

Note

MORPHOLOGICAL TRANSITION BETWEEN VESICLES AND TUBULES FOR A GLYCOPOLYMER-CONTAINING AMPHIPHILIC DIBLOCK COPOLYMER IN AQUEOUS SOLUTIONS*

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Abstract The morphological transition of molecular assemblies in aqueous solutions for a new amphiphilic diblock copolymer induced by changing the initial solvent conditions was studied by transmission electron microscopy (TEM). The copolymer was polystyrene(77)-*b*-poly[2-(β -D-glucopyranosyloxy)ethyl acrylate (6)] (PSt₇₇-*b*-PGEA₆) and the solvent was a mixture of DMF and THF. PSt₇₇-*b*-PGEA₆ yields vesicles and tubules when it is initially dissolved in THF and DMF respectively. The morphological transition between vesicles and tubules can be achieved by simply varying the amounts of THF and DMF, or changing the temperature at which the aggregates were prepared.

Keywords Block copolymer, Amphiphile, Glycopolymer, Self-assembly, Tubule, Vesicle

INTRODUCTION

Amphiphilic diblock copolymers can self-assemble into a variety of molecular assemblies in aqueous media^[1-5]. Among these diblock copolymers, those which contain a relatively shorter hydrophilic block give very rich morphologies of molecular assemblies and have been studied systematically by Eisenberg's group^[6-10]. These molecular assemblies, commonly known as "crew-cut" aggregates, are normally obtained by first dissolving the block copolymer in a common solvent and then slowly adding water to the solution. Compared with analogues formed from small surfactant molecules, these crew-cut aggregates exhibit the following characteristics. (1) The range of molecular assemblies can be controlled by simply changing the copolymer composition; (2) the ordered structure can be easily changed from one type to the other by slightly changing the preparation methods of a single polymer; and (3) these aggregates are much more stable in water.

Vesicles and tubules are the two important forms of molecular assemblies. Vesicles are bilayer structures which could be used as cell models or encapsulation systems for drug delivery, while tubules have been used in a variety of applications, including electro-active composites and controlled-release systems^[11, 12]. So far, vesicles have been prepared from many amphiphilic diblock copolymers^[8, 13-19], but tubules can be formed from only a few of them. Eisenberg *et al.* prepared tubular crew-cut aggregates from polystyrene-*b*-poly(ethylene oxide) (PSt-*b*-PEO) diblock copolymer in a mixture of DMF and water^[10]. They also reported the formation of tubules from polystyrene-*b*-poly(acrylic acid) (PSt-*b*-PAA) diblock copolymer from a mixture of DMF and dioxane^[9c]. Hammer *et al.* obtained tubules from polyethylethylene-*b*-poly(ethylene oxide) (PEE-*b*-PEO) and observed the transition from tubules to vesicles^[14]. The kinetics and mechanism of the transition from rods to vesicles have also recently been reported^[10d].

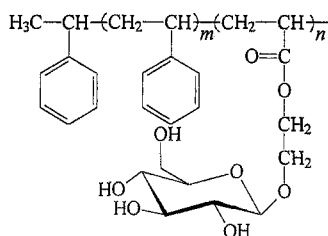
We are interested in constructing molecular assemblies from amphiphilic block copolymers with glycopolymer as hydrophilic segment. These assemblies should have the potential to be used as models for

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cellular-specific target drug delivery system or as building blocks for highly ordered supramolecular architectures. We have recently reported a new type of well-defined amphiphilic diblock copolymer, polystyrene-*b*-poly[2-(β -D-glucopyranosyloxy) ethyl acrylate] (PSt-*b*-PGEA) which could form a variety of molecular assemblies in aqueous medium by first dissolving in an organic solvent, followed by addition of water^[20]. In this note, we report the study of the morphological transition between vesicular and tubular crew-cut aggregates of PSt-*b*-PGEA by changing the composition of the cosolvent or the temperature at which the aggregates were prepared.



EXPERIMENTAL

PSt-*b*-PGEA diblock copolymer was synthesized by atom transfer radical polymerization (ATRP) and characterized by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR). The diblock copolymer was fractionated, and the fraction used in this study was PSt₇₇-*b*-PGEA₆ with a polydispersity of 1.27 (polydispersity of PSt block is 1.10), while the subscripts, 77 and 6, give the number of the repeat units of PSt block and PGEA block, respectively. The procedures for the preparation of aggregates and their characterization with transmission electron microscopy (TEM) were the same as described previously^[21]. The solvents used were DMF and THF, or their mixtures. The initial copolymer concentration was 1.0 wt % for aggregate preparation, and the final concentration for TEM analysis was 0.08 wt %.

