Electronic Supplementary Information

Shape-Changing Linear Molecular Bottlebrushes with Dually