

## Supporting information

### **Synthesis of monodisperse nano colloidal microspheres with controlled size by vesicle bilayer templating**

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## 1. Experimental section

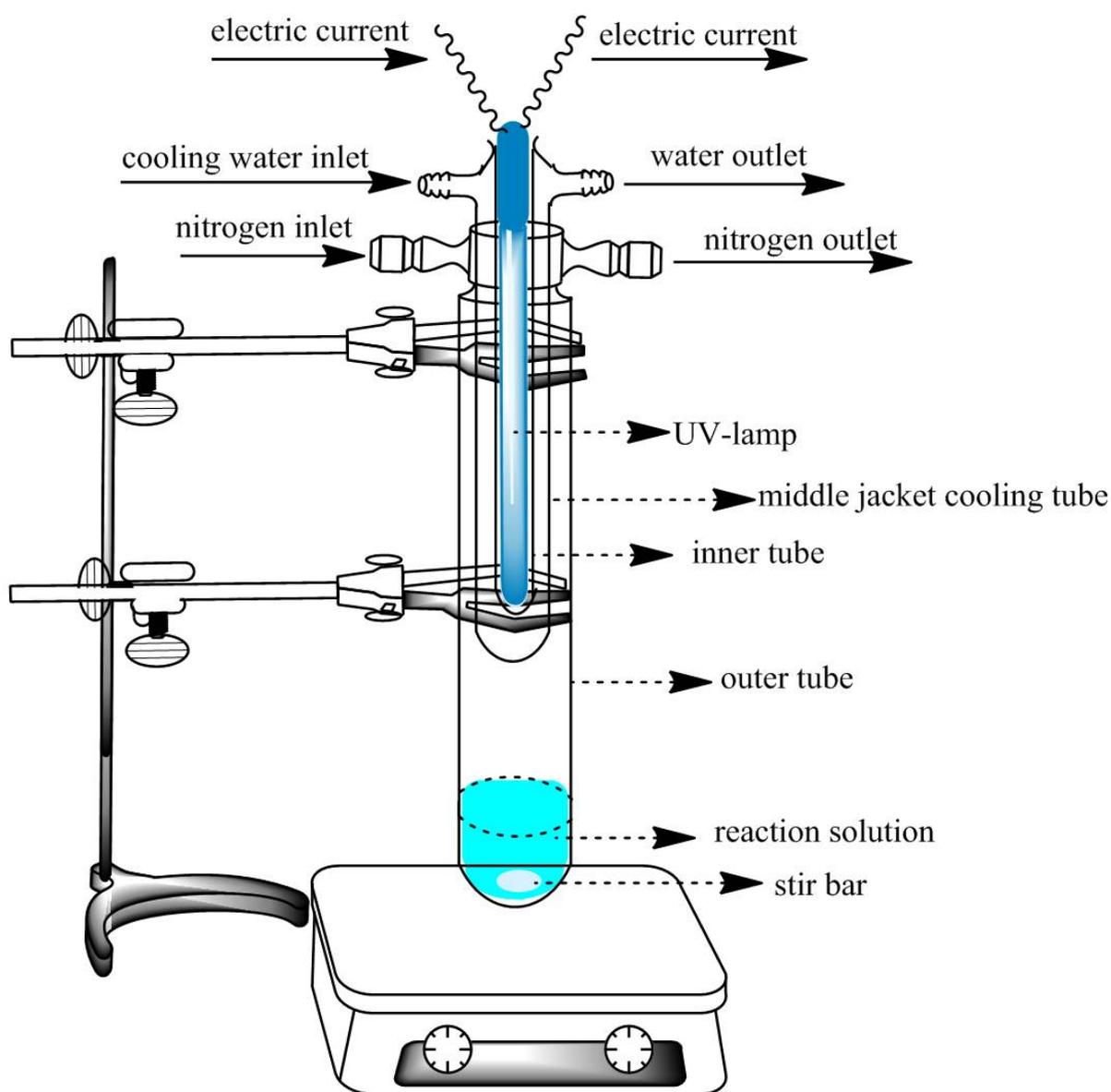
### 1.1 Materials

HBPO-star-PEO was synthesized based on our previous reports through cationic ring-opening polymerization (CROP).<sup>1,2</sup> The number-average molecular weight ( $M_n$ ) measured by GPC is about 7400. Polydispersity index ( $M_w/M_n$ ) = 2.5. The number-average degree of polymerization (DP) of the PEO arms is 2.7. Styrene (St, Shanghai Chemical Reagent CO., AR) was purified by distillation under reduce pressure. Divinylbenzene (DVB, 55%, mixture of isomers, Aldrich), 2, 2-Dimethoxy-2-phenylacetophenone (DMPA, 99%, Acros) and Pyrene (98%, Aldrich) were used without further purification.

### 1.2 Preparation of uniform PS particles and colloidal crystals

The quartz reactor was shown in Figure S1, which is composed of an inner tube, a middle jacket cooling tube, and an outer tube. A UV light source (DY 250, 250 W) was located in the inner tube of the reactor. The range of wavelengths of the lamp ( $\lambda_{max}$ =366 nm) matched the UV-absorbing region of the photo initiator. The heat generated by the UV lamp was removed by the middle jacket cooling tube. Prior to polymerization, oxygen in the reactor was removed by repeated evacuation cycles followed by flushing with nitrogen. For the reaction, HBPO-star-PEO was first put into the water inside the outer tube with a concentration of 1 mg/mL to get a vesicle solution. The initiator DMPA was first dissolved in the monomers (St and DVB) at a mass fraction of 0.2%, and was then added to the vesicle aqueous dispersion at room temperature and stirred by a magnetic bar for 24 hrs to dissolve the monomers completely in dark. After reaction for 3 hrs, reaction solutions were disposed with a further sonication step (2 hrs, 300W, 40KHz) to totally rupture vesicles and separate the particles from the vesicle templates. A small amount of reaction solution was collected at different time intervals through a syringe for the following TEM, SEM and DLS analyses.

