

# Disk-Like Micelles with a Highly Ordered Pattern from Molecular Bottlebrushes

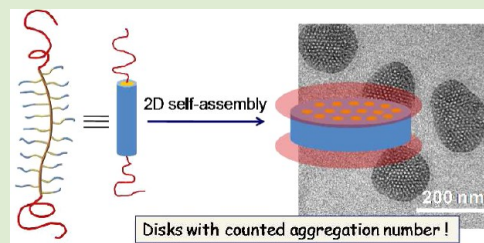
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## Supporting Information

**ABSTRACT:** Self-assembling amorphous macromolecules into nanoparticles with a highly ordered internal structure and a defined shape is always a big challenge. Herein we present formation of soft disk-like micelles by hexagonally packing *AbBA* amphiphilic triblock copolymers, whose *bB* block is the molecular bottlebrush with densely grafted poly(*t*-butyl acrylate)-*b*-polystyrene (PBA-*b*-PS) branches and *A* block is poly(*N*-(2-methacryloyloxyethyl)pyrrolidone) (PNMEP). In a selective solvent of *A* segment, it was found that the *AbBA* molecular bottlebrushes with stiffened middle blocks self-assembled two-dimensionally into disks with a uniform thickness of about 33 nm and a diameter of hundreds of nanometers. A hexagonal pattern of molecular bottlebrushes aligned perpendicularly to the disk plane with a periodic spacing of 9 nm was visualized by TEM through selective staining the PS shells of brushes. The aggregation number of *AbBA* molecular bottlebrushes in each disk was counted directly from the stained TEM image.

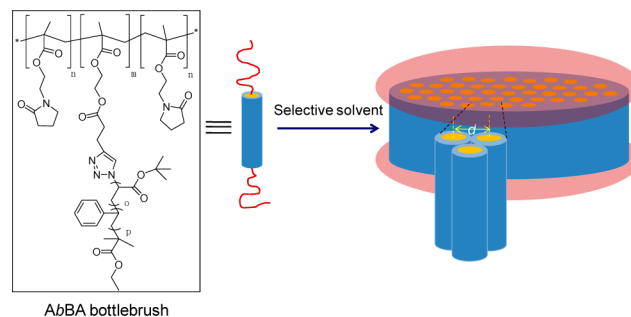


Self-assembly of amphiphilic block copolymers may form nanomaterials with various morphologies in selective solvents. Micellar morphologies of sphere, cylinder, vesicle, and toroid have been reported.<sup>1</sup> In recent years, multicompartiment micelles of block copolymers have attracted increasing attention since the micelles from amorphous synthetic macromolecules have a subdivided compartment, which can be considered as analogues of biological entities like eukaryotic cells.<sup>2</sup> However, disk- or sheet-like morphology of block copolymer micelles has been reported scarcely.<sup>3</sup> Few examples of disk-like micelles were obtained from coil-rod-coil molecules,<sup>4</sup> coil-coil diblock copolymers with a perfluoropolymer segment,<sup>5</sup> triblock copolymers in the presence of additives,<sup>6</sup> coil-rod diblock copolymers,<sup>7</sup> supramolecular block copolymers,<sup>8</sup> and diblock copolymers with a crystallizable segment.<sup>9</sup> However, none of these researches could be a generalized strategy for preparation of the disk-like micelles. Recently, emulsion approach to prepare disk-like nano-objects of block copolymers was reported.<sup>10</sup> It is known that block copolymers assembled into vesicles by enclosing molecular membranes into a closed structure in order to diminish high free energy of the hydrophobic edges. It is believed that the bending energy of the membrane to form a vesicle is lower than the released free energy of diminishing edge. Thus, disk-like micelles could be prepared in the case that the membrane would be difficult to bend.

Molecular bottlebrush is a kind of cylindrical molecular nano-objects.<sup>11</sup> Attributed to the densely tethered bulky polymer chains, the backbone is stretched and the morphology shows worm-like shape.<sup>1c,11</sup> Moreover, molecular bottlebrushes may

form lyotropic phase in a concentrated solution and at monolayer film by orderly packing cylindrical molecular bottlebrushes.<sup>12</sup> Thus we proposed that well-defined rigid molecular bottlebrushes with two terminals tethered with coil-like polymers may be packed in two-dimensionally (2D) and form disk-like micelles since such thick block copolymer membranes could be difficult to bend (Scheme 1). In this Letter, we present a rational approach to form disk-like micelles by packing molecular nanoobjects in 2D in a selective solvent. The building block was amphiphilic *AbBA* triblock copolymer,

## Scheme 1. Molecular Structure of Amphiphilic *AbBA* Triblock Molecular Bottlebrush and Schematic Presentation of Its 2D Packing



