

# Preparation of Organic/Inorganic Hybrid Nanomaterials Using Aggregates of Star Block Copolymer Consisting of Poly(stearyl methacrylate) and Poly(3-(trimethoxysilyl) propyl methacrylate) as Precursor

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**ABSTRACT:** A series of star block copolymer consisting of poly(stearyl methacrylate) and poly(3-(trimethoxysilyl)propyl methacrylate) was synthesized via atom transfer radical polymerization technique. The resultant polymers were characterized by gel permeation chromatography and  $^1\text{H}$  NMR. The copolymer can self-assemble into the aggregates in selective solvents, the resulting aggregates can be used as precursor to prepare hybrid nanomaterials

conveniently via the hydrolysis reaction of  $-\text{Si}(\text{OCH}_3)_3$  groups and the condensation reaction of  $-\text{Si}(\text{OH})_3$  groups. Moreover, the effect of the star copolymer-solvent interaction on the aggregation behavior was also discussed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2010–2016, 2008

**Key words:** star polymer; hybrid nanomaterial; self-assembly

## INTRODUCTION

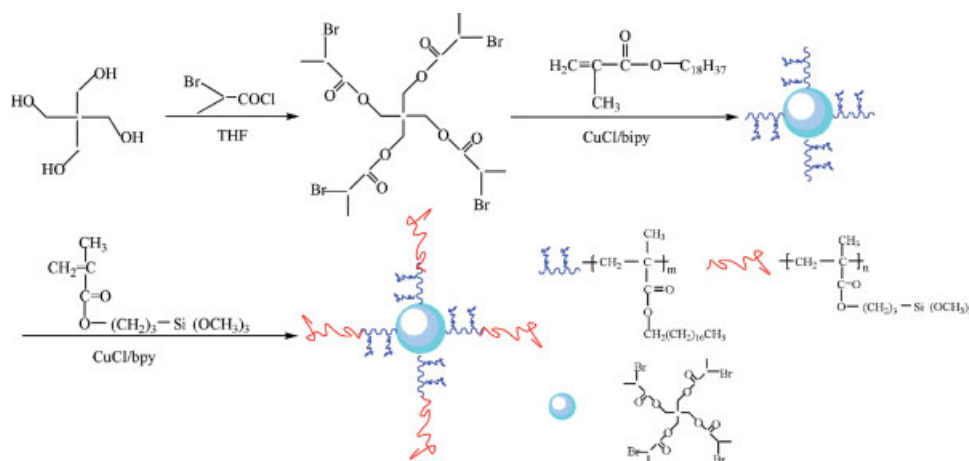
Organic/inorganic hybrid nanomaterials (one kind of novel functional materials) are of considerable interest since their unique microstructures are composed of organic and inorganic moieties in one single material at nanoscopic level, therefore, they possess special characteristics and have potential appliance foreground such as optical materials, biomaterials, catalyst, and so on.<sup>1–5</sup> It has been reported to date that a large number of methods can be used to prepare these organic/inorganic hybrid nanomaterials.<sup>6–8</sup> As one of significant methods mentioned above, one molecule bearing hydrolysable trimethoxysilane groups can be used as precursor for the preparation of hybrid nanomaterials by the sol-gel procedure at ambient temperature.<sup>9,10</sup> For instance, Chen et al. had reported that a novel amphiphilic diblock copolymer, poly(ethylene oxide)-*b*-poly[3-(trimethoxysilyl) propyl methacrylate], containing reactive trimethoxysilane groups in one segment, was used as precursor of hybrid vesicles to prepare hybrid hollow particles based on the hydrolysis and polycondensation reactions within the polymeric vesicles in a selective solvent.<sup>11</sup> In our previous study, a multi-block copolymers containing organoferrocenyl (Fc) units, poly[3-

(trimethoxysilyl) propyl methacrylate]-*b*-poly(stearyl methacrylate)-ferrocene-poly(stearyl methacrylate)-*b*-poly[3-(trimethoxysilyl) propyl methacrylate], was also used as precursor to prepare various morphological hybrid materials.<sup>12</sup> However, to our knowledge, while some studies have been reported on the preparation of organic/inorganic hybrid nanomaterials using the aggregates of linear block copolymer as precursor, few have been performed on those using the aggregates of star block copolymers as precursor.