Colloidal crystals were grown on quartz plate by vertical deposition technique.<sup>3</sup> Prior to use, all quartz plates and vials were soaked overnight in a chromic-sulfuric acid cleaning solution, rinsed with ultra-pure water, and dried in a steam of nitrogen. The PS nanoparticle supernatant was filtered through filters with the pore size of 0.45  $\mu\text{m}$  to remove agglomeration, and then a clean quartz plate was placed vertically into a vial containing diluted aqueous solution of filtrate. The vial is subsequently placed in a temperature- and humidity-controlled chamber. The evaporation temperature was controlled at about 50  $^{\circ}\text{C}$ , the relative humidity was about 80%.



**Figure S1.** The scheme for quartz sleeve reactor

## 2. Instruments and measurements

**2.1 Optical and Fluorescent microscope (OM).** The morphologies of the vesicles were observed by optical microscopy microscope on a Leica DM4500 B. For the microscope observation, the aqueous solution was dropped onto a glass slide and then observed directly under the microscope.

**2.2 Scanning electron microscope (SEM).** SEM experiments were performed on JEOL 7401F field emission scanning electron microscope, with an accelerating voltage 1 kV or 5 kV. The samples were prepared by dropping a small drop of the polymer solution onto silicon wafer, and then quickly frozen by liquid nitrogen, or dried at room temperature for 24 hrs. The samples were coated with a thin film of gold before measuring.

**2.3 Transmission electron microscopy (TEM).** TEM results were obtained on a JEM-2010/INCA OXFORD instrument operating at an accelerating voltage of 200KV. For TEM measurement, a small drop of the polymer solution was placed onto 400 mesh copper grids coated with Parlodion film stabilized with vacuum evaporated carbon, and then were dried at room temperature for 24 hrs.

**2.4 Dynamic Light Scattering (DLS).** DLS measurements were performed on aqueous solutions at 25°C with a Malvern Zetasizer Nano S (Malvern Instruments, Ltd.) equipped with a 4 mW He-Ne laser light operating at  $\lambda=633$  nm and a scattering angle of 90°.

