

# Multiple morphologies of molecular assemblies formed by polystyrene-block-poly[2-( $\beta$ -D-glucopyranosyloxy)ethyl acrylate] in water

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Received (in Montpellier, France) 9th December 1999, Accepted 29th February 2000

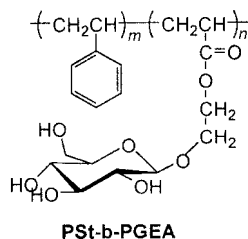
Published on the Web 13th April 2000

A variety of molecular assemblies have been prepared from a new kind of amphiphilic diblock copolymer, polystyrene-block-poly[2-( $\beta$ -D-glucopyranosyloxy)ethyl acrylate] (PSt-b-PGEA). The morphologies include spheres, vesicles, tubules, porous spheres and large compound vesicles. These molecular assemblies are similar in morphology to the so-called "crew-cut" aggregates that have been systematically studied by Eisenberg's group and were prepared in the same manner. The preparation of such molecular assemblies was carried out by first dissolving the copolymer in a common solvent, followed by addition of water to freeze the polystyrene block. The solvents used in this report were *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), dioxane and their mixtures. It has been observed that by changing the solvent, or the solvent mixture, different morphologies can be obtained from a single copolymer, and the transformation of these morphologies can be easily adjusted by changing the composition of the solvent mixture. One typical example is the morphological transitions between tubules and vesicles of PSt<sub>77</sub>-b-PGEA<sub>6</sub>, which is initially dissolved in mixed THF-DMF solvent. These molecular assemblies contain a high density of glucose moieties on the surface, therefore, they may find applications as cellular-specific drug delivery systems or be used as building blocks for highly ordered supramolecular architectures.

It is well known that when AB diblock copolymers are dissolved in a selective solvent, *i.e.* one that solvates only one of the blocks, aggregates form as a result of the association of the insoluble blocks. The aggregates have a characteristic core-shell architecture, in which the solvophilic block forms the outer shell to surround the inner core composed of the solvophobic block.<sup>1–4</sup> When amphiphilic AB diblock copolymers are used, micelles and other types of molecular assemblies are formed in water through the association of the hydrophobic segments.<sup>5–10</sup> Recently, it has been reported that some hydrophilic diblock copolymers can also form such molecular assemblies in water.<sup>11–14</sup> These molecular assemblies are important for their potential applications as novel drug delivery systems for both hydrophobic and hydrophilic drugs.<sup>15,16</sup> Another important contribution to the study of molecular assemblies of amphiphilic diblock copolymers is the pioneering, systematic work on so-called "crew-cut" aggregates by Eisenberg's group.<sup>17–19</sup> These aggregates are formed from AB diblock amphiphilic copolymers in which the hydrophilic block is much shorter than the hydrophobic one. The importance of these studies is that even from a single copolymer a variety of morphologies of crew-cut aggregates are easily obtainable by simply changing the copolymer composition, the nature of the solvent, or the initial copolymer concentration, *etc.* The multiple morphologies that have been identified so far for polystyrene-block-poly(acrylic acid) (PSt-b-PAA),<sup>20</sup> polystyrene-block-poly(ethylene oxide) (PSt-b-PEO),<sup>21</sup> polystyrene-block-poly(4-vinylpyridine) (PSt-b-P4VP)<sup>22</sup> and polybutadiene-block-poly(acrylic acid) (PBD-b-PAA)<sup>23</sup> in water include spheres, rods, lamellae, vesicles, tubules, large compound micelles (LCM), and large compound vesicles (LCV). Other morphologies of block copolymers

formed in selective solvents have also been reported.<sup>24</sup> To prepare stable solutions of crew-cut aggregates, highly asymmetric diblock copolymers are first dissolved in a common solvent such as DMF or THF. Then, a precipitant (*e.g.* water) for the long hydrophobic blocks is added gradually to the copolymer solution. The long block starts to aggregate when the water content reaches a critical point. More water is added to freeze the morphologies and the solvents are finally removed by dialysis.