Compared with the corresponding linear block copolymers, star block copolymers with chemically different arms exhibit various properties and functions. They possess unusual molecular architectures that more than two different types of polymers converge together at a single junction. These novel copolymers present a promising system for studying highly branched polymeric architectures and can be applied in many areas such as drug delivery systems, lubricant nanomaterials and so on.<sup>13–15</sup>

Star-typed hybrid nanomaterials may have better hydrodynamic properties and higher degree of chain end functionality compared with the corresponding linear hybrid nanomaterials,<sup>16</sup> may be therefore of great interest for emerging nanomaterials and nanotechnologies. Many groups have taken their efforts to prepare such nanomaterials, but few examples that we have ever known are successfully reported due to the difficulties of synthesis and characterization of these precursors.

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**Scheme 1** Synthesis procedure of S-(PSMA-*b*-PTMSPMA)<sub>4</sub>. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

With these characteristics in mind, a novel star polymer with four arms is designed. It is composed of the hydrolysable block bearing trimethoxysilane groups, poly[3-(trimethoxysilyl) propyl methacrylate], and the brush-type block, poly(stearyl methacrylate). It is first used as precursor to prepare various morphological hybrid nanomaterials by the hydrolysis reaction of  $-\text{Si}(\text{OCH}_3)_3$  groups and the condensation reaction of  $-\text{Si}(\text{OH})_3$  groups within the polymeric aggregates in selective solvents. Finally, the effect of the star copolymer-solvent interactions on these aggregations is discussed.

## EXPERIMENTAL

### Materials

3-(trimethoxysilyl) propyl methacrylate (TMSPMA) from Wuhan University Silicon New Material was dried over  $\text{CaH}_2$  overnight.<sup>12</sup> Stearyl methacrylate (SMA) from Shanghai No.1 Chemical Reagent Factory was treated according to the literature method.<sup>17</sup> 2,2-Bipyridyl (bipy), an analytical reagent, was used as obtained from Shanghai No.1 Chemical Reagent Factory. Copper(I) chloride ( $\text{CuCl}$ , AR grade) was purified by stirring in acetic acid, washed with methanol, and then dried under reduced pressure. Pentaerythritol tetrakis(2-bromo-isobutyrate) (PT-Br) was synthesized according to the literature method.<sup>18</sup> All other reagents were of analytical grade and used as received.

### Synthesis of star-shaped macroinitiator[S-(PSMA-Br)<sub>4</sub>] by atom transfer radical polymerization

$\text{Cu}(\text{I})\text{Cl}$  (10.0 mg; 0.10 mmol), bipy (31.20 mg; 0.20 mmol), PT-Br (17.00 mg; 0.025 mmol), SMA (5.0 g; 14.80 mmol), and anisole (6.0 mL) were added to a 50-mL dried Schlenk flask containing a magnetic stir