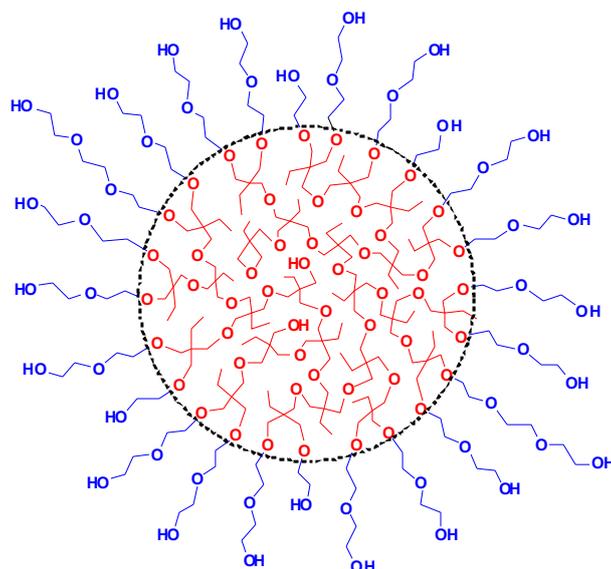
**2.5 NMR measurement.** <sup>1</sup>H NMR and <sup>13</sup>C NMR were performed on a Varian Mercury Plus 400-MHz spectrometer using deuterated chloroform or deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>) as solvents at 20°C, and tetramethylsilane (TMS) was used as the internal reference.

**2.6 Gel Permeation Chromatography (GPC).** The molecular weights of the products were measured by GPC on a HLC-8320GPC (TOSOH, EcoSEC GPC System) system at 40°C with N,N-dimethylformamide as mobile phase at a flow rate of 0.6 ml/min.

### 3. Characterizations

#### 3.1 Synthesis of HBPO-star-PEO

The  $^{13}\text{C}$  NMR spectra of HBPO is shown in Figure S3, degree of branching (DB) calculated by comparing the integral of peaks (D, L, T) according to the formula  $(D+T)/(D+L+T)$  was about 39%. The  $^1\text{H}$  NMR spectra of HBPO-star-PEOs (Figure S2) is shown in Figure S4, the number-average degree of polymerization (DP) of the PEO arms calculated by comparing the integral of peaks d with that of peak a according to the formula  $(3S_d/4S_a)$  was about 2.7. The GPC measurements (Figure S5) showed a unimodal distribution with a number-average molecular weight of 7400 and a polydispersity of 2.5.



**Figure S2.** Schematic representation of the HBPO-star-PEO multiarm copolymer. The dashed circle shows the boundary between the HBPO core (red) and the PEO arms (blue).