The variety of quantitative theories available to treat the crew-cut aggregate system is very limited compared to the many theoretical treatments of spherical micelles of the star type.<sup>25</sup> It has been found that the factors influencing the final morphologies of the aggregate are quite complicated.<sup>18</sup> However, the following three parameters: are found to be the most essential factors, the stretching of the core-forming blocks in the core, the surface tension between core and the outside solvents, and the repulsive interactions among the corona chains. These factors are governed by the nature and composition of the block copolymer, and most important is the nature of the common solvents and the amount of water added.<sup>18,20c,d,21c</sup> We have been interested in the construction of molecular assemblies from amphiphilic block copolymers with a glycopolymer as the hydrophilic segment, aimed at the utilization of these assemblies as models for cellular-specific targeting drug delivery systems or as building blocks for highly ordered supramolecular architectures. A preliminary study of such a amphiphilic block copolymer that forms crew-cut aggregates in water has been reported recently.<sup>26</sup> The copolymer is polystyrene-block-poly[2-( $\beta$ -D-glucopyranosyloxy)ethyl acrylate] (PSt-b-PGEA), shown in Scheme 1. In this paper, we detail the morphological study of a series of these



Scheme 1

block copolymers in water; of particular interest is the effect of solvent on the morphologies and the transitions between them.

## Experimental

### Materials

THF, DMF and dioxane were used as the common solvents for the copolymers and were the highest grade commercially available in China. They were further purified according to conventional methods. Water was doubly distilled and deionized.

The copolymer samples used in the present study are polystyrene-block-poly[2-(β-D-glucopyranosyloxy)ethylacrylate] (PSt-b-PGEA) diblock copolymers, whose characteristics are summarized in Table 1. They were synthesized by atom transfer radical polymerization (ATRP). Styrene was first polymerized with 1-phenylethyl bromide, Cu<sup>I</sup>Br and 2,2'-bipyridine in chlorobenzene at 110 °C for about 20 h (conversion was about 90%) to obtain bromo-terminated polystyrenes of different molecular weights. Then, they were used as macro-initiators for the polymerization of the second monomer [2-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyloxy)ethyl acrylate] (AcGEA) in chlorobenzene under ATRP conditions. The purified polystyrene-block-poly[2-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucosyloxy)ethyl acrylate] (PSt-b-PAcGEA) was obtained by precipitating in methanol and drying *in vacuo*, and was deacetylated in mixed chloroform-methanol (10% vol MeOH) solvent with MeONa at room temperature. Detailed synthetic procedures and characterization can be found elsewhere.<sup>27</sup>

### Preparation of crew-cut aggregates in water

To study the aggregation behavior of these new block copolymers in water, a known amount of the completely dried block copolymer sample was dissolved in a common solvent for the two blocks to give a final concentration of 1.0 wt%. The solvents were DMF, THF, dioxane or their mixtures. The organic solvent solution was stirred at room temperature for 24 h. While vigorously stirring the solution, deionized water was then added very slowly. When *ca.* 5–20 wt% of water had been added, the clear solution became turbid, indicating that aggregation had taken place. The water content at which aggregation starts is called the critical water content (cwc).

**Table 1** Characteristics of bromo-terminated polystyrenes and PSt-b-PGEA block copolymers

Homopolymer <sup>a</sup>	$M_w/M_n$	Copolymer <sup>a</sup>	PGEA content mol%	$M_w/M_n$
PSt <sub>101</sub>	1.11	PSt <sub>101</sub> -b-PGEA <sub>25</sub>	25.0	1.34
PSt <sub>55</sub>	1.08	b-PGEA <sub>55</sub> -b-PGEA <sub>9</sub>	16.4	1.28
PSt <sub>77</sub>	1.10	PSt <sub>77</sub> -b-PGEA <sub>6</sub>	7.8	1.27
PSt <sub>88</sub>	1.10	PSt <sub>88</sub> -b-PGEA <sub>4</sub>	4.5	1.21

<sup>a</sup> PSt<sub>101</sub> represents a homopolystyrene containing 101 styrene units; PSt<sub>101</sub>-b-PGEA<sub>25</sub> represents a diblock copolymer containing 101 styrene units and 25 GEA units.

The critical water content is obtained by observing the onset of turbidity of the copolymer solution. For example, the cwc of PS<sub>55</sub>-b-PGEA<sub>9</sub> at an initial concentration of 1.0 wt% is 6 wt% in DMF, 9 wt% in 1,4-dioxane, and 18 wt% in THF. When mixed solvents were used, cwc was a function of the solvent composition. The addition of water was continued until 25 wt% of water had been added. Then the sample was put into a dialysis bag (molecular weight cut: 10 000) and dialyzed against deionized water for 4 days to remove the organic solvents.

