Electronic Supplementary Information:

Convex Lens-Shaped Polymer Particles by Tuning Interfacial Interaction

Jiangping Xu, Yi Yang, Ke Wang, Yuqing Wu, Jintao Zhu*

Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education

School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

*Corresponding authors, E-mail: jtzhu@mail.hust.edu.cn (J. Z.)

EXPERIMENTAL SECTION

1. Materials

Diblock copolymer PS_{51K}-*b*-$P4VP_{18K}$ (M_w/M_n = 1.15) and triblock copolymer $P4VP_{4.5K}$-*b*-PS_{38K}-*b*-$P4VP_{4.5K}$ (M_w/M_n = 1.10) were purchased from Polymer Source, Inc., Canada. Poly(vinyl alcohol) (PVA, M_w: 13K−23K g mol^{-1}, 87-89% hydrolyzed), cetyltrimethylammonium bromide (CTAB, purity ≥ 99%), and 3-*n*-pentadecylphenol (PDP, purity ≥ 90 %, recrystallized twice from hexane before use) were purchased from Aldrich. 1, 4-diiodobutane (DIB, purity 99 %) was supplied by Alfa Aesar. All of the materials were used as received without further purification unless mentioned specifically.

2. Preparation of the Convex Lens (CL)-Like Particles

Emulsion-solvent evaporation method was applied to prepare the CL particles.[1, 2] The BCPs and PDP were respectively dissolved in chloroform at a concentration of 10 mg/mL. Then, the copolymer solution was mixed with desired amount of PDP solution, followed by stirring for 24 h to form PS-*b*-

$P4VP(PDP)_x$ comb-like supramolecules, where x was the molar ratio of PDP to 4VP unit. Subsequently, 0.1 mL of the mixed solution was emulsified with 1.0 mL aqueous solution of surfactants (CTAB or PVA or their mixture, 3 mg/mL) by using a hand-driven membrane-extrusion emulsification. Chloroform was then allowed to slowly evaporate for 3 days at 30 °C. Finally, the microparticles were separated by centrifugation (14 000 rpm, 6 min) to remove the surfactants.

3. Solvent-Adsorption Annealing

In a typical annealing process, 0.05 mL of the particle suspension was firstly centrifuged to remove the surfactant (for example, PVA). Then, 0.5 mL of another surfactant solution (*e.g.*, CTAB) was added to redisperse the particles. Afterward, the suspension with particle content of ~ 0.1 mg/mL in a small vial (5 mL) was placed inside a large vial (25 mL) with 1.0 mL of chloroform at 30 °C for 8 h. Subsequently, the inner small vial was taken out to the ambient atmosphere to release the absorbed chloroform for 12 h at 30 °C. Finally, structure of the particles is kinetically frozen after removal of chloroform, and the particles were separated by centrifugation (14 000 rpm, 6 min) to remove the surfactants.[3]

4. Disassembly of the CL Particles

For the preparation of porous particles, the CL particles were first centrifuged to remove the supernatant, then redispersed in ethanol at 25 °C for 24 h or at 60 °C for 20 min. The P4VP(PDP) domains would be swollen and pores were formed after removal of ethanol. On the other hand, nano-objects with P4VP as the core and PS as the shell could be obtained by firstly crosslinking P4VP domains and then dissolving PS domains. In a typical experiment, DIB was used to selectively crosslink $P4VP(PDP)_x$ block. DIB was first dissolved in ethanol at a concentration of 50 mg/mL and then added to the CL particle suspension (DIB:4VP unit = 5:1). After being stirred at 45 °C for 3 days, the crosslinked particles were separated by centrifugation (14 000 rpm, 6 min) and washed in ethanol for 3 times. Then, the particles were dispersed in chloroform, which could dissolve PS domains.

5. Characterization

Internal structure of the BCP particles was investigated using FEI TecnaiG^2 20 transmission electron microscope (TEM) operated at an accelerated voltage of 200 kV. Before TEM characterization, the samples were selectively stained with iodine vapor for 2 h (for P4VP(PDP) domains). The surface topology of the particles was characterized by Sirion 200 scanning electron microscope (SEM).

6. Construction of the Voronoi Diagram

The Voronoi diagram is used to indicate the degree of order of P4VP domains. To construct the Voronoi diagram, each P4VP domain in the CL-like particles is regarded as a point. These points are connected to all of their nearest neighbors without making a line that crosses another. The next step is to draw the perpendicular bisector of each line. These perpendicular bisectors will construct a polygon, which is named as a Voronoi cell. Generally, each point has a corresponding cell. All of these cells form the Voronoi diagram, which can indicate the presence of defects in the stacking of P4VP domains.[4]