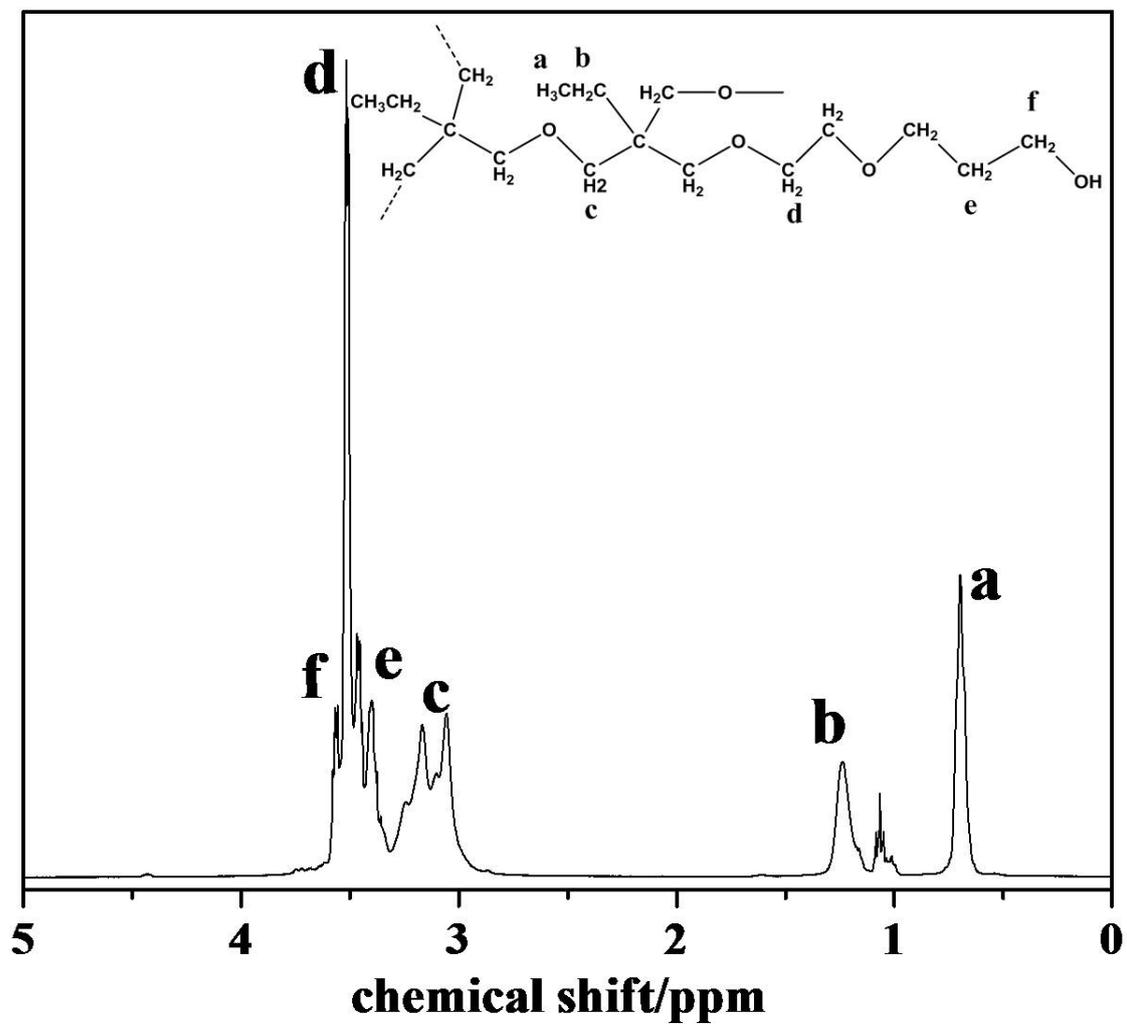
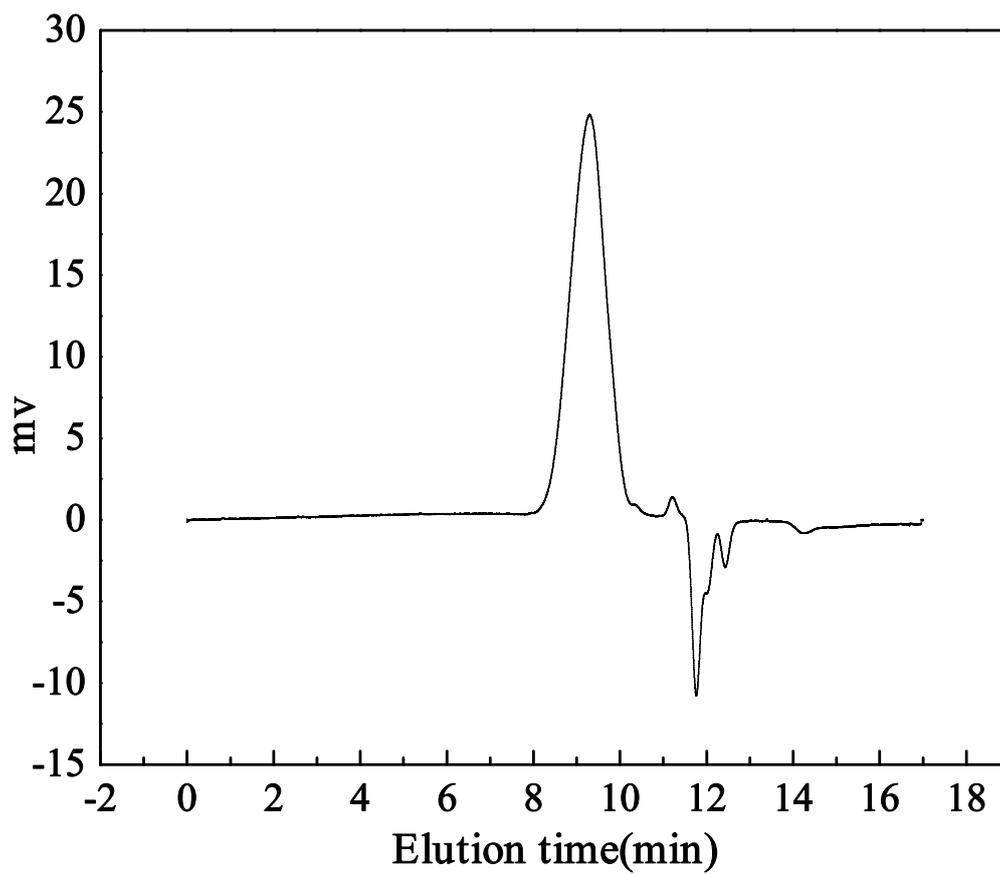