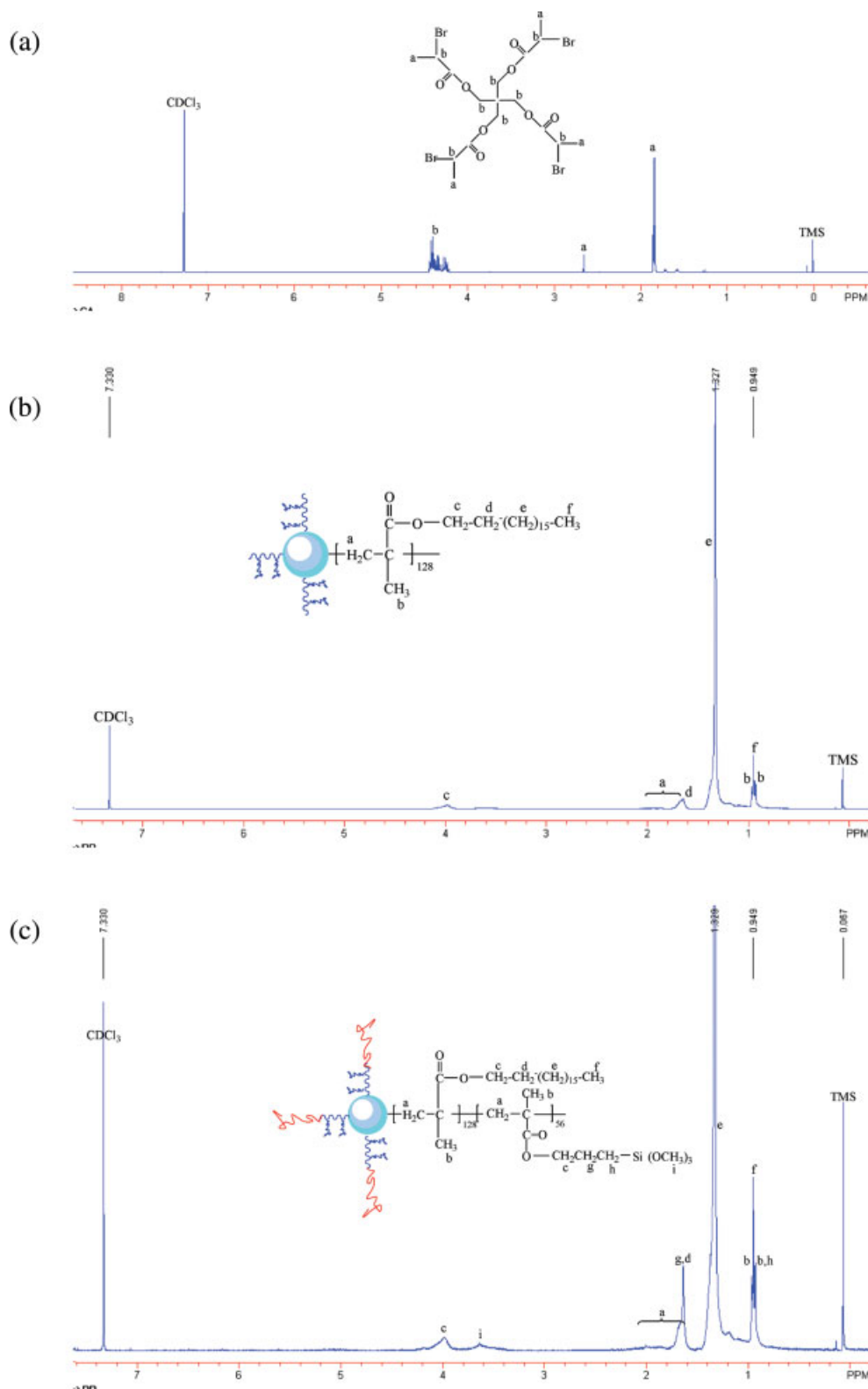
bar. The flask was degassed by three freeze-vacuum-thaw cycles, and then immersed in an oil bath thermostated at  $90^\circ\text{C}$ . After 10 h, the flask was taken away from the bath and the reaction mixture was cooled to slow the polymerization, and then anhydrous THF was added to dilute the polymer solution. The solution of crude product was transferred into a neutral alumina column by a syringe to remove the catalyst. The excess THF was evaporated under reduced pressure and the polymer was precipitated in anhydrous ethanol two times to remove the unreacted monomer and anisole.

### Synthesis of four-armed star-block copolymers [S-(PSMA-*b*-PTMSPMA)<sub>4</sub>]

In a typical synthesis, bipy,  $\text{Cu}(\text{I})\text{Cl}$ , S-PSMA-Br (8 : 4 : 1 in molar ratio), TMSPMA with a certain molar ratio and some anisole were added to a dry tube. The tube was degassed by three freeze-vacuum-thaw cycles to remove the oxygen. Then the tube was sealed and placed in a thermally regulated oil bath at  $90^\circ\text{C}$ . After a certain period of polymerization, the tube was removed from the oil bath and allowed to cool for a few minutes. Several milliliters of  $\text{CHCl}_3$  were added to the tube, and the mixture was placed for a period of time at room temperature to complete the dissolution of the polymer. The resulting solution was passed through a short column on neutral aluminum oxide to remove most of the Cu complex. The excess  $\text{CHCl}_3$  was evaporated under the reduced pressure, the product was precipitated from a large amount of anhydrous ethanol, filtered, and dried under vacuum to constant weight.

