Supplementary Information

Regulation of self-assembly morphology of azobenzene-bearing double hydrophobic block copolymers in aqueous solution based on host-guest recognition

Zai-Zai Tong, Rui-Yang Wang, Jie Huang, Jun-Ting Xu, Zhi-Qiang Fan
MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China
Synthesis of initiator 2-hydroxyethyl 2-bromo-2-methylpropanoate (2-HBMP). 93.06 g (1.50 mol) of dry glycol and 6.48 g (0.064 mol) of dry triethylamine were placed in a 500 mL round-bottom flask, kept under a nitrogen atmosphere. Within 2 h, 14.6 g (0.063 mol) of 2-bromoisobutyryl bromide was added at 0°C. After an additional hour the reaction mixture was slowly warmed to room temperature and stirred overnight. Then, 200 mL of water was added and extracted with 3×80 mL of chloroform. The organic phase was subsequently washed with 50 mL of 1 N hydrochloric acid and saturated sodium carbonate solution. After drying over magnesium sulfate, the product was filtered. Finally, the crude product was separated through a silicon column using mixture solvent (petroleum ether and ethyl acetate, 1:1) as eluent, and the second ingredient was collected.

![NMR spectrum of 2-HBMP.](image)

**Fig. S1.** NMR spectrum of 2-HBMP.

![TEM images of PLLA-PMMAZO/β-CD complex at β-CD/azo=1.](image)

**Fig S2.** TEM images of PLLA-PMMAZO/β-CD complex at β-CD/azo=1. a) without staining; b) the sample was stained with PTA for 10 min.
Fig. S3. Effect of β-CD/azo ratio on the micellar morphology of PLLA_{44-b-PMMAZO_{26}/β-CD complexes (c=0.1 mg mL^{-1}): a) 0.5:1; b) 1:1 and c) 2:1. The scale bar is 200 nm.

Fig. S4. The size distribution of PLLA_{44-b-PMMAZO_{26}/CD (CD:AZO=1) in aqueous solution a) before annealing, b) after annealing at 65 ºC for 24h; and PLLA_{92-b-PMMAZO_{26}/β-CD (β-CD:AZO=1), c) before annealing, d) after annealing at 65 ºC for 24h.

Fig. S5. (a) UV/vis spectra of PLLA_{17-b-PMMAZO_{26}/β-CD complex (β-CD/azo=1) at different irradiation times of 365 nm UV light. (b) UV/vis spectra of PLLA_{17-b-PMMAZO_{26}/β-CD complex (β-CD/azo=1) at different irradiation times of 450 nm visible light. (c) Change of the absorbance at 360 nm due to the azobenzene/β-CD inclusion upon alternate irradiations with 365 nm UV light and 450 nm visible light.
for 300 s. The concentration of the sample is 0.1 mg mL\(^{-1}\).

**Fig. S6.** The effect of UV irradiation time on absorbance at 360 nm and 450 nm.

**Fig. S7.** Size distribution of PLLA\(_{92}\)-b-PMMAZO\(_{26}\)/β-CD complex at β-CD/azo=1 before (black) and after (red) UV irradiation, and the after irradiation with visible light (blue).