

**Supporting Information**

**Host–guest complexation modulated aqueous  
polymerization-induced self-assembly for monodisperse  
hierarchical nanoflowers**

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## 1. Experimental Section

### 1.1 Materials

Randomly methylated- $\beta$ -cyclodextrin (MCD,  $M = 1320$  Da, with average degree of substitution = 1.8, 98%, Zhiyuan Biotech) was used as received. Styrene (J&K Chemical) was passed through alkaline aluminum oxide column. 4,4'-Azobis(4-cyanopentanoic acid) (ACVA; 98%, J&K Chemical, mPEG<sub>45</sub>-OH ( $M_n = 2000$  g mol<sup>-1</sup>, J&K Chemical), and Oxalyl chloride (98%, J&K Chemical) were used as received. 2-Methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid (TTC) and PEG-TTC macro-CTA were synthesized according to published procedures. [S1, S2]

### 1.2 Host-guest modulated aqueous polymerization

Macro-CTA (PEG<sub>45</sub>-TTC 0.115 g, 0.05 mmol) and St (2.08 g, 0.02 mol), MCD (27.7 g, 0.021 mol) were dispersed in 45 mL H<sub>2</sub>O. The molar ratio of MCD to St was 1.05, and the weight ratio of MCD to St was 13.3. The total solid content of copolymer was ca. 3 wt %. After stirring overnight, and pass through nylon filter, a homogeneous MCD solution was obtained. ACVA (4.9 mg, 0.0175 mmol, ACVA/macro-CTA = 0.35:1) was added, and the solution was purged with N<sub>2</sub> for 30 min. Then, the mixture was heated at 70 °C in an oil bath for 8 h. After polymerization, the dispersion was quenched by cooling in iced water and exposure to air. The stable dispersion of nanoflowers was obtained by dialysis against water for two days to remove free MCD.

### 1.7 Characterization

**<sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H NMR):** <sup>1</sup>H NMR spectra were recorded using 400 MHz JEOL JNM-EA 400 spectrometer (D<sub>2</sub>O and CDCl<sub>3</sub> as solvent). To determine the degree of polymerization, PEG-*b*-PSt samples for NMR was further purified by precipitated in CH<sub>3</sub>CN and dried under reduced pressure at room temperature.

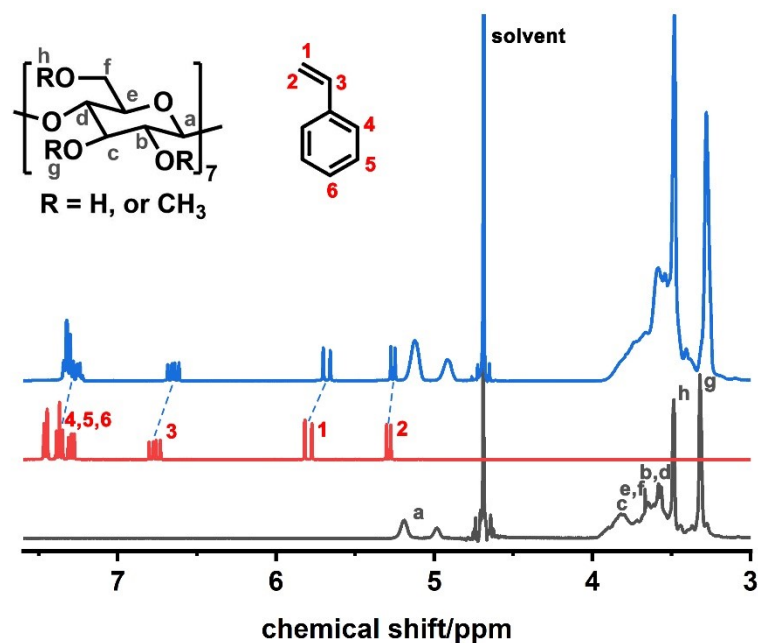
**Size-Exclusion Chromatography (SEC):** The number-average molecular weight ( $M_n$ ) and dispersity ( $\mathcal{D}$ ) of the PEG-*b*-PSt were characterized by a Waters GPC instrument, using THF (containing 2% trimethylamine) with a flow rate of 1.0 mL min<sup>-1</sup> as eluent, at 35 °C. PEG-*b*-PSt samples was extracted and freeze-dried, then dissolved in THF. A series

of near-monodisperse linear polystyrenes ( $M_p = 580$  to  $281000$  g/mol) were used for calibration.