### Preparation of organic/inorganic hybrid nanomaterials

Hybrid nanomaterials were prepared using aggregates from star block copolymer as precursor. The



**Figure 1**  $^1\text{H}$  NMR spectrum of PT-Br (A), S-(PSMA<sub>128</sub>)<sub>4</sub> (B), and S-(PSMA<sub>128</sub>-b-PTMSPMA<sub>56</sub>)<sub>4</sub> (C). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

influences of the solvent composition ( $W_{\text{THF}}/W_{\text{ethanol}}$ : from 95/5 to 60/40) and the copolymer composition on the morphologies were investigated. To prepare

the self-assembly solution, anhydrous ethanol, as a precipitant, was added to the copolymer solution in THF at a rate of 0.5 wt % per minute with vigorous

TABLE I  
Molecular Weight and Molecular Weight Distribution of the Polymers

Polymer	$M_n^a$ (g/mol)	$M_w/M_n^a$	Polymer composition
S-(PSMA-Br) <sub>4</sub>	$4.41 \times 10^4$	1.67	S-(PSMA <sub>128</sub> -Br) <sub>4</sub>
S-(PSMA- <i>b</i> -PTMSPMA) <sub>4</sub> -1	$5.80 \times 10^4$	1.79	S-(PSMA <sub>128</sub> - <i>b</i> -PTMSPMA <sub>56</sub> ) <sub>4</sub>
S-(PSMA- <i>b</i> -PTMSPMA) <sub>4</sub> -2	$4.62 \times 10^4$	1.76	S-(PSMA <sub>128</sub> - <i>b</i> -PTMSPMA <sub>9</sub> ) <sub>4</sub>

S-(PSMA-Br)<sub>4</sub> polymerization conditions:  $n_{\text{SMA}}/n_{\text{PT-Br}}/n_{\text{CuCl}}/n_{\text{Bipy}} = 14.80 \text{ mmol} : 0.025 \text{ mmol} : 0.10 \text{ mmol} : 0.20 \text{ mmol}$  at 90°C in 6.0 mL of anisole solution for 10 h. S-(PSMA-*b*-PTMSPMA)<sub>4</sub>-1 polymerization conditions:  $n_{\text{TMSPMA}}/n_{\text{S-(PSMA-Br)}_4}/n_{\text{CuCl}}/n_{\text{Bipy}} = 12.0 \text{ mmol} : 0.01 \text{ mmol} : 0.04 \text{ mmol} : 0.08 \text{ mmol}$  at 90°C in 2.0 mL of anisole solution for 11 h. S-(PSMA-*b*-PTMSPMA)<sub>4</sub>-2 polymerization conditions:  $n_{\text{TMSPMA}}/n_{\text{S-(PSMA-Br)}_4}/n_{\text{CuCl}}/n_{\text{Bipy}} = 16.0 \text{ mmol} : 0.02 \text{ mmol} : 0.08 \text{ mmol} : 0.16 \text{ mmol}$  at 90°C in 6.0 mL of anisole solution for 11 h.

<sup>a</sup>  $M_n$  determined by GPC.

stirring. The final polymer concentration of the above solutions was maintained at 0.05 wt %.

After 3 h, triethylamine (TEA) as the catalyst (0.1 wt %) was added to the above solutions to induce the hydrolysis and condensation reactions of the star block copolymers. The solutions were stirred at room temperature for 5 days, thus the organic/inorganic hybrid nanomaterials were obtained conveniently by the sol-gel process.