### Transmission electron microscopy (TEM)

After being diluted by a factor of 10, the aggregate solutions free of organic solvent were used to make TEM samples. A drop of the aqueous solution of aggregates was mixed with a drop of a saturated aqueous solution of uranyl acetate (concentration *ca.* 2.0 wt%). The mixed solution was placed onto a copper EM grid that had been precoated with a thin film of Formvar and coated with carbon. About 15 min later, the aqueous solution was blotted away with a strip of filter paper. After drying in air for an hour, the grids were observed by TEM (JEM-100CXII operated at an acceleration voltage of 100 kV). The sizes of aggregates were measured directly from the prints of the microscope photographs.

## Results and discussion

In this part, we first describe different morphologies of PSt-b-PGEA crew-cut aggregates obtained from a single solvent: DMF, THF or dioxane. These morphologies include spheres, vesicles, tubules, porous spheres and large compound vesicles. Then, morphologies such as rods and lamellae of PS<sub>55</sub>-b-PGEA<sub>9</sub> from the mixed common solvent of DMF and dioxane are discussed. Finally, morphological transitions for a single block copolymer were observed by using mixed solvents.

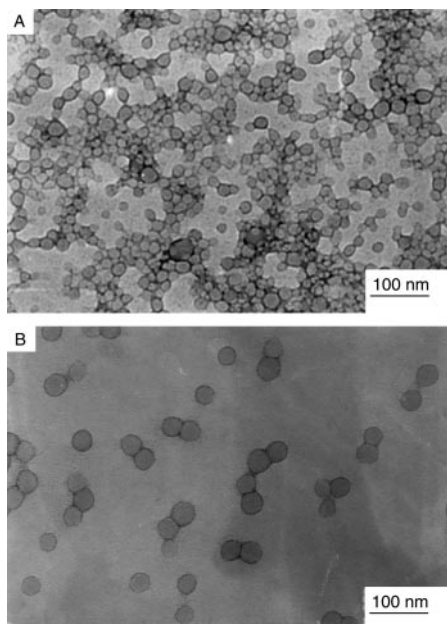
### Morphologies of PSt-b-PGEA crew-cut aggregates from a single solvent

All of the four PSt-b-PGEA copolymers are soluble in DMF, THF and dioxane. Because of the different solubility parameters and polarities of these solvents,<sup>18</sup> different morphologies of aggregates can be obtained for a single block copolymer in different solvents. These morphologies are summarized in Table 2.

**Sphere.** When the glycopolymer content in the block copolymers increases, spherical aggregates are usually formed. In this case, the effect of solvent on the morphology is not obvious. For example, PSt<sub>101</sub>-b-PGEA<sub>25</sub> has the highest glycopolymer content (relative to PSt block length, 25.0 mol%) among the four copolymers and yields spheres from all three solvents used at an initial copolymer concentration of 1.0

**Table 2** Morphologies of PSt-b-PGEA crew-cut aggregates formed by dissolving in different single solvents (1.0 wt%)

Copolymer	DMF	Dioxane	THF
PSt <sub>101</sub> -b-PGEA <sub>25</sub>	Sphere	Sphere	Sphere
PS <sub>55</sub> -b-PGEA <sub>9</sub>	Sphere	Vesicle	Sphere
PSt <sub>77</sub> -b-PGEA <sub>6</sub>	Tubule	LCV	Vesicle
PSt <sub>88</sub> -b-PGEA <sub>4</sub>	Vesicle	Porous sphere	Porous sphere



**Fig. 1** Spherical morphology of PSt-b-PGEA crew-cut aggregates made from DMF. (A) PSt<sub>101</sub>-b-PGEA<sub>25</sub>, (B) PSt<sub>55</sub>-b-PGEA<sub>9</sub>.

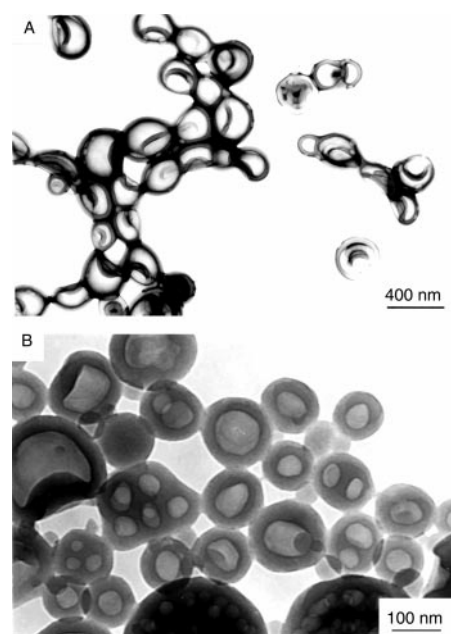
wt%. PSt<sub>55</sub>-b-PGEA<sub>9</sub> yields spheres in DMF or THF. The typical spheres formed by PSt<sub>101</sub>-b-PGEA<sub>25</sub> and PSt<sub>55</sub>-b-PGEA<sub>9</sub> in DMF are shown in Fig. 1(A) and (B), respectively. The diameters of the spheres formed by PSt<sub>101</sub>-b-PGEA<sub>25</sub> vary from 12 to 25 nm and are polydisperse. The average diameter of the spheres formed by PSt<sub>55</sub>-b-PGEA<sub>9</sub> is *ca.* 25 nm with low polydispersity. From the nature and composition of the block copolymer, it is clear that the core of the spheres consists of the hydrophobic PSt block and the corona layer on the core surface consists of the hydrophilic PGEA block, which allows the spheres to remain suspended for a long time in water without settling. The corona layer must be very thin because of the short hydrophilic PGEA block, so it is impossible to distinguish the corona layer from the core region in the TEM images.