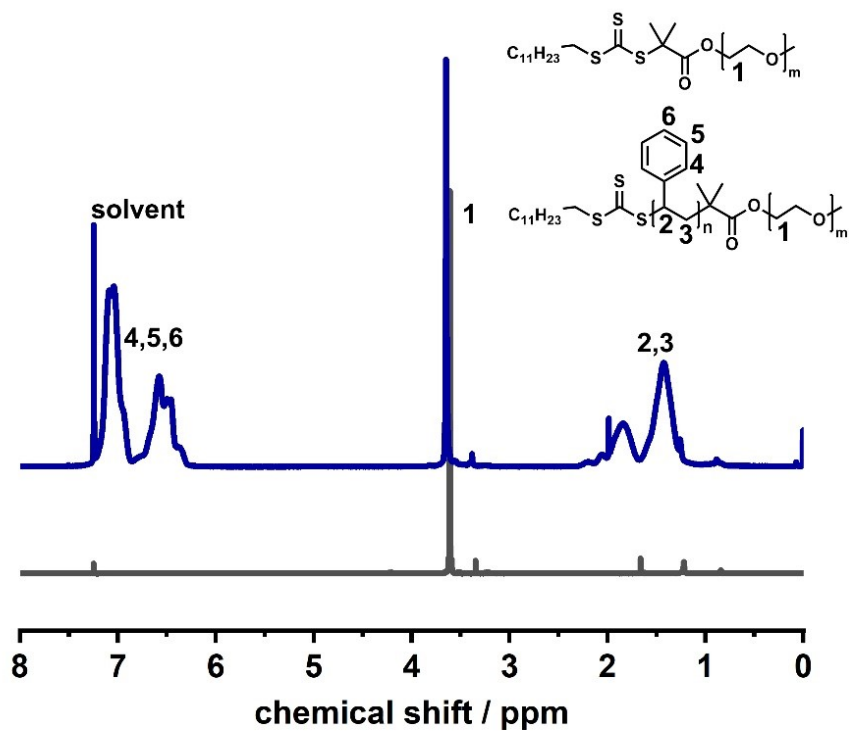
**High performance liquid chromatography (HPLC):** The styrene conversion was measured using Agilent 1200 series HPLC equipped with G1315B diode array detector. (245 nm) The samples were diluted 100 folds by  $\text{CH}_3\text{CN} : \text{H}_2\text{O} = 4:1$ , and filtered through  $80\ \mu\text{m}$  filters. The following conditions were used for measurement: 20 min, eluent contained  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$ , with  $\text{CH}_3\text{CN}$  gradually increased from 65 to 95 v/v%.

**Dynamic Light Scattering (DLS):** DLS measurements were recorded using Malvern Zetasizer Nano ZS90 at  $25\ ^\circ\text{C}$  with a He-Ne laser (633 nm). Scattering light at  $90^\circ$  was detected. The dispersions were diluted for DLS measurements. All the DLS tests were repeated three times.