Samples for TEM measurement were prepared by mounting a drop (ca. 10  $\mu\text{L}$ ) of the above solutions on the carbon-coated Cu grids and air-dried at room temperature before measurement.

### Characterizations

<sup>1</sup>H NMR spectra of polymers were recorded with a 400 MHz AVANCE NMR spectrometer (Model DMX400) in CDCl<sub>3</sub>, using TMS as the standard. The gel permeation chromatography measurements were carried out on a Waters 201 with an  $\mu$ -styragel column and THF as an eluent, and the molecular weight was calibrated with standard PS. TEM micrographs were obtained on a JEOL model 1200EX instrument operated at an accelerating voltage at 160 kV.

## RESULTS AND DISCUSSION

### Synthesis and characterization of PT-Br and star polymer

Synthesis of PT-Br and the synthetic strategy followed for a well-defined S-(PSMA-*b*-PTMSPMA)<sub>4</sub> via the atom transfer radical polymerization (ATRP) route are depicted in Scheme 1.

The chemical structures of PT-Br, S-(PSMA-Br)<sub>4</sub>, and S-(PSMA-*b*-PTMSPMA)<sub>4</sub> were characterized by <sup>1</sup>H NMR spectra, as shown in Figure 1.

The <sup>1</sup>H NMR spectrum of PT-Br shows peaks with following shifts [Fig. 1(A)]: 4.17–4.41 (12H, C—CH<sub>2</sub>—O—C(O)—CH—Br), 2.62, 1.81 (12H, CH(Br)—CH<sub>3</sub>).<sup>18</sup> The NMR spectrum of the product indicates that PT-Br is successfully synthesized.

The <sup>1</sup>H NMR spectrum of S-(PSMA-Br)<sub>4</sub> shows peaks with following shifts [Fig. 1(B)]: 0.88 (3H, in CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>—), 0.86, and 0.90 (3H, in CH<sub>3</sub>C—), 1.20–1.40 (30H, in —(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 1.53–1.66 (2H, in —CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 1.60–2.03 (2H, in —CH<sub>2</sub>C—), 3.84–4.12 (2H, in —OCH<sub>2</sub>—). The NMR spectrum of the product indicates that S-(PSMA-Br)<sub>4</sub> is successfully prepared.

