case, a vesicle solution prepared from PEO$_{45}$-*b*-PTMSPMA$_{42}$ has been left more than 1 year in the absence of catalyst (Figure S4 in the Supporting Information). This result indicates that the vesicles can be fixed by the gelation even without catalyst because the polycondensation occurs quickly once the partial hydrolysis happens.

Once TEA was added after the vesicles formed for several hours, the hybrid vesicles could be observed easily by TEM. No difference had been found in terms of the sizes and wall thickness of the vesicles regardless the time of TEM analysis. It seems that the quality of the TEM image of the vesicles with shorter gelation time was not as good as those with longer gelation time. This might be owing to the lower cross-linking degree of the vesicle walls in a short time. The concentrations of TEA showed no obvious effect on the gelated vesicles as studied by TEM, either. (Figure S5 in the Supporting Information).

A small amount of acid such as hydrochloric acid, trifluoroacetic acid, or acetic acid was added into the vesicle solution. However, the characteristic blue tint of the vesicle solution disappeared quickly; instead, insoluble gels were obtained. Only a trace of acetic acid (pH is very close to 7 in the final solution) was needed to obtain an unsoiled hybrid vesicle (see Supporting Information for details). This result was very different from that of TEA, which works well to fix the vesicle morphology. In general, both acidic and alkali catalysts are effective for the hydrolysis and polycondensation of −Si(OCH$_3$)$_3$, but the catalytic mechanisms are different. The acid catalyzes the hydrolysis quickly while relatively slowly for the polycondensation and may switch the polarity of PTMSPMA blocks from the hydrophobic to the hydrophilic. The vesicular morphologies would be destroyed due to the rapid hydrolysis before the polycondensation process starts; as a result, macroscopic gelation happened. However, the hydrolysis reaction catalyzed by the base is slower whereas the polycondensation is faster. Once the partial hydrolysis reaction occurred in the PTMSPMA domain, the polycondensation would proceed simultaneously. As a result, the vesicle structure was remained and became more stable after the gelation process.

2.2. Stability of the Hybrid Vesicles. The gelated vesicles in solution are very stable, and no change has been observed after the preparation for over 1 year. If the hybrid vesicle solution was diluted with water to 0.001 mg/mL and then followed by a sonication process for half an hour, neither the size nor the morphology change was observed by TEM. Such shape persistence apparently owes to the gelation process, which has led to the cross-linked polysilsesquioxane within the vesicle walls. This is different dramatically from the vesicles without gelation, as discussed in the previous section. Furthermore, the polysiloxane structure also possesses another unusual property, i.e., the shape-persistent at high temperature. After calcination at 450 °C for 7 h in air, the morphology showed no change except less shrinkage in the volume of vesicle, which was related to the decomposition of the organic PEO chains.
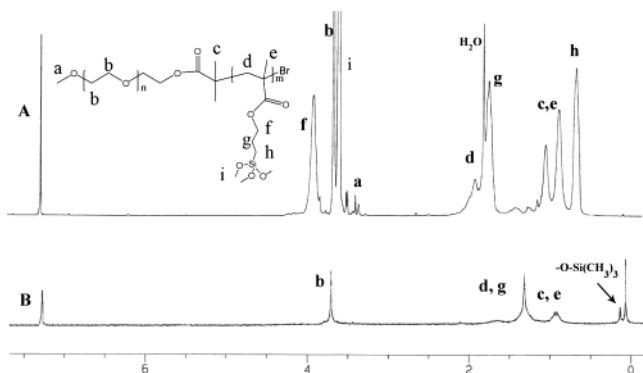
Figure 6. ^{1}H NMR spectra in CDCl$_3$: (A) PEO-*b*-PTMSPMA diblock copolymer; (B) the capped vesicles.