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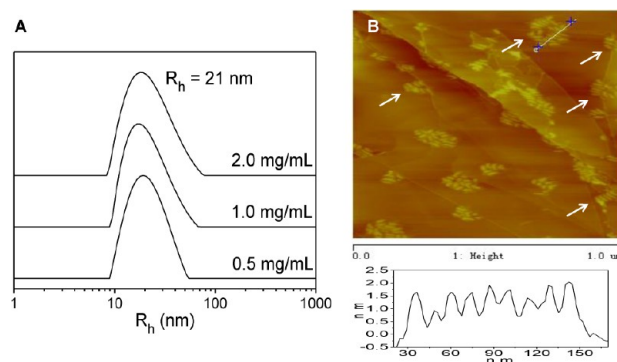
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where the *bB* segment was the brushes with densely grafted PBA-*b*-PS branches and the A segment was PNMEP. The middle block *bB* showed rod-like shape that was visualized by AFM image and thus it was a PBA core/PS shell nano-object. Therefore, the *AbBA* triblock copolymer had a coil-*b*-nanorod-*b*-coil conformation, and in selective solvent of the A segment, the nano-objects packed in 2D, which was defined by the A blocks. It is noteworthy that the PBA-*b*-PS block copolymers were used as side chains, which in one hand allowed us to identify how the brushes were packed along the disks and in the other hand endowed the disks with an ordered pattern.

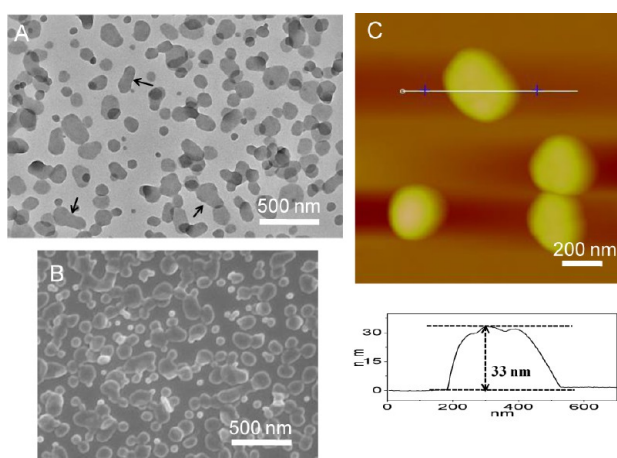
To prepare well-defined *AbBA* molecular bottlebrush (Scheme S1), the main chain PNMEP-*b*-PHEMA-*b*-PNMEP was first synthesized via sequential reversible addition-fragmentation chain transfer radical polymerization and was then postmodified with pentanoic acid to give PNMEP-*b*-PMAPA-*b*-PNMEP. The side chain, PS-*b*-PBA- $N_3$ , was obtained separately by atom transfer radical polymerization and then by terminal transformation into azido terminals. The brush was prepared by copper-catalyzed azide-alkyne cycloaddition click reaction between the PNMEP-*b*-PMAPA-*b*-PNMEP backbone and the PS-*b*-PBA- $N_3$  side chains.<sup>13</sup> Figures S1 and S2 gave the SEC traces of preparation of PS-*b*-PBA- $N_3$ , PHEMA-TMS, PNMEP-*b*-PHEMA-*b*-PNMEP, and PNMEP-*b*-PMAPA-*b*-PNMEP. All the traces with low polydispersity indices indicated that the polymerizations were controlled. The composition of these polymers in each step was given by <sup>1</sup>H NMR spectra (Figure S4 and Table S1). Figures S3A and S3B show the SEC traces of the mixtures of PNMEP-*b*-PMAPA-*b*-PNMEP and PS-*b*-PBA- $N_3$  before and after click reaction. After the click reaction, appearance of a new peak at much shorter eluent time indicated an efficient grafting reaction (Figure S3B). The grafting density, given by conversion ratio of PS-*b*-PBA- $N_3$  via SEC trace using toluene as internal standard, was 97%. After removal of excessive PS-*b*-PBA- $N_3$ , the composition and the molecular weights were estimated by its <sup>1</sup>H NMR spectrum as shown in Figure S4(C). By comparing the segment ratio, the grafting density was 94%, very close to the result from SEC method. Thus, the repeating units of the middle block were nearly fully tethered with PBA-*b*-PS branches. The formula with detail composition was PNMEP<sub>300</sub>-*b*-P(MAPA-*g*(PBA<sub>17</sub>-*b*-PS<sub>43</sub>))<sub>126</sub>-*b*-PNMEP<sub>300</sub>.