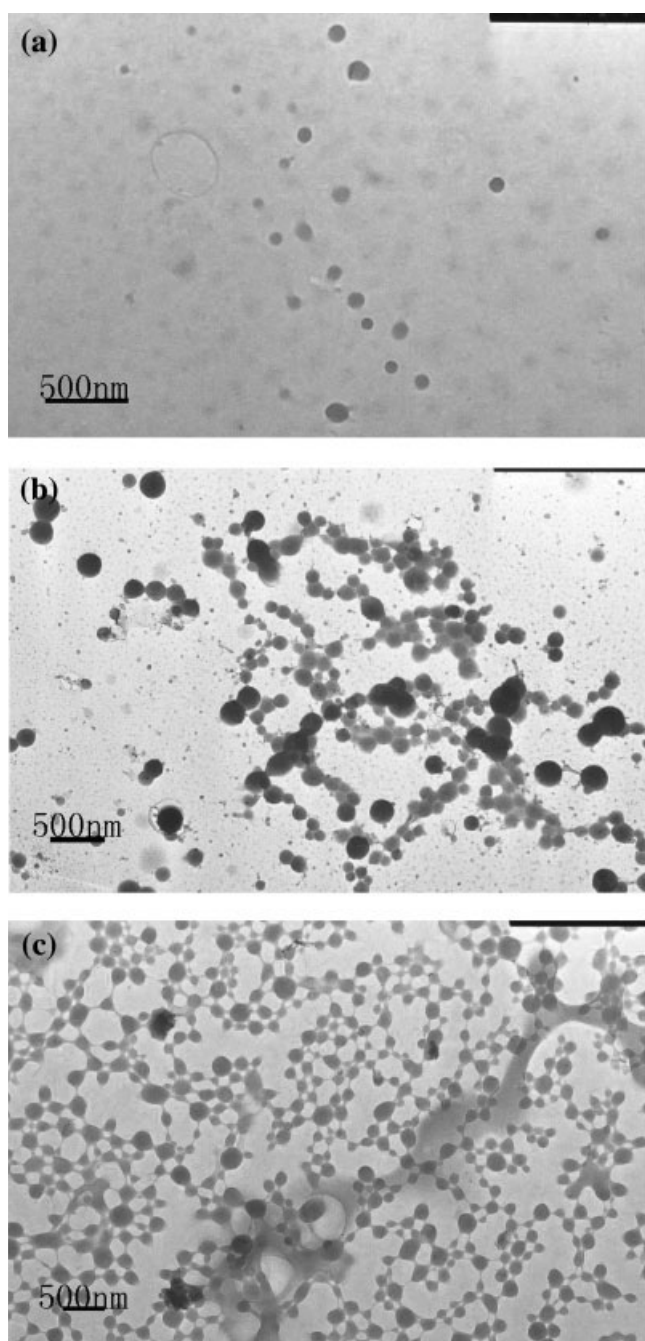
The <sup>1</sup>H NMR spectrum of S-(PSMA-*b*-PTMSPMA)<sub>4</sub> shows peaks with following shifts [Fig. 1(C)]: 0.88 (3H, in CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>—), 0.86, and 0.89 (6H, in CH<sub>3</sub>C—), 1.22–1.34 (30H, in —(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 1.53–1.64 (2H, in —CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>; 2H, in —CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>), 1.60–2.03 (2H, in —CH<sub>2</sub>C—), 3.57 (9H, in —Si(OCH<sub>3</sub>)<sub>3</sub>), 3.84–4.10 (4H, in —OCH<sub>2</sub>—). It is found that there exist SMA moiety and methoxysilyl moiety in the prepared copolymer, so S-(PSMA-*b*-PTMSPMA)<sub>4</sub> is obtained successfully via the ATRP technique.

The molecular weight and molecular weight distribution of the resultant polymers are listed in Table I.

### Preparation of organic/inorganic hybrid nanomaterials using aggregates of star block copolymer as precursor

The novel star block copolymers can form a large number of morphological aggregates in selective solvents. Because the polymer contains reactive trimethoxysilane groups in one block, therefore, the novel organic/inorganic hybrid nanomaterials can be prepared conveniently via the hydrolysis and the condensation reactions within the polymeric aggregates in selective solvents.

It is well-known that the precipitant content plays an important role in the self-assembly process of aggregates as precursor.<sup>19</sup> Illustrated in Figure 2 are typical TEM pictures of hybrid nanomaterials, which are resulted from these aggregates at different ethanol contents. The small hybrid nanoballs with average diameters of about 80 nm are found at ethanol content of 10.0 wt % [Fig. 2(A)]. As ethanol content is raised to 20.0 wt %, besides a few small hybrid



**Figure 2** TEM micrographs of hybrid nanomaterials from  $S\text{-(PSMA}_{128}\text{-}b\text{-PTMSPMA}_{56})_4$  at various ethanol contents at the polymer concentration of 0.05 wt % in THF/ethanol. Ethanol content: (A) 10.0 wt %; (B) 20.0 wt %, and (C) 40.0 wt %.

nanoballs, large hybrid nanoballs are formed [Fig. 2(B)]. With ethanol content further increasing to 40.0 wt %, as shown in Figure 2(C), the number of the large hybrid nanoballs increases although the average radius is still maintained at about 200 nm. Considering the chemical structure of  $S\text{-(PSMA}_{128}\text{-}b\text{-PTMSPMA}_{56})_4$ , the dimension of hybrid nanomaterial is very large. If the polymer chains stretch out in the solution, the diameter of hybrid nanomaterial

