

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.

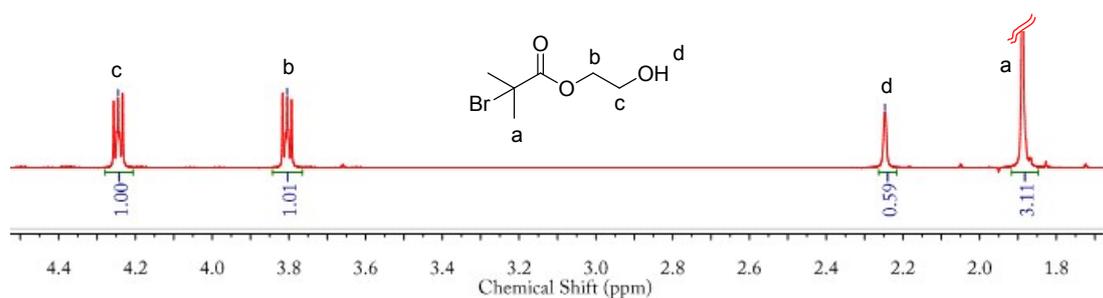


Fig. S1. NMR spectrum of 2-HBMP.

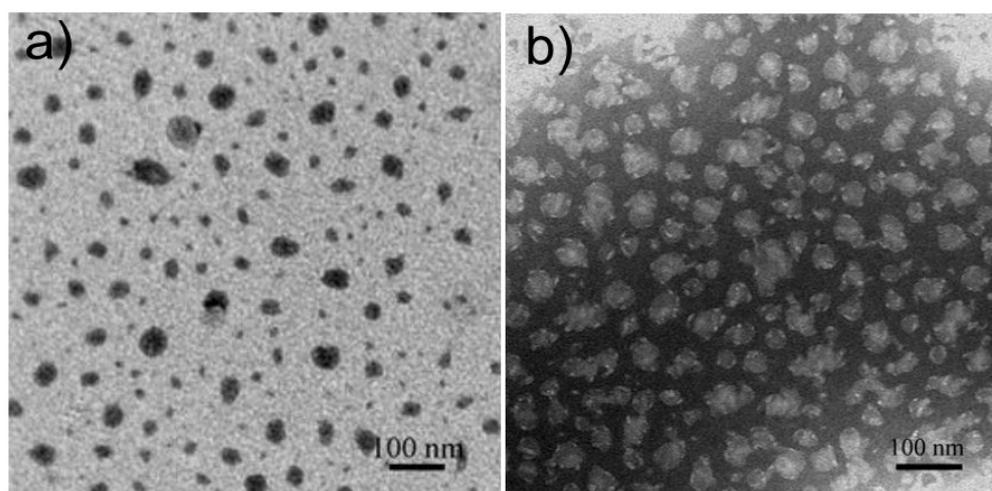


Fig S2. TEM images of PLLA₄₄-*b*-PMMAZO₂₆/β-CD complex at β-CD/azo=1. a) without staining; b) the sample was stained with PTA for 10 min.

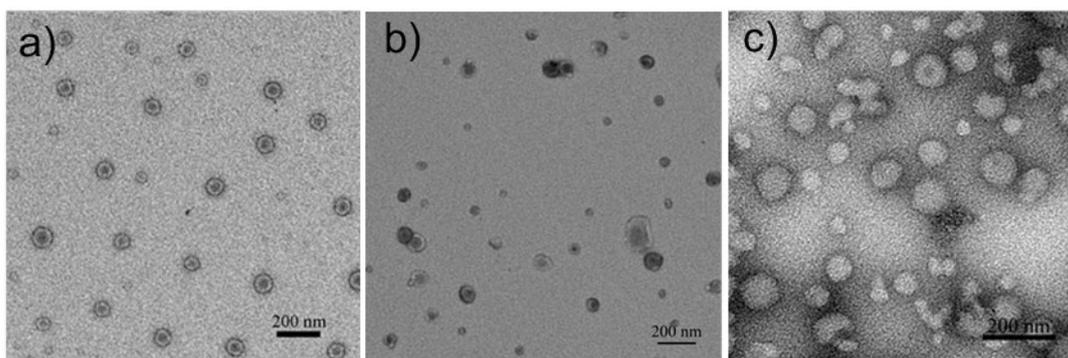


Fig. S3. Effect of β -CD/azo ratio on the micellar morphology of PLLA₄₄-*b*-PMMAZO₂₆/ β -CD complexes ($c=0.1 \text{ mg mL}^{-1}$): a) 0.5:1; b) 1:1 and c) 2:1. The scale bar is 200 nm.