ADDITIONAL FIGURES

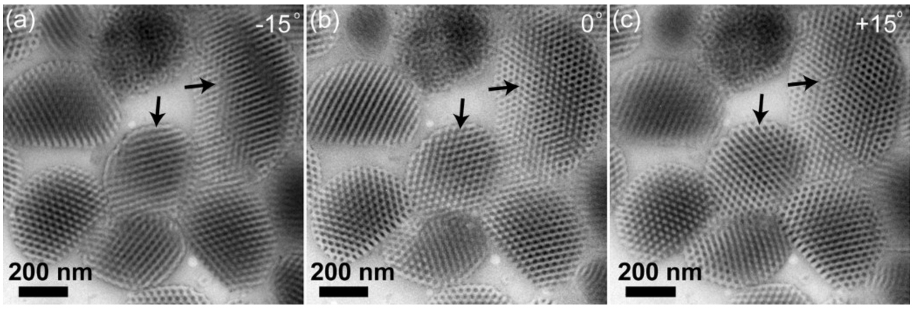


Fig. S1 TEM images of the CL-like particles tilted at (a) -15°, (b) 0°, and (c) +15°. The arrows show the obvious changes of the TEM images. The P4VP(PDP) domains are selectively stained by I_2 vapor before TEM investigation.

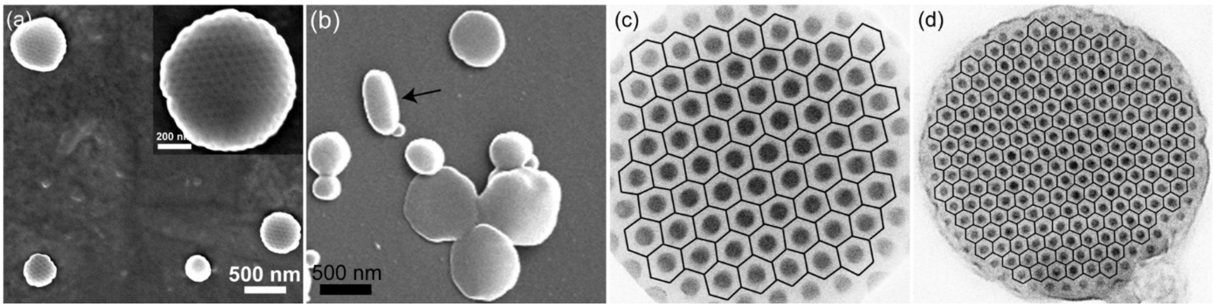
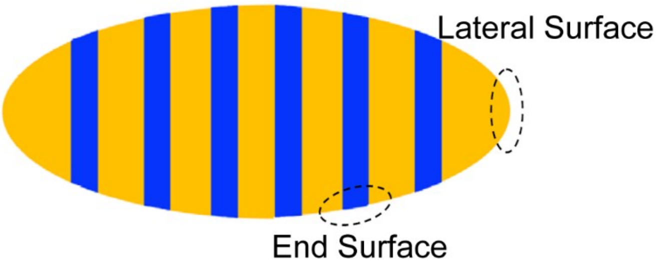


Fig. S2 (a, b) SEM images of the CL-like particles shown in Figure 1d. (c, d) Voronoi diagram constructed from the locations of the P4VP(PDP) domain center in the convex-lens shaped particles from (c) PS_{51K}-*b*-$P4VP_{18K}(PDP)_{0.2}$, and (d) $P4VP_{4.5K}$-*b*-PS_{38K}-*b*-$P4VP_{4.5K}(PDP)_{0.25}$, respectively. The center of every P4VP(PDP) domain has six nearest neighbors. This high degree of lateral order is found to extend over the entire area of the particles.



Scheme S1. Schematic diagram showing the side-view of CL-like particles. The surface energies are different at different positions of the particles, due to the different packing structures of polymer chains at the lateral surface and end surface. The difference in the surface energy induces the shape transition from the spherical shape to the CL-like shape.[5]

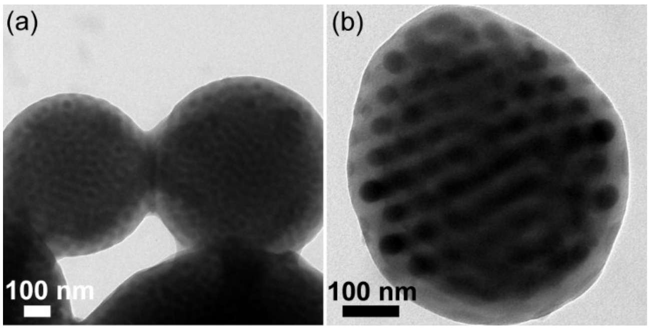


Fig. S3 TEM images of the PS_{51K}-*b*-$P4VP_{18K}(PDP)_{0.2}$ obtained in CTAB of 5 mg/mL. Two dominating structures (a) random cylinders and (b) stacked rings can be observed in the particles. No CL-like particles can be obtained in this case. The P4VP(PDP) domains are selectively stained by I_2 vapor before TEM investigation.