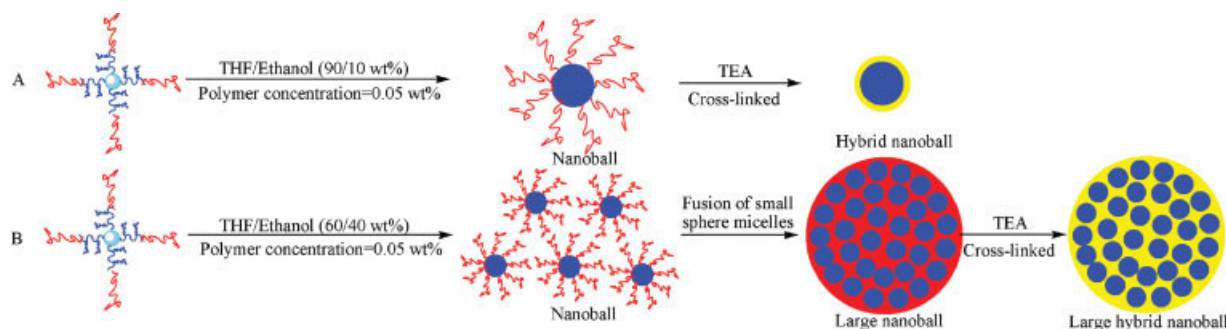
should not exceed  $(128 + 56) \times 0.25 \times 2 \text{ nm} = 92 \text{ nm}$ . Thus, hybrid nanomaterials are not prepared from simple spherical aggregates and may be ascribed to resulting from large compound micelles.

First, the possible mechanism of the morphological transition from small nanoballs to large nanoballs is presented in Scheme 2 according to previous studies.<sup>19,20</sup> It is well-known that the formation of aggregates is controlled by a force balance principally involving three factors, i.e., the stretching (deformation) of the core-forming blocks in the core, the surface tension between the aggregate core and the solvent outside of the core, and the intercorona-chain interactions.<sup>21</sup> In the present system, as ethanol content increases, the solvent become poorer for the PSMA block, so the interfacial energy between the PSMA aggregate core and the solvent must be improved. However, the corona repulsion may have no change since both ethanol and THF are good solvents for the PTMSPMA block. Consequently, small nanoballs should form to reduce the total interfacial energy of this system.

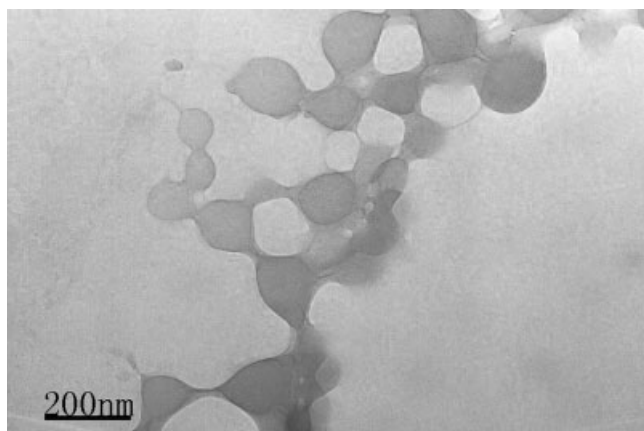
Secondly, it is also known that the increase of ethanol content will lead to the increase in aggregation number because of the increase in the interfacial energy between the PSMA core and the solvent.<sup>20</sup> Moreover, since the PTMSPMA block length is very short, the interactions between the corona chains and the solvent no longer stabilize the small nanoballs. As a result, it results in the formation of large nanoballs by undergoing a secondary aggregation.

After TEA as the catalyst was added into the above self-assembly solutions, the PTMSPMA blocks were transferred into the cross-linked polysilsesquioxane via the hydrolysis and condensation reactions within the polymeric aggregates, so the organic/inorganic hybrid nanoparticles can be prepared conveniently by the sol-gel procedure. Moreover, there are no changes of the morphology of the aggregate before or after gelation. In this case, the hydrolysis reaction catalyzed by the base is slower than the polycondensation reaction.<sup>10</sup> Consequently, the polycondensation reaction within these aggregates proceeds simultaneously once partial hydrolysis occurs in the PTMSPMA blocks.