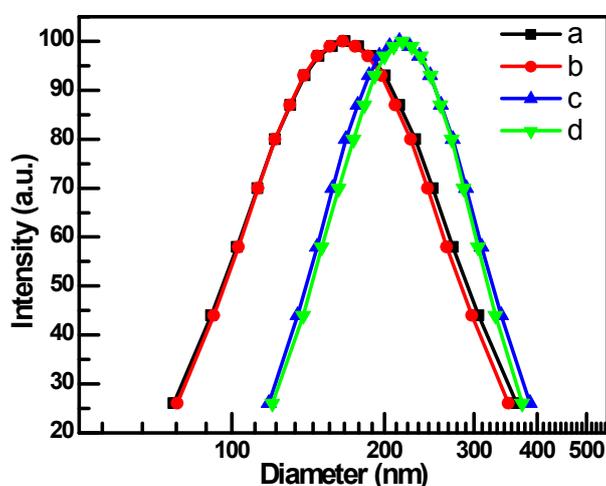


Fig. S4. The size distribution of PLLA₄₄-*b*-PMMAZO₂₆/CD (CD:AZO=1) in aqueous solution a) before annealing, b) after annealing at 65 °C for 24h; and PLLA₉₂-*b*-PMMAZO₂₆/ β -CD (β -CD:AZO=1), c) before annealing, d) after annealing at 65 °C for 24h.

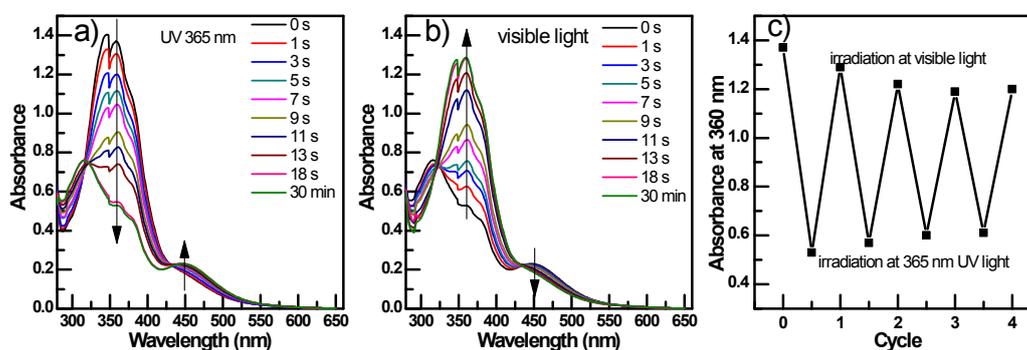


Fig. S5. (a) UV/vis spectra of PLLA₁₇-*b*-PMMAZO₂₆/ β -CD complex (β -CD/azo=1) at different irradiation times of 365 nm UV light. (b) UV/vis spectra of PLLA₁₇-*b*-PMMAZO₂₆/ β -CD complex (β -CD/azo=1) at different irradiation times of 450 nm visible light. (c) Change of the absorbance at 360 nm due 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.

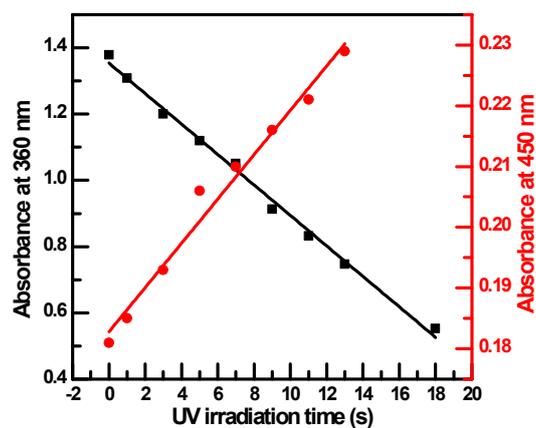


Fig. S6. The effect of UV irradiation time on absorbance at 360 nm and 450 nm.

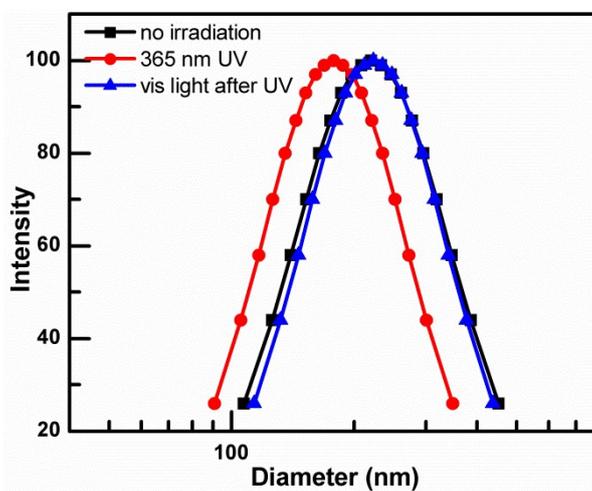


Fig. S7. Size distribution of PLLA₉₂-*b*-PMMAZO₂₆/β-CD complex at β-CD/azo=1 before (black) and after (red) UV irradiation, and the after irradiation with visible light (blue).