As discussed in the literature,<sup>18</sup> the diameter of the spheres is mainly controlled by the degree of stretching of the PSt block. The degree of stretching is defined as the ratio of the micelle core radius to the PSt chain end-to-end distance in the unperturbed state. As mentioned above, the diameter of spheres obtained from PSt<sub>101</sub>-b-PGEA<sub>25</sub> is less than that from PSt<sub>55</sub>-b-PGEA<sub>9</sub>, although the PSt block length of PSt<sub>101</sub>-b-PGEA<sub>25</sub> is longer than that of PSt<sub>55</sub>-b-PGEA<sub>9</sub>. Therefore, the degree of stretching of the PSt chain in PSt<sub>101</sub>-b-PGEA<sub>25</sub> is less than that in PSt<sub>55</sub>-b-PGEA<sub>9</sub>. The length of the hydrophilic block of PSt<sub>101</sub>-b-PGEA<sub>25</sub> is longer than that of PSt<sub>55</sub>-b-PGEA<sub>9</sub>. Thus, the cwc of PSt<sub>101</sub>-b-PGEA<sub>25</sub> is higher than that of PSt<sub>55</sub>-b-PGEA<sub>9</sub>. PSt blocks of copolymers begin to associate reversibly to form micelles at the cwc and are frozen kinetically above the cwc. The core of PSt<sub>101</sub>-b-PGEA<sub>25</sub> aggregates has a lower organic solvent content than that of PSt<sub>55</sub>-b-PGEA<sub>9</sub> aggregates due to the high cwc. The lower the organic solvent content in the core, the lower the degree of PSt chain stretching.

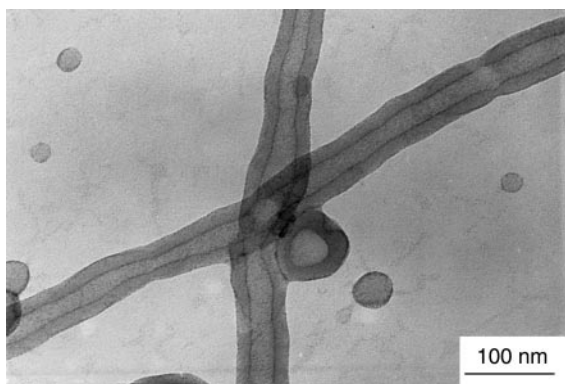
PGEA-solvent interactions also affect the diameter of spherical aggregates. Zhang and Eisenberg found that the diameters of spheres formed by PSt-b-PAA in the different solvents follow the sequence: dioxane > THF > DMF.<sup>18</sup> The same sequence is also found for PSt-b-PGEA. The average diameter of spheres from PSt<sub>101</sub>-b-PGEA<sub>25</sub> is 30 nm from dioxane, 24 nm from THF, and 18 nm from DMF, although the diameter is polydisperse. The average diameter of spheres from PSt<sub>55</sub>-b-PGEA<sub>9</sub> is 32 nm in THF and 25 nm in DMF.