The copolymer composition has an effect on the morphologies of the aggregates as precursor.<sup>22</sup> As shown in Figure 3,  $S\text{-(PSMA}_{128}\text{-}b\text{-PTMSPMA}_9)_4$  forms small hybrid vesicles with average diameters of 150 nm at the polymer concentration of 0.05 wt % in THF/ethanol W/W 90/10 (Fig. 3). As far as we know, this phenomenon of vesicles is few in the self-assembly of star block copolymers. Moreover, in the same condition,  $S\text{-(PSMA}_{128}\text{-}b\text{-PTMSPMA}_{56})_4$  only yields alone small hybrid nanoballs with average diameters of 80 nm [Fig. 2(A)].

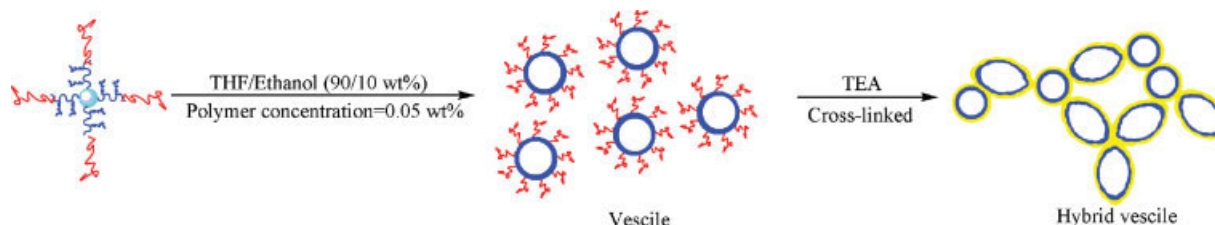


**Scheme 2** Schematic model of hybrid nanomaterials with the increase in ethanol content. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3** TEM micrographs of hybrid nanomaterial from  $S-(\text{PSMA}_{128}\text{-}b\text{-PTMSPMA}_9)_4$  at the polymer concentration of 0.05 wt % in THF/ethanol W/W 90/10.

According to Eisenberg's studies about the aggregates of the linear block copolymer,<sup>22,23</sup> the possible mechanisms of the morphologies obtained from star block copolymers is depicted in Scheme 3. It is well-known that the morphologies of aggregates can be controlled by a balance between three major forces mentioned above. In the present study, the self-assembly procedure of  $S-(\text{PSMA}_{128}\text{-}b\text{-PTMSPMA}_9)_4$  is the same to that of  $S-(\text{PSMA}_{128}\text{-}b\text{-PTMSPMA}_{56})_4$  except for the PTMSPMA block length. Therefore, the intercorona chain repulsion will be more important than other forces when the PSMA block length is constant. With the PTMSPMA block length decreasing,



**Scheme 3** Schematic model of hybrid nanomaterial of  $S-(\text{PSMA}_{128}\text{-}b\text{-PTMSPMA}_9)_4$  as precursor. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the higher intercorona chain repulsion favors the stretching of the core-forming block (PSMA), thus the resulting morphologies of vesicles form to reach the minimum of the energy of the system.

When TEA as a catalyst was added into the solution, the hydrolysis and cross-linking reactions occurred within the corona of each individual vesicle. Because the distance between each individual vesicle is very short, the PTMSPMA chains maybe be cross-linked each other between these vesicles, thus these vesicles adhere together. Moreover, some circular vesicles would change into elliptical ones to adapt the environment because of the existence of some forces between these hybrid vesicles.

## CONCLUSION

In summary, a series of star block copolymers of TMSPMA and SMA were prepared by ATRP in anisole solution. The aggregation behaviours of the resultant copolymers in the THF/ethanol mixtures were investigated. By controlling the solvent composition and the copolymer composition, these various morphologies of aggregates could be prepared. The aggregates can be used as precursors to prepare hybrid nanomaterials conveniently via the hydrolysis reactions of  $-\text{Si}(\text{OCH}_3)_3$  groups and the condensation reaction of  $-\text{Si}(\text{OH})_3$  groups. The convergence of star block copolymers and organic/inorganic hybrid nanomaterial can offer a great opportunity for new materials with unique properties.

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