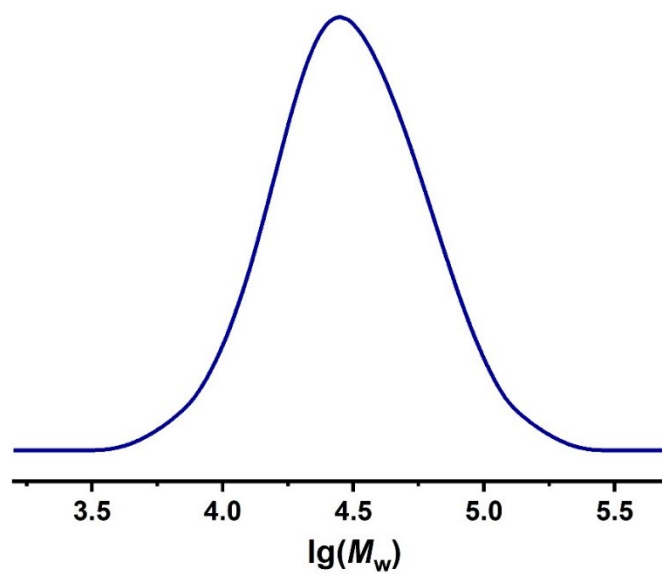
**Transmission Electron Microscope (TEM):** Morphologies of the samples were characterized using a JEM-2010 microscope with an accelerating voltage of 120 kV, equipped with a CCD camera. The dispersion was dialysis against water for two days to remove free MCD. Then, the dispersion was diluted and a droplet of dispersion was dropped onto a carbon-coated copper grid. The samples onto the copper grid were dried at room temperature for 24 h.



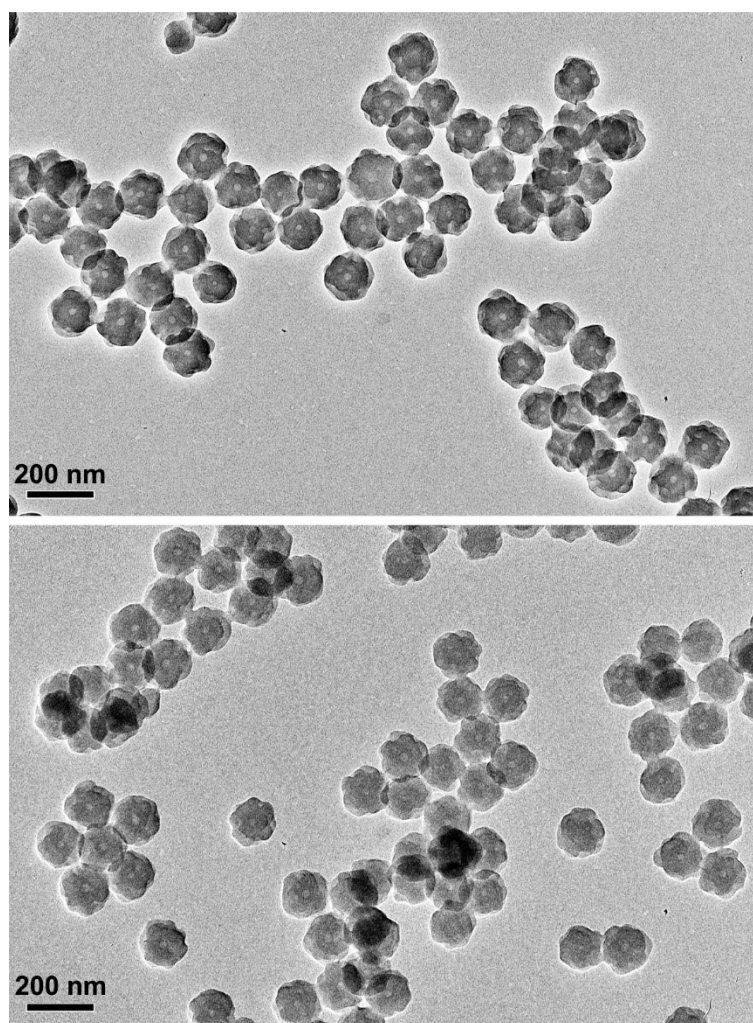
**Fig. S1**  $^1\text{H}$  NMR spectra of MCD (grey, solvent:  $\text{D}_2\text{O}$ ), styrene (red, solvent:  $\text{CDCl}_3$ ), and MCD/styrene complex (blue, solvent:  $\text{D}_2\text{O}$ ).