**Vesicles.** Vesicles can be obtained from three of the block copolymers (see Table 2). Fig. 2 shows typical TEM pictures of vesicles. PSt<sub>55</sub>-b-PGEA<sub>9</sub> yields predominantly single-compartment vesicles in dioxane at an initial copolymer concentration of 1.0 wt% [Fig. 2(A)]. The vesicular nature is evidenced from the higher transmission in the center of the aggregates compared to the periphery. The outer diameter of vesicles ranges from 70 to 180 nm. The wall thickness of the vesicles is uniform, at *ca.* 25 nm, and independent of the overall size of the vesicles. The vesicles formed by PSt<sub>88</sub>-b-PGEA<sub>4</sub> in DMF are shown in Fig. 2(B). It can be seen that besides single-compartment vesicles, two-compartment and multiple-compartment vesicles are formed. The outer diameter of the vesicles is quite polydisperse, ranging from 70 to 350 nm. The wall thickness of the vesicles is uniform, at *ca.* 20 nm. The structure of multiple-compartment vesicles is very interesting. Although it is known that some small molecule surfactants form multiple-compartment vesicles, the formation of multiple-compartment vesicles from block copolymers has only occasionally been reported.<sup>18</sup> Their detailed structure needs to be studied further. PSt<sub>77</sub>-b-PGEA<sub>6</sub> also yields only single-compartment vesicles from THF. The diameters of the vesicles range from 70 to 300 nm.

**Tubules.** PSt<sub>77</sub>-b-PGEA<sub>6</sub> yields predominantly tubules from DMF at an initial copolymer concentration of 1.0 wt%. A typical TEM picture of the tubular aggregates is shown in Fig. 3. The tubular nature is evident from the higher transmission in the central part of the aggregates compared with their periphery, indicating that the structure is hollow. The diameter of the tubules is uniform, at *ca.* 50 nm. The wall thickness is also uniform, at *ca.* 15 nm. The length of the tubules is polydisperse, varying from 4 to 10  $\mu$ m. There is a hemispherical structure at the end of the tubules. To our knowledge, the only previously cited block copolymers that yield tubules are PSt-b-PEO<sup>21</sup> and polyethylene-block-poly(ethylene oxide) (PEE-b-PEO),<sup>10</sup> as well as PSt-b-PAA, which occasionally yields tubules from mixed dioxane-DMF solvents.<sup>20</sup> In our case, PSt-b-PGEA can yield tubules under a broad range of conditions. For example, PSt<sub>77</sub>-b-PGEA<sub>6</sub> also yields tubules from the mixed solvent of THF and DMF. PSt<sub>55</sub>-b-PGEA<sub>9</sub> yields fragments of tubules in dioxane at an initial copolymer concentration of 2.5–3.0 wt%.



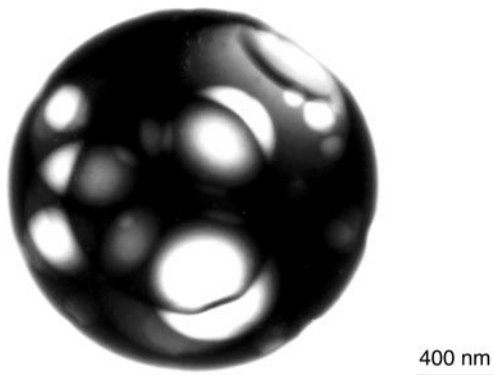
**Fig. 2** Vesicular morphology of PSt-b-PGEA crew-cut aggregates. (A) PSt<sub>55</sub>-b-PGEA<sub>9</sub> from dioxane, (B) PSt<sub>88</sub>-b-PGEA<sub>4</sub> from DMF.



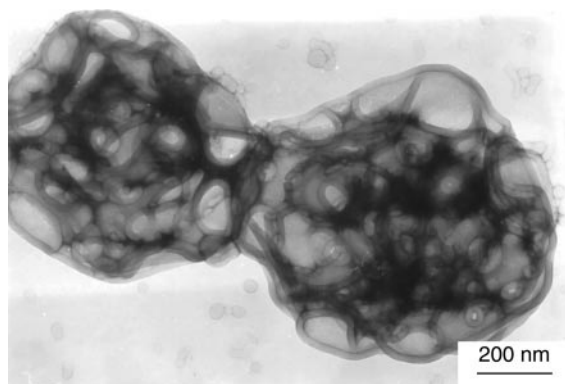
**Fig. 3** Tubular morphology of PSt<sub>77</sub>-b-PGEA<sub>6</sub> crew-cut aggregates made from DMF.

**Porous spheres.** PSt<sub>88</sub>-b-PGEA<sub>4</sub> yields another kind of aggregate from dioxane or THF at an initial copolymer concentration of 1.0 wt%. A typical picture is shown in Fig. 4. This morphology is very similar to that obtained from PSt-b-PEO and is considered to be a porous sphere.<sup>21b</sup> This morphology has not been observed from other copolymer samples. Unlike the spheres, tubules and vesicles whose structures can be observed clearly from TEM pictures, the structure of a porous sphere is quite complicated and of multiple phases, the diameter of which is highly polydisperse. Some porous spheres are so large that they settle out in the preparation of micelles. The inside phases of porous spheres are spherical, which is evidenced by the different transmission densities in the TEM pictures. Because most porous spheres can remain suspended in water, the outer surface of the porous spheres must consist of the hydrophilic PGEA segment. The hydrophilicity of the outer surface gives porous spheres considerable stability and allows those that have settled to the bottom of the container to be resuspended.