However, the dried hybrid vesicles cannot be redispersed neither in water nor other polar media, suggesting that the intervesicle coupling has occurred during the period of dryness. This result is expected since not all the active −SiOH groups have been consumed completely during the gelation process in the solution. The PEO corona prevents such intervesicle interaction in solution successfully but fails in the absence of solvents. When the free −SiOH groups were capped by a termination reagent, e.g., methoxytrimethylsilane, and then further terminated by a more effective termination reagent, chlorotrimethylsilane, the soluble solid vesicles were obtained. Shown in Figure 6B is the ^{1}H NMR spectrum of the vesicles being capped. Compared in Figure 6A is the ^{1}H NMR spectrum of the block copolymer precursor, from which we found that all of protons assigned to −(C*H*$_2$)$_3$−Si(OC*H*$_3$)$_3$ groups disappeared while the protons assigned to PEO block still remained unchanged. The peaks assigned to the backbone of the PTMSPMA chain were highly broadened and nearly disappeared, indicating far less mobility of these polymer chain segments. The monomodal peak at δ 0.1 ppm was assigned to −OSi(C*H*$_3$)$_3$, which came from the capping reagent.

2.3. Formation Mechanism of the Vesicles. From the above studies, we have found the vesicles evolving from the lamellae as the water content in the binary solvent increases. In the literature, the morphological transition of the crew-cut micelles based on the PS-*b*-PAA diblock copolymers follows the order of spheres, sphere and rod mixtures, rods, rod and vesicle mixtures, and pure vesicles as the water content in a binary mixture solvent (water/dioxane) increases.[4,26] It is clear that our vesicles are developed from the enclosure of the lamellae. Pure hybrid vesicles are formed over a wide range of the water contents. In general, our results are consistent with the reported results in the literature. However, neither pure spheres nor rods were obtained exclusively under the present conditions.

It should be mentioned that the present block copolymers with various composition could form vesicles very easily. Actually, the vesicles have been obtained for the block copolymers with short core-forming block relative to the long corona-forming block, i.e., PEO$_{45}$-*b*-PTMSPMA$_{29}$. This is different from the requirement of highly asymmetric composition (short hydrophilic block forms the corona) for the vesicles based on PS-*b*-PAA and PS-*b*-PEO reported in the literature.[6,10b] Considering the coil−rod block copolymers may self-assemble into the vesicles as well and the asymmetry requirement appears not necessary,[11,12] we assume the

PTMSPMA polymer may have a wormlike conformation due to its bulky side groups. The interfacial curvature between the core and the corona of the aggregates in solution would be small enough to form the vesicles in bilayer structure. Moreover, the PTMSPMA is a medium hydrophobic polymer, and its glass transition temperature is lower than room temperature.[27] During the self-assembly process, PTMSPMA blocks in the core are likely to be swollen by the solvent mixture of methanol and water. Such a factor could also help the vesicle formation.[28] On the contrary, it is not easy to find the conventionally spherical star micelles for this family of block copolymers, PEO$_{45}$-*b*-PTMSPMA$_x$, over a range of conditions attempted, even in the other common solvents (unpublished results).

The bilayer vesicles consist of the orderly aggregated blocks with the solvated PEO blocks stretching toward both sides of the wall, whereas the gelation occurred exclusively in the PTMSPMA phases in the presence of the catalyst. Because of the protection of the PEO corona, the macroscopic gelation was avoided effectively.[29] As a result of gelation in the walls, the hybrid vesicles were not the aggregates composed of many polymer chains anymore but the hollow microgels in nanoscale. The outer and the inner surfaces of the vesicles were covered with PEO chains that chemically attached to the surfaces. Obviously, there is a solvent pool enclosed by the nanowall of the hybrid vesicle. Scheme 1 shows the structure of the nanocapsule.

3. Experimental Section

3.1. Materials. The diblock copolymers were synthesized by ATRP of TMSPMA monomer using poly(ethylene oxide) methyl ether 2-bromoisobutyrate (PEO-Br) as macroinitiator. The detailed kinetic studies and synthetic procedure of the block copolymers were described elsewhere.[30] Triethylamine (TEA; >99%, Beijing Chemical Reagent Co.) was dried over KOH. Anhydrous methanol (>99%, Beijing Chemical Reagent Co.) and double distillated water were used directly. Chlorotrimethylsilane (Me$_3$SiCl; >98%, Beijing Chemical Reagent Co.) was used after distillation. Methoxytrimethylsilane (Me$_3$SiOCH$_3$) was obtained by the reaction of Me$_3$SiCl with anhydrous methanol in the presence of equal molar of TEA. Other reagents used as purchased.