**Fig. S2**  $^1\text{H}$  NMR spectra of  $\text{PEG}_{45}$ -derived macro-CTA (grey) and  $\text{PEG}_{45}$ -*b*- $\text{PSt}_{289}$  block copolymer (blue) prepared by host–guest modulated aqueous RAFT polymerization. ( $\text{CDCl}_3$  as solvent, at  $25^\circ\text{C}$ )



**Fig. S3** SEC trace of PEG<sub>45</sub>-*b*-PSt<sub>400</sub> ( $M_n = 24700$ ,  $M_w = 37300$ ,  $D = 1.51$ )

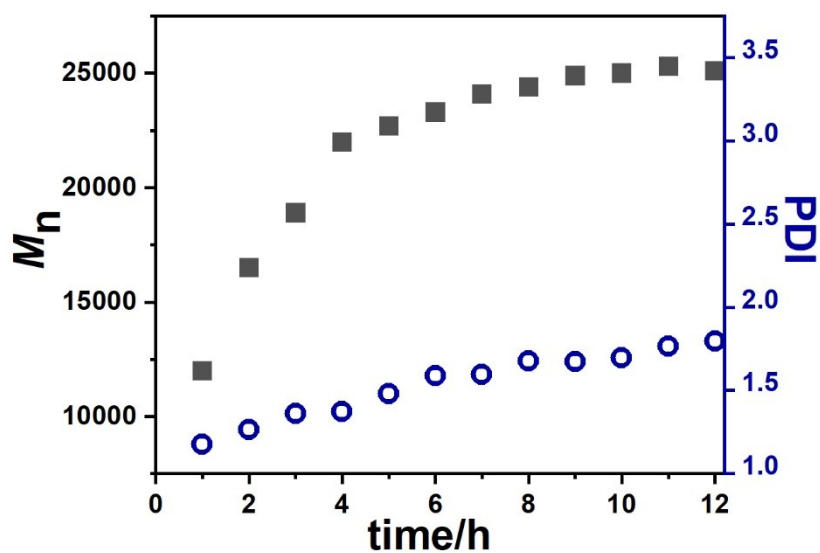
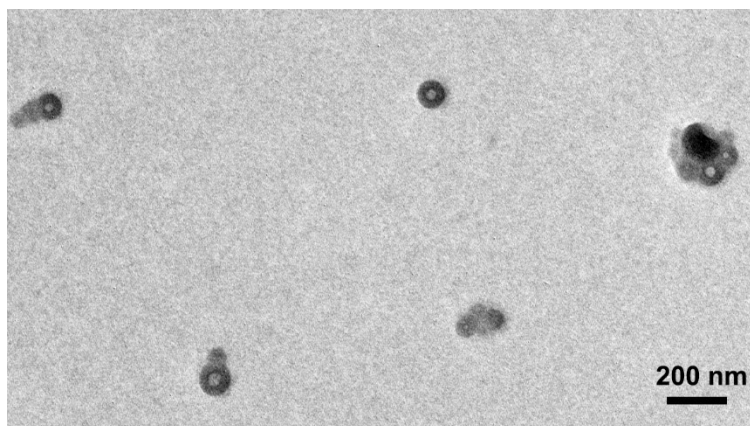


**Fig. S4** Supplemented TEM images of PEG<sub>45</sub>-*b*-PSt<sub>289</sub> nanoflowers.

**Table S1** Molecular weight and nanoparticle hydrodiameter of PEG-*b*-PSt

Time/h	HPLC		SEC		DLS		
	Conv./ %	DP <sub>theo</sub>	$M_n$	$M_w$	$\bar{D}$	$D_h$ /nm	PDI
1	18	72	12000	14100	1.18	51	0.26
2	31	126	16500	20900	1.27	89	0.14
3	43	174	18900	25700	1.36	132	0.11
4	57	227	22000	30200	1.37	155	0.04
5	65	258	22700	33600	1.48	167	0.03
6	74	295	23300	37000	1.59	176	0.03
7	79	317	24100	38500	1.60	186	0.02
8	84	335	24400	40900	1.68	189	0.03
9	86	344	24900	41700	1.67	*	-
10	87	347	25000	42400	1.70	*	-
11	88	352	25300	44700	1.77	*	-
12	88	353	25100	45100	1.80	*	-

\* No stable results, due to a fraction of aggregates.