**Large compound vesicles (LCV).** LCVs are another type of complicated crew-cut aggregates formed from PSt-b-PGEA. PSt<sub>77</sub>-b-PGEA<sub>6</sub> yields LCVs from dioxane at an initial concentration of 1.0 wt%, as shown in Fig. 5. LCVs consist of many vesicles interconnecting with each other. The overall size of LCVs is polydisperse and the outer surface is not uniform. The structure of LCVs resembles that of aggregated soap bubbles. Similar to porous spheres, some LCVs are so large that they settle to the bottom of containers, but they can be resuspended in water. The fusion process of vesicles made from block copolymers is very low because of the low mobility of macromolecules compared with the fusion of vesicles made from small molecule surfactants.



**Fig. 4** Porous sphere of PSt<sub>88</sub>-b-PGEA<sub>4</sub> crew-cut aggregates made from THF.



**Fig. 5** LCV morphology of PSt<sub>77</sub>-b-PGEA<sub>6</sub> crew-cut aggregates made from dioxane.

LCVs are self-assembled spontaneously from vesicles. These higher ordered structures might be of interest in leading to new methods for processing tissue-like composites and soft biomaterials. It is possible that the self-assembly of vesicles made from PSt-b-PGEA can be adjusted by adding the lectins that are specific to carbohydrates.

#### Morphologies of PSt-b-PGEA crew-cut aggregates from mixed solvents

The morphologies of crew-cut aggregates can also be controlled by using a mixed solvent to adjust the polymer-solvent interactions. For PSt-b-PAA, the morphogenic effect of solvents on the crew-cut aggregates has been reported.<sup>20c,d</sup> Following these original reports, we have studied the morphologies of crew-cut aggregates from PSt-b-PGEA by using solvent mixtures of DMF-dioxane and DMF-THF.

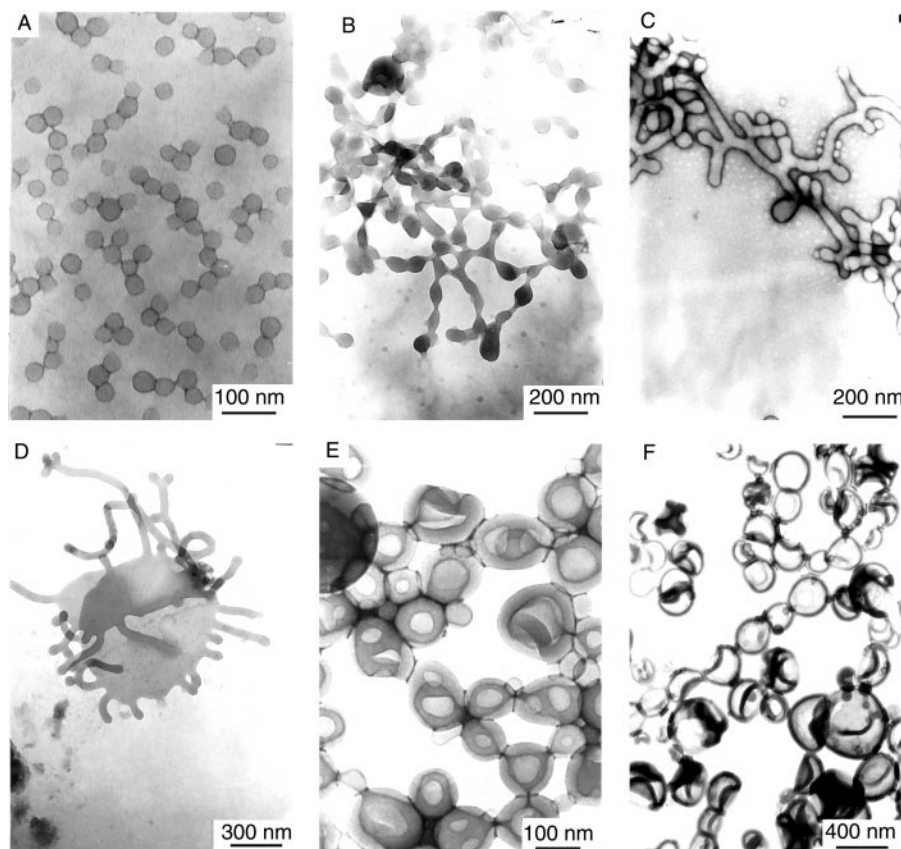
Two fundamental morphologies of crew-cut aggregates, rods and lamellae, can be obtained from PSt<sub>55</sub>-b-PGEA<sub>9</sub> by first dissolving it in mixed dioxane-DMF solvent.