Dynamic light scattering (DLS) was used to estimate the size of this molecular bottlebrush in DMF, which is its good solvent. At the concentration region of 0.5–2.0 mg/mL,  $R_h$  data, as shown in Figure 1A, were nearly the same, ~21 nm, an expected size of individual molecules. The shape of molecular bottlebrush was visualized by AFM by spin-casting the sample solution of chloroform onto HOPG. As shown in Figure 1B, the brushes exhibited a rod-like morphology in a large area of observation window, demonstrating that the backbones were stretched. The height and the width of brushes were about 1.9 and 15 nm. By the statistics of 50 molecules, the average length was  $40 \pm 4$  nm. It is noteworthy that this data included the size of the A blocks besides that of the brush segments. The persistent length of fully tethered bottlebrushes in literatures was at least 50 nm.<sup>12,14</sup> Thus, the present brush segments may be considered as short stiff rods. It is interesting to notice from the AFM image that some brushes formed ordered clusters as indicated by arrows in Figure 1B, implying that the molecular rods had a tendency to align orderly along the substrate during sample preparation.



**Figure 1.** (A) DLS traces of *AbBA* molecular bottlebrushes in DMF with varied concentration. (B) AFM height image of the brushes on HOPG.

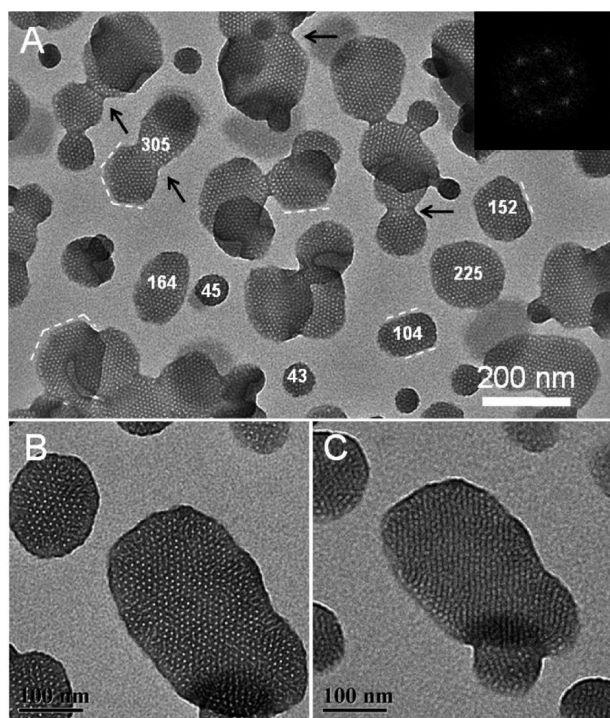
Organization of the molecular nano-objects in solution was induced by dropping methanol, a selective solvent of PNMEP, into a solution of sample in DMF with an initial concentration,  $c_{\text{ini}} = 5$  mg/mL, under stirring until methanol content ( $c_{\text{MeOH}}$ ) reached 90 vol %. The obtained colloidal dispersion was kept still without stirring and small amount of sample was taken at different interval for morphology observation. The TEM images of dispersion without staining at 0 h (the as-prepared dispersion, Figure SSA), 8 h (Figure 2A), and 2 d (Figure SSB)



**Figure 2.** (A) TEM, (B) SEM, and (C) AFM height images of self-assemblies of *AbBA* molecular bottlebrushes in DMF/MeOH solution at 8 h;  $c_{\text{ini}} = 5$  mg/mL;  $c_{\text{MeOH}} = 90$  vol %. Sample for TEM was not stained.

demonstrated similar irregular-shaped morphologies with uniform thickness and varied diameters in range of 100–300 nm. The SEM and AFM height images (Figure 2B,C) further confirmed their morphology being a disk-like shape. By the AFM image, the thickness of the disk was given to be about 33 nm. This data matched to length of the brushes, supporting monolayer packing of rod-like molecular objects. It is noteworthy that small disks seemed to have a round circular rim while some larger disks showed an elongated shape. As shown in Figure S6 of the morphologies at 8 and 26 d, the number of those elongated disks became more, implying the further aggregation of small disks with the time.

To confirm exact packing manner of molecular brushes, the PS shells of brushes were selectively stained with  $\text{RuO}_4$  vapor at room temperature. As shown in Figure 3A,B (by HRTEM), it is

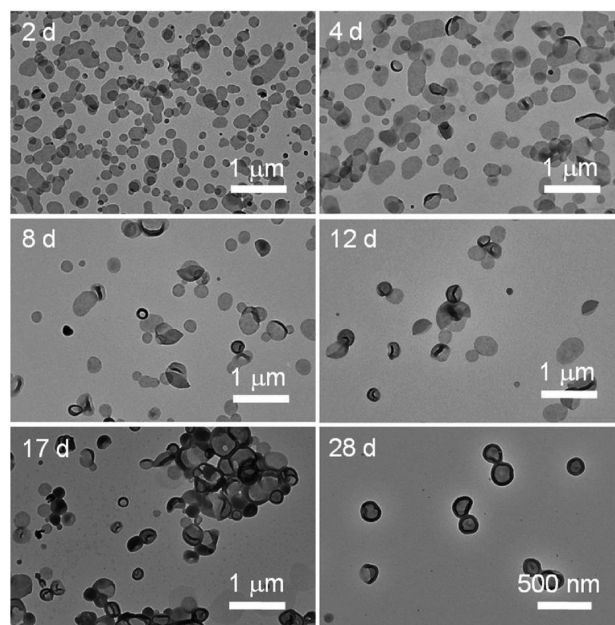


**Figure 3.** TEM (A) and HRTEM (B, C) images of self-assembled *AbBA* molecular bottlebrushes at 8 h. Image (C) was titled for 30° of (B). Sample was stained by RuO<sub>4</sub> vapor. Inset in (A) was Fourier-transformed from pattern of disk. Digits in (A) were aggregation number of *AbBA* molecules.

remarkable that there were many white dots in each disk that were organized in a highly ordered way. Since the PS components were stained, the continuous dark areas were attributed to the PS microdomains and the white dots were the PBA cores. The inset pattern was the Fourier-transformed image and it shows a symmetric hexagonal pattern. Moreover, it is noteworthy that the edges of some disks, highlighted by dash lines, were straight instead of arc, a crystalline-like packing character of rigid rods. Please also notice those elongated disks pointed by the black arrows in Figure 3A. It is apparently that the elongated disks were the merged disks at the straight edges. The specimen for HRTEM (Figure 3B) was also titled for 30°, and the image (Figure 3C) demonstrates a characteristic pattern of titled rods, proving that the axes of brush segments were perpendicular to the disk plane. From the TEM image, the periodic spacing  $d$  between axes of neighboring brushes was given to be 9 nm and it corresponded to the diameter of cross-section of brush segments. It is also noteworthy that the aggregation number for each disk may be counted directly from the TEM image. The digits of selected disks in Figure 3A are the aggregation number of *AbBA* to form one disk. As far as we know, this is the first example that the aggregation number of block copolymers can be counted precisely with TEM image.

Above results showed an intriguing 2D packing character of block copolymer nanoobjects to form disk-like micelles with a hexagonal pattern. It is apparently that the nanosized rigid middle blocks were organized in a parallel manner during micellization. Probably due to the rigidity of brushes, the self-assembled membranes with an edge thickness of ~30 nm should have a high bending energy that could not be compensated by the free energy released by membrane closure. Instead, the disks should have a tendency to propagate from the

edge and grow two-dimensionally. Because the backbone was prepared by controlled radical polymerization, the length of brush segments still had a distribution and the shorter one might end-cape the edge to terminate further growth. In order to prove above speculation, we also conducted self-assembly of the *AbBA* brushes with lower  $c_{\text{MeOH}}$ , namely, more DMF content in the mixed solvent that may soften the brush membranes. At 8 h (Figure S7) and 2 d (in Figure 4) of self-



**Figure 4.** TEM images of self-assembled *AbBA* molecular bottlebrushes in DMF/MeOH solution;  $c_{\text{ini}} = 5 \text{ mg/mL}$ ;  $c_{\text{MeOH}} = 80 \text{ vol } \%$ . Sample for TEM was not stained.

assembly, exclusive disk-like micelles were also given. The disks under such a condition still had a highly organized packing structure (Figure S8). Then, at 4 d, they became even larger and few disks began to bend. At 8 and 12 d, more bending disks and even vesicles could be found. At 17 and 28 d, the vesicles with a wall thickness of ca. 33 nm became the majority. Therefore, the disk-like micelles were indeed stabilized by the stiffened *AbBA* membranes. Please also notice that such a very slow process allows a direct observation of vesicle formation through the membrane closure, supplying a unique evidence of vesicle formation mechanism.

In summary, disk-like micelles with a highly ordered molecular packing structure were obtained by self-assembly of *AbBA* core/shell bottlebrush in solution. Since the rigid middle blocks stiffened the assembled membranes, this is a straightforward strategy and thus is a generalized approach to fabricate the disk shaped nano-objects. Furthermore, the results have intrigued even more interesting topics. For example, the disk composed of the core/shell building blocks has many highly packed subdivided compartments with only few nanometers. It may be applied as the template to organize tiny functional particles into 2D pattern. Also, the core/shell building blocks allow generating uniform pores along the membrane of vesicles, which supplies an amazing character for release loaded molecules.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details of synthesis of molecular bottlebrushes and additional TEM, SEM, and AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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