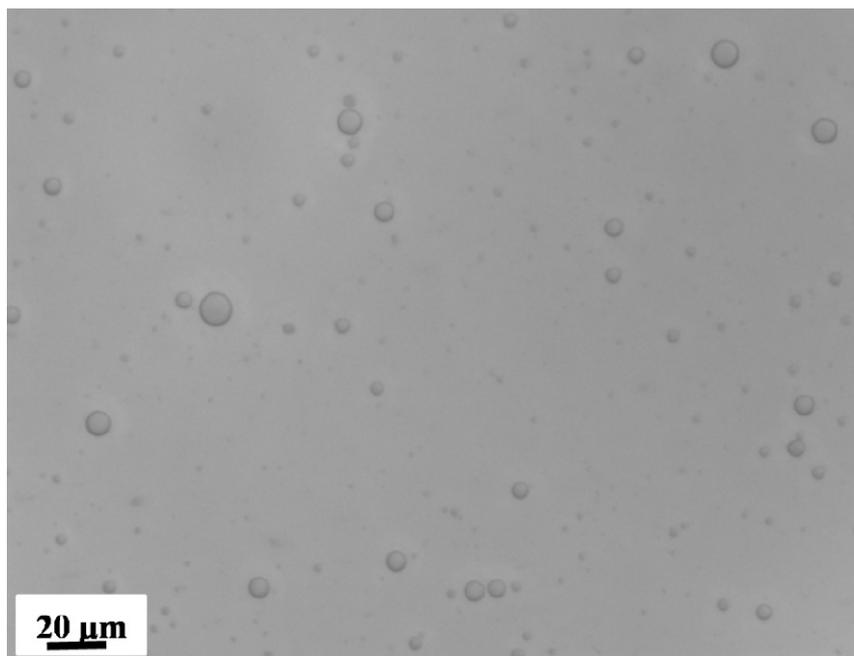