**Rods.** PSt<sub>55</sub>-b-PGEA<sub>9</sub> yields rod-like aggregates from dioxane-DMF (30 wt% dioxane) at an initial copolymer concentration of 1.0 wt%. Fig. 6(C) shows the typical structure of rods. The rod-like nature is evidenced by the uniformity over the entire feature. Most of the rods are bent rather than straight. Hemispherical caps form at the rod end. The diameter of rods is uniform, at *ca.* 40 nm, but the length of rods is quite polydisperse. Some rods interconnect with each other and some are quite short, at *ca.* 60 nm. The rods are usually found to coexist with a few spheres.

**Lamellae.** Lamellar aggregates are obtained from the same block copolymer if the content of dioxane in the mixed solvent is increased to 50 wt%. Fig. 6(D) shows the typical structure of lamellae. The lamellar nature is evidenced by the uniformity of the light intensity over the entire feature and no overlapping in their extended positions. Usually, lamellae interconnect with rods. The size of lamellae is quite polydisperse.

#### Morphological transitions of crew-cut aggregates by changing the composition of the solvent mixture

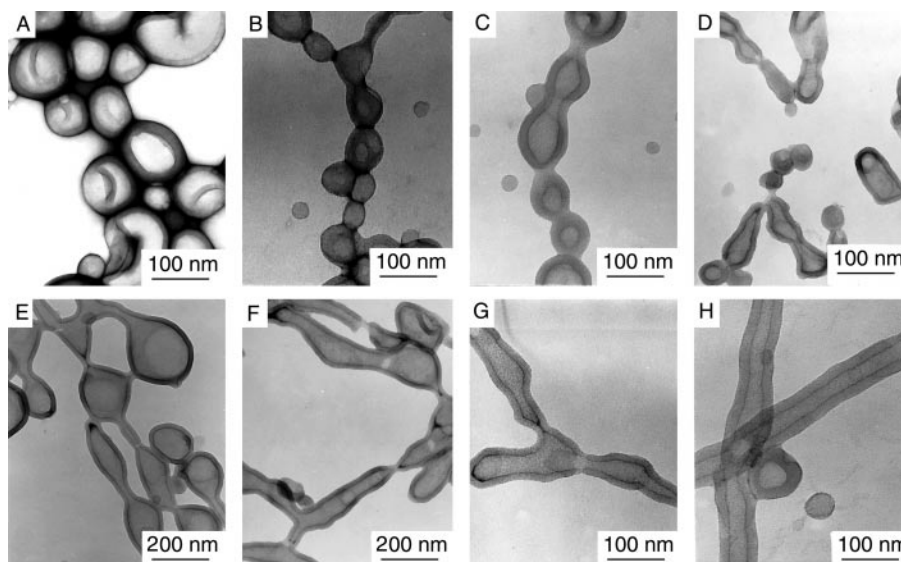
**Morphological transition between spheres and vesicles.** The morphological transitions from spheres to rods, to lamellae, and to vesicles can be carried out from PSt<sub>55</sub>-b-PGEA<sub>9</sub> by changing the composition of the solvent mixture of DMF-dioxane as shown in Fig. 6. PSt<sub>55</sub>-b-PGEA<sub>9</sub> yields completely spherical aggregates in pure DMF [Fig. 6(A)]. The diameter of the spheres is *ca.* 25 nm and of low polydispersity, as discussed in a previous section. With an increase of the dioxane



**Fig. 6** Morphological transitions between spheres and vesicles made from  $\text{PSt}_{55}\text{-b-PGEA}_9$  by initially dissolving it in mixed dioxane–DMF solvent. Content of dioxane (wt%): (A) 0, (B) 10, (C) 30, (D) 50, (E) 80, (F) 100.