RESULTS AND DISCUSSION

Morphological Transition Induced by Changing Solvent

The morphological transition between tubules and vesicles was first performed at 25°C by changing the solvent composition of DMF and THF. Figure 1 shows different morphologies obtained by dissolving PS₇₇-*b*-PGEA₆ in different solvent compositions. When the solvent was 100% THF, PS₇₇-*b*-PGEA₆ produced predominantly vesicles after the addition of water. One of the typical structures is shown in Fig. 1(a). The vesicles are very polydispersed in size, with diameters ranging from 60 nm to 200 nm; however, the wall thickness of the vesicles is relatively uniform at ca. 15 nm. The vesicular nature of these vesicles is evident from the higher transmission in the center of the aggregates compared with the periphery, as demonstrated by the TEM results. The bilayer in the center of vesicles is believed to be due to the shrinkage of vesicles after drying in air. Almost all the vesicles are of single-room. When the common solvent was changed to a mixture of 80% THF and 20% DMF (wt%), the dominant aggregates formed from PS₇₇-*b*-PGEA₆ were still vesicles. But most of the vesicles started to associate with each other, with some even beginning to transform (Fig. 1b). These interconnected vesicles seem to be the intermediates of the transition from vesicles to tubules. When the DMF content in the solvent mixture was increased to 50%, most of the vesicles transformed into aggregates with irregular shape and size. Some short tubules began to form during the transformation. When the DMF content was further increased to 70%, the structure of aggregates became less regular, but most of them were still short tubules associating with each other (Fig. 1d). The length of the tubules increases in comparison with that in Fig. 1(c), but the longest tubule is still only 1 μm. At this solvent composition, a few vesicles could still be observed. Much longer tubules with lengths ranging from 4 μm to 9 μm were observed when the DMF composition was increased to 90%, and very little

vesicles could be detected in the solution. These tubules have very different diameters (ranging from 40 nm to 80 nm), but with very similar wall thickness (ca. 15 nm). Figure 1(e) represents a typical tubule structure with an oscillatory perturbation in the center at this solvent composition. When the solvent was changed to 100% DMF, PS₇₇-*b*-PGEA₆ yielded mostly long tubules (Fig. 1f). The diameter of the tubules became very uniform, at ca. ~50 nm, while the length of tubules ranged from 6 μ m to 12 μ m. Again the wall thickness of the tubules was very uniform at ca. 15 nm. Based on these experimental results, it is apparent that the diameter of tubules decreases and the length of the tubules increases with the process of the transition from vesicles to tubules. However, the thickness of the bilayer (wall thickness) in both vesicles and tubules remained the same.

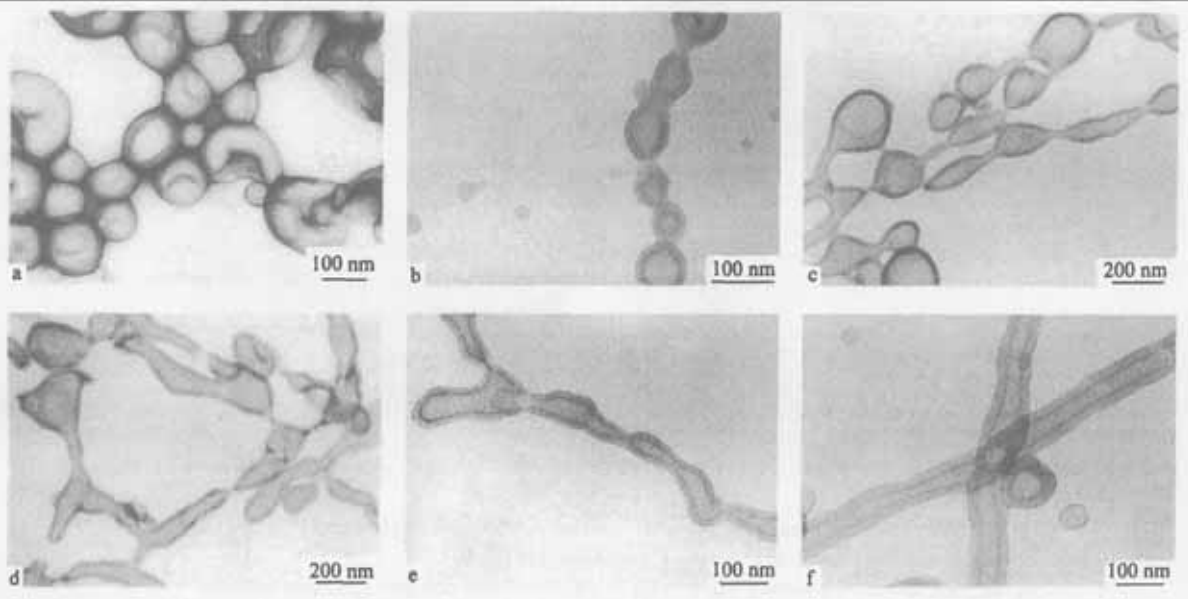


Fig. 1 Morphological transitions between vesicles and tubules made from PS₇₇-*b*-PGEA₆ by initially dissolving it in a mixture of THF and DMF. Content of DMF (wt%): (a) 0, (b) 20, (c) 50, (d) 70, (e) 90 and (f) 100. The initial copolymer concentration was 1.0 wt%.