Figure S4. The  $^1\text{H}$  NMR spectra of HBPO-star-PEOs ( $\text{CDCl}_3$  as solvent).



**Figure S5.** The GPC traces of HBPO-star-PEOs with DMF as eluent.

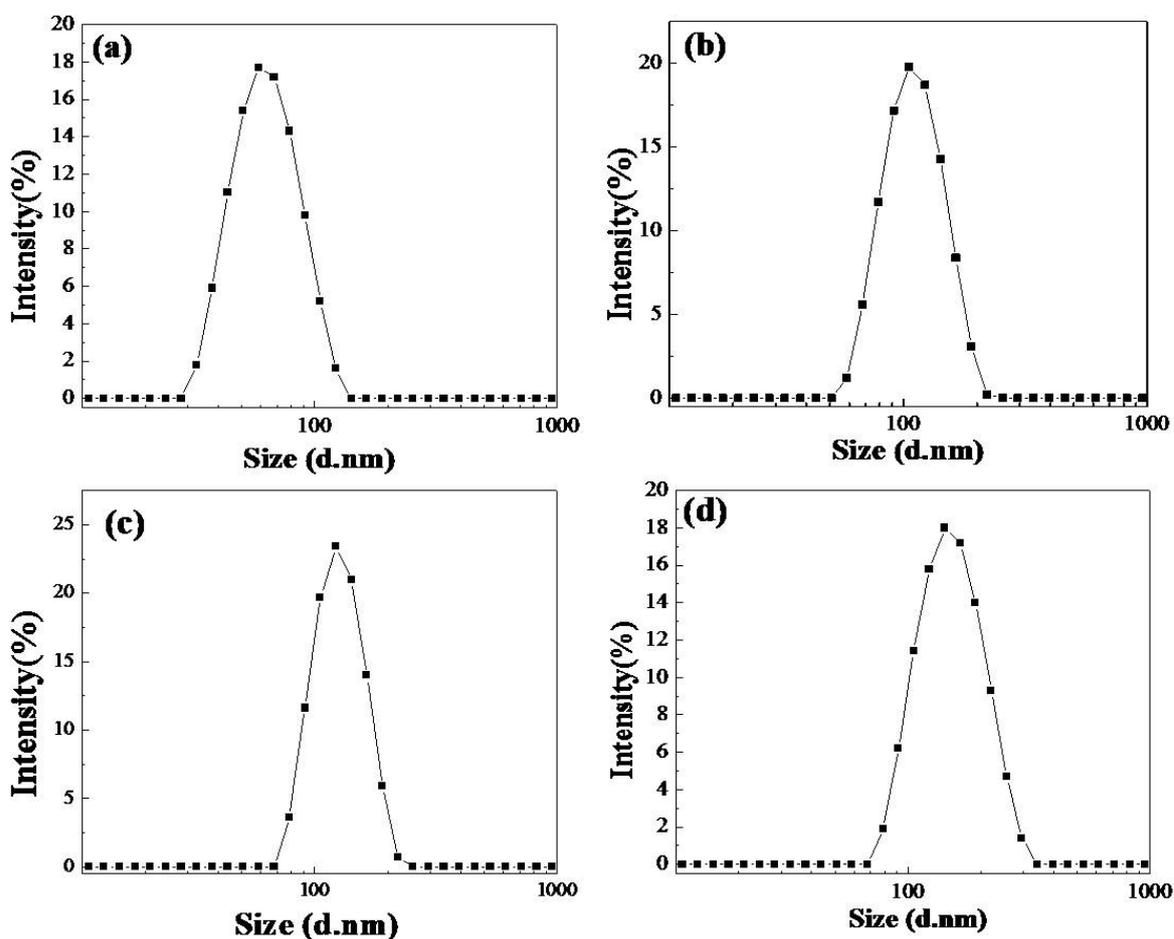
### 3.2 The morphology characterization of BPs from HBPO-star-PEOs



**Figure S6.** Optical micrograph of BPs obtained from the self-assembly of HBPO-star-PEOs in water.

### 3.3 The size distributions of PS particles

By changing the feed ratios in the monomer compositions during the intervesicular polymerization, we obtained a series of monodisperse PS microspheres. The intensity-weighted particle size distributions of PS colloidal particles (Figure S7) were obtained at different HBPO-star-PEO/St mass ratios of 1:1 (a); 1:2 (b); 1:4 (c) and 1:6 (d).



**Figure S7.** The intensity-weighted particle size distributions of PS colloidal particles obtained at different HBPO-star-PEO/St mass ratios of 1:1 (a); 1:2 (b); 1:4 (c) and 1:6 (d).

#### References and Notes

1. Y. F. Zhou, D. Y. Yan, *Angew. Chem. Int. Ed.* 2004, **43**, 4896.
2. Y. F. Zhou, D. Y. Yan, W. Y. Dong, Y. Tian, *J. Phys. Chem. B* 2007, **111**, 1262.
3. S. L. Kuai, X. F. Hu, A. Haché and V. V. Truong, *J. Cryst. Growth*, 2004, **267**, 317.