content in the mixture, the morphologies of the formed aggregates begins to change. When the dioxane content is 10 wt%, spheres interconnect with each other and tend to form rod-like structures [Fig. 6(B)]. The rod-like structure is irregular and there is an oscillatory perturbation in the diameter of the rods like pearls on a string. When the dioxane content in DMF is raised to 30 wt%, rods are obtained [Fig. 6(C)]. Further increase of the dioxane content to 50 wt% results in the formation of lamellae coexisting with rods [Fig. 6(D)]. Subsequently, when the dioxane content is further raised to 80

wt%,  $\text{PS}_{55}\text{-b-PGEA}_9$  yield vesicles, as from pure dioxane [Fig. 6(E) and (F), respectively]. The outer diameter of vesicles varies from 70 to 250 nm. The wall thickness of the vesicles is uniform, at *ca.* 25 nm. A few two-compartment and multiple-compartment vesicles are formed at the same time. The diameter of the largest multiple-compartment vesicles reaches 250 nm. The outer diameters of vesicles from pure dioxane vary from 120 to 600 nm and are larger than those of the vesicles from the mixed solvent. But the wall thickness is unchanged, at *ca.* 25 nm.



**Fig. 7** Morphological transitions between tubules and vesicles made from  $\text{PSt}_{77}\text{-b-PGEA}_6$  by initially dissolving it in mixed THF–DMF solvent. Content of DMF (wt%): (A) 0, (B) 10, (C) 20, (D) 35, (E) 50, (F) 70, (G) 90, (H) 100.

**Morphological transitions between tubules and vesicle.** This transition was observed for PSt<sub>77</sub>-b-PGEA<sub>6</sub> from mixed DMF-THF solvent. As shown in Fig. 7, the morphological transition from vesicles to tubules with the increase of DMF content in the mixture can be seen very clearly. When the content of DMF is 10 wt%, the morphology does not change obviously as compared with that from pure THF. The dominant aggregates are still vesicles, but most of them connect with each other and tend to be arranged in line [Fig. 7(B)], the interior of the vesicles being separated by bilayers. When the DMF content is raised to 20 wt%, a few vesicles start to transform at the connections [Fig. 7(C)]. These interconnected vesicles may be the intermediates in the transition from vesicles to tubules. Further increase of the DMF content to 35 wt% results in the formation of transformed vesicles, shown in Fig. 7(D). When the DMF content reaches 50 wt%, most of the vesicles are changed with an irregular shape, some are short tubules and attach with transformed vesicles in the end [Fig. 7(E)]. It is obvious that the short tubules are transformed from vesicles. On increasing the DMF content to 70 wt%, the structure of the aggregates remains as irregular tubules [Fig. 7(F)]. Though a few vesicles are still observed, most of the aggregates are tubule-like. The length of these tubules increases compared with that in Fig. 7(E). The longest tubule is about 1  $\mu$ m. When the DMF content is increased to 90 wt%, long tubules are observed. But these tubules are not uniform in diameter, ranging from 40 to 80 nm. One of the typical tubules with an oscillatory perturbation in its diameter is shown in Fig. 7(G). The lengths of the tubules range from 4 to 9  $\mu$ m. The wall thickness is still very uniform, at ca. 20 nm. When the solvent is pure DMF, PS<sub>77</sub>-b-PGEA<sub>6</sub> yields longer tubules with a uniform diameter as discussed above [Fig. 7(H)]. The diameter of the tubules is ca. 50 nm and the lengths range from 6 to 12  $\mu$ m.

The formation of different morphologies of crew-cut aggregates and the transformation between these morphologies are governed by many factors, some morphologies are formed thermodynamically, while others are just kinetically stable. A detailed explanation of these factors which is also applicable to the present study, has been reviewed by Zhang and Eisenberg, especially for the PSt-b-PAA system.<sup>18</sup> Although these explanations may be considered to be qualitative or semi-quantitative, they can at least give us ideas to guide further studies in this field.

## Conclusion

It has been shown that multiple morphologies of crew-cut aggregates can be obtained from a new type of amphiphilic block copolymer, which contains a short glycopolymer segment as the hydrophilic block. These morphologies are very stable once they are formed in water. The surfaces of the aggregates are covered with a high density of glucose groups as deduced from the morphologies. Although the composition of the block copolymer affects the final morphologies of the aggregates in water, the effect of solvent was found to be very important. The observation of morphological transformations from a single copolymer by just changing the common solvent composition suggests that this may be a useful and simple method to prepare different morphologies from a single compound. These morphologies may find applications as models

for cellular-specific drug delivery systems, and they may also be used as building blocks for highly ordered supramolecular architectures.

## Acknowledgements

This work was partially supported by the National Natural Science Foundation of China (29992590-4, 59603004).

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