**Fig. S5** Molecular weight and polydispersity versus polymerization time.**Fig. S6** Supplemented TEM images of PEG-*b*-PSt vesicles obtained at 2h.

**Table S2** Comparison of molecular weight and nanoparticle hydrodiameter of PEG-*b*-PSt

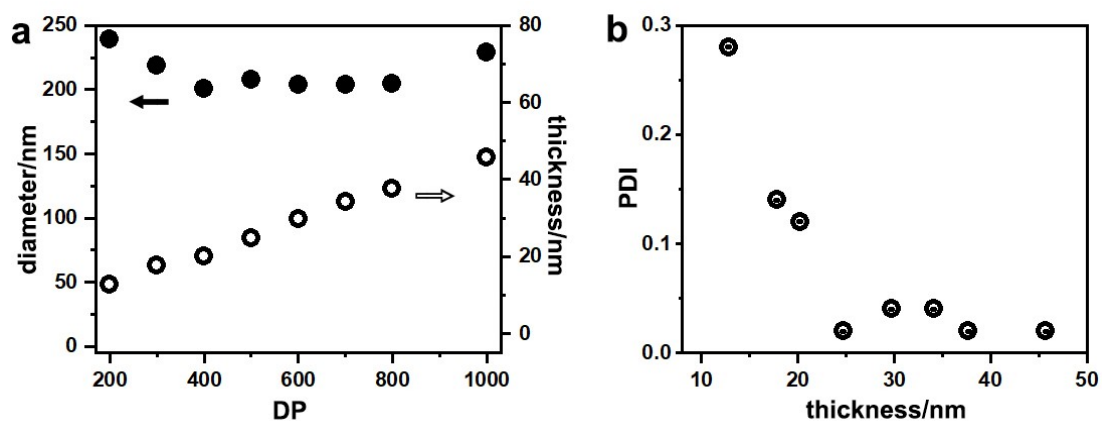
PGMA <sub>55</sub> - <i>b</i> -PHPMA <sub>x</sub> <sup>a</sup>				PEG <sub>45</sub> - <i>b</i> -PSt <sub>y</sub>			
DP	Size <sub>DLS</sub> / nm	PDI <sub>DLS</sub>	<i>T</i> <sub>SAXS</sub> /nm	DP	Size <sub>DLS</sub> / nm	PDI <sub>DLS</sub>	<i>T</i> <sub>calculation</sub> <sup>b</sup> /nm
200	239	0.28	12.8	72	51	0.26	–
300	219	0.14	17.8	126	89	0.14	24.5
400	201	0.12	22.2	174	132	0.11	46
500	208	0.02	24.7	227	155	0.04	57.5
600	204	0.04	29.7	258	167	0.03	63.5
700	204	0.04	24.1	295	176	0.03	68
800	205	0.02	37.7	317	186	0.02	73
1000	229	0.02	45.7	335	189	0.03	74.5

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<sup>b</sup> *T*<sub>calculation</sub> represents wall thickness of vesicles and nanoflowers;

$$T_{\text{calculation}} = (\text{Outer diameter} - \text{inner diameter})/2$$

For a simple calculation, we fixed inner diameter = 20 nm and used Size<sub>DLS</sub> as outer diameter of vesicles and nanoflowers, which would certainly bring in some deviation between calculated vesicle thickness and real vesicle thickness.



**Fig. S7** a) Evolution of vesicle diameter and vesicle thickness with DP, for PGMA<sub>55</sub>-*b*-PHPMA<sub>x</sub>, x=200, 300, 400, 500, 600, 700, 800, and 1000, respectively. Spheres represent diameter, hollow spheres represent vesicle thickness, b) evolution of PDI of vesicle diameter with vesicle thickness for PGMA<sub>55</sub>-*b*-PHPMA<sub>x</sub>, reproduced from S3 with permission from copyright 2014 American Chemical Society.

#### References

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- [S2] X. Chen, L. Liu, M. Huo, M. Zeng, L. Peng, A. Feng, X. Wang, and J. Yuan, *Angew. Chem. Int. Ed.* 2017, 56, 16541
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