3.2. Characterization. To prepare the samples for transmission electron microscope (TEM) analysis, a micelle solution (2−10 μL) was dropped onto a carbon-coated copper grid and left until dry. TEM images were obtained using a JEM 100 instrument operated at 100 kV. To obtain a scanning electron microscope (SEM) image, the micelle solution (5 μL) was placed onto the surface of a silica wafer and left until dryness. It was coated with platinum and viewed by a Hitachi S-4300 electron microscope operated at 15 kV. The images were recorded by a digital camera. Turbidity measurements were performed on a UV-1601PC UV−vis spectrophotometer (Shimadzu) using a UVPC Personal Spectroscopy Software (version 3.91). ^{1}H NMR spectra were recorded on a Bruker DMX300 spectrometer with CDCl$_3$ as solvent at room temperature.

3.3. General Procedures for the Vesicle Preparation and Gelation. To prepare vesicles, PEO-*b*-PTMSPMA (10.0 mg) was dissolved in methanol (2.0 mL), and then water (2.0 mL) was added dropwise by syringe at a rate of 1 drop every 10 s under vigorous stirring. After 5 h, TEA (40.0 μL) was added to induce the hydrolysis and polycondensation within micelles.

3.4. Capping the Free SiOH Groups in Vesicles. Vesicles (∼20 mg in 20 mL of water/methanol) were stirred for 48 h after the addition of TEA, and then Me$_3$SiOCH$_3$ (∼100 μL) was added and stirred for 2 days to terminate free −SiOH groups on the surface of vesicles preliminarily. Then the vesicle solution was concentrated to ∼5 mL, and then anisole (20 mL)

was added to extract vesicles. The organic phase was collected and dried over anhydrous Na_2SO_4. Me_3SiCl ($\sim$100 μL) was added to further terminate the residual free $-SiOH$ groups. The solid product was obtained after removing the solvents and extra Me_3SiCl under vacuum. The product can be dissolved in $CDCl_3$ for NMR analysis.

3.5. Turbidity Study. The polymer was first dissolved in methanol, and then quantitative water was added gradually into the sample cell. After stirring for several minutes, which was long enough for the micelle stabilization, the sample was scanned from a wavelength of 400−800 nm. The transmittance (*T*) data at 650 nm were collected for the turbidity analysis because the adsorption is the lowest for both the polymer and the aggregate solutions. The turbidity data were obtained from *T* data, i.e., 100 − *T*%. Methanol was used as the reference for all the measurements.

4. Conclusion

A simple approach to prepare organic/inorganic hybrid nanocapsules has been developed. It is based upon the gelation of the polymer vesicles preformed by self-assembly of the reactive block copolymers, PEO-*b*-PTMSPMA, in a binary solvent mixture of methanol and water. Detailed conditions for the vesicle formation were explored for PEO$_{45}$-*b*-PTMSPMA$_{59}$. It demonstrates that the hybrid vesicles can be formed exclusively over a wide range of water contents in the mixed solvent. Spheres, rods, and lamellae as the coexisting morphologies were observed at lower water contents. The formation of the vesicles was believed to be the closure of the lamellae. Exclusive vesicles were also obtained for the initial polymer concentrations ranging from 0.1 to 20 mg/mL when the water content was kept at 55.8 wt %. However, high initial polymer concentration would lead to the vesicles in large size with a broader size distribution. TEA was found to be a good catalyst for the gelation reaction while the gelation with acid failed to keep the vesicular structure. The block copolymers with the same PEO block length while different PTMSPMA lengths; i.e., 29, 42, 59, and 180 may also produce the vesicles. The hybrid hollow particles are stable against the environmental changes due to the cross-linked polysilsesquioxane structure in the vesicle walls once the gelation occurs.

The vesicles reported in this paper possess the following novelties: (1) the vesicles are produced by self-assembling of an amphiphilic block copolymer bearing reactive trimethoxysilane groups along one block in a solution; (2) the simple gelation in the wall of the preformed vesicles can stabilize the vesicle permanently; (3) the product is soluble, which will benefit further characterizations and applications; (4) water is the medium for vesicle formation, and the products composed of PEO and polysilsesquioxane can be made biocompatible. These shape-persistent nanocapsules will also become a scaffold to stimulate further research on the preparation and application of nanomaterials. The robust hollow nanoparticles may find applications not only in encapsulation and release just like other types of polymer vesicles but also in encapsulation uses for high-temperature application.

Supporting Information Available: Figures S1−S5 and the experimental observations when acid was used as the catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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