Morphological Transition by Changing Temperature

The morphological transition between tubules and vesicles was also carried out by changing the temperature at which the crew-cut aggregates were formed. The results are shown in Fig. 2. PS₇₇-*b*-PGEA₆ was dissolved in DMF at an initial concentration of 1.0 wt%. When the temperature of the solution was kept at 80 °C during water addition, vesicles were the only aggregates formed (Fig. 2a). The diameter of the vesicle ranged from 50 nm to 150 nm, and the wall thickness was ca. 15 nm. If the preparation temperature was decreased to 60 °C, transformed vesicles associated with a few tubules started to form. But the dominant aggregates were still vesicles. The tubules were very short and irregular (Fig. 2b). Further decreasing the temperature to 50 °C resulted in the formation of short tubules coexisting with vesicles (Fig. 2c). When the temperature was further lowered to 40 °C, the main aggregates became tubules (Fig. 2d). The length of these tubules was ca. 2 μ m–6 μ m. Similarly, during the morphological transition, the wall thickness of both vesicles and tubules did not change significantly (ca. 15 nm).

The morphology of PS-*b*-PGEA aggregates in water is affected by many factors. The effects of copolymer composition, the solvent nature and copolymer concentration have been discussed in previous papers^[21]. In most cases, the morphologies observed at certain water content is under equilibrium control, a little water jump may induce the transition of aggregate morphologies^[10d]. It has been suggested that the formation of block copolymer tubules might be a result of conversion from vesicles, one of the contributions to driving force might be a decrease of stretching of the PS chains^[10b]. Since the solubility parameter value of THF is closer to that of homo-

PS than that of DMF, PS chains of PS₇₇-*b*-PGEA₆ have a higher degree of swelling ratio in THF than in DMF^[7]. This can help to explain the result that the vesicular morphology from THF gradually changes to transformed vesicle, short tubule and finally long tubule with the successive increase of DMF in the solvent mixture. In the case of temperature induced vesicle to tubule transition, the results can also be explained by the fact that the degree of stretching of PS chains is higher at high temperature than at low temperature.

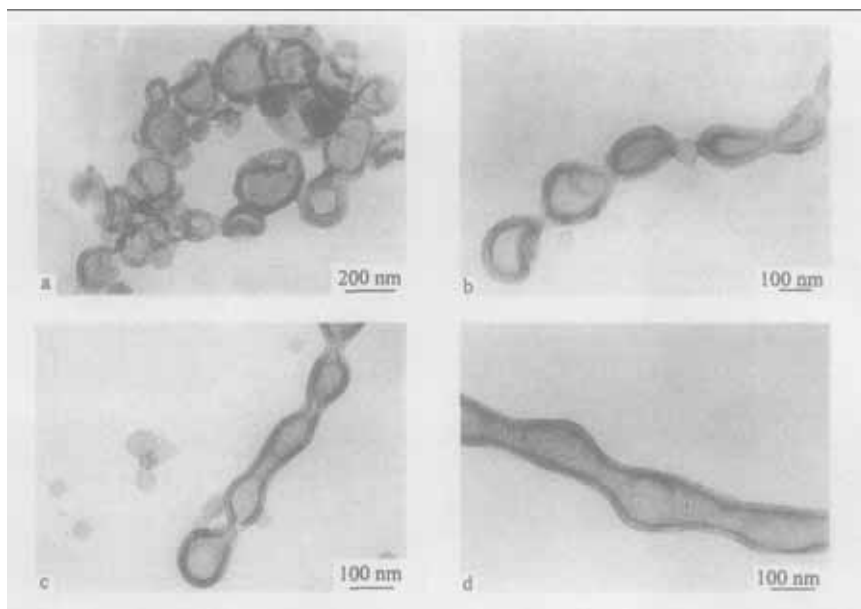


Fig. 2 Morphological transition between vesicles and tubules made from PS₇₇-*b*-PGEA₆ at different temperatures: (a) 80°C, (b) 60°C, (c) 50°C and (d) 40°C
The organic solvent used was DMF and the initial copolymer concentration was 1.0 wt%.

In summary, the well-defined amphiphilic diblock copolymer PS₇₇-*b*-PGEA₆ was demonstrated to yield vesicles and tubules when it was initially dissolved in THF and DMF respectively, at a copolymer concentration of 1.0 wt%. When a mixture of THF and DMF was used as the common solvent, various intermediate morphologies between tubules and vesicles were obtained from the same copolymer depending on the compositions of the common solvent. The morphological transformation between vesicles and tubules can be readily observed using TEM. Similar morphological transition could also be achieved by changing the temperature of the solution at which aggregates were prepared, with higher temperature favoring the formation of vesicles.

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