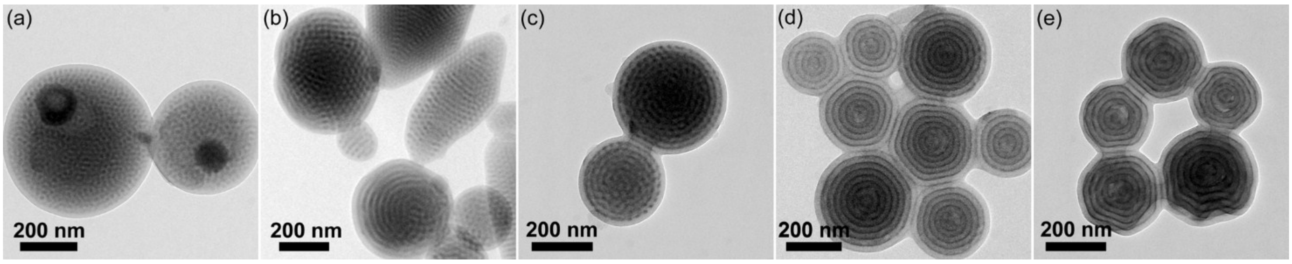


Fig. S4 TEM images of the P4VP$_{4.5K}$-*b*-PS$_{38K}$-*b*-P4VP$_{4.5K}$(PDP)$_x$ particles obtained when PVA (3 mg/mL) acting as surfactant, where x equals to (a) 0, (b) 0.25, (c) 0.50, (d) 0.75, and (e) 1.0. The P4VP(PDP) domains are selectively stained by I$_2$ vapor before TEM investigation. The outermost layer of the particles is proven to be P4VP(PDP), based on the selective iodine staining. In this case, the affinity of PVA to PS block is not strong enough to pull PS chains to the interface. Thus, the interface is not neural for both PS and P4VP(PDP) blocks and no CL-like particles can be observed.

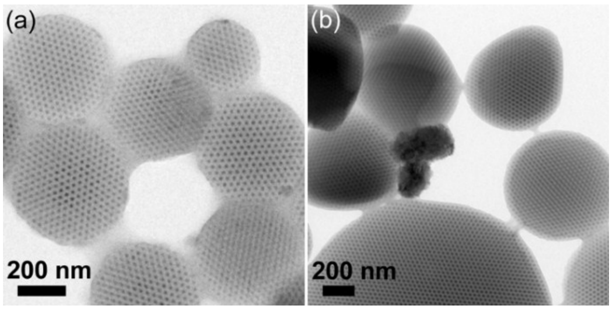


Fig. S5 TEM images of the CL-like particles obtained through solvent-absorption annealing the particles in mixed surfactants of CTAB and PVA. The P4VP$_{4.5K}$-*b*-PS$_{38K}$-*b*-P4VP$_{4.5K}$(PDP)$_x$ particles which have twisted cylindrical structures (**Figure 3**a) are used as the initial state of the annealing process. The weight ratios (w) of CTAB to PVA are (a) 1:5 and (d) 1:3, respectively. The P4VP(PDP) domains are selectively stained by I$_2$ vapor before TEM investigation.

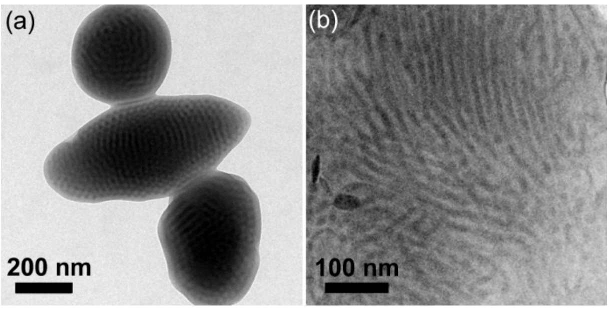


Fig. S6 TEM images of (a) the $P4VP_{4.5K}$-*b*-PS_{27K}-*b*-$P4VP_{4.5K}$ particles obtained in PVA and (b) the cylindrical micelles obtained by crosslinking and disassembling of the particles in (a). The P4VP domains are selectively stained by I_2 vapor before TEM investigation.

REFERENCES

1. R. Deng, S. Liu, J. Li, Y. Liao, J. Tao and J. Zhu, *Adv. Mater.*, 2012, **24**, 1889-1893.

2. R. Tangirala, R. Revanur, T. P. Russell and T. Emrick, *Langmuir*, 2007, **23**, 965-969.

3. J. Xu, K. Wang, J. Li, H. Zhou, X. Xie and J. Zhu, *Macromolecules*, 2015, **48**, 2628-2636.

4. K. H. Ku, J. M. Shin, M. P. Kim, C.-H. Lee, M.-K. Seo, G.-R. Yi, S. G. Jang and B. J. Kim, *J. Am. Chem. Soc.*, 2014, **136**, 9982-9989.

5. H. Yang, K. H. Ku, J. M. Shin, J. Lee, C. H. Park, H.-H. Cho, S. G. Jang and B. J. Kim, *Chem. Mater.*, 2016, **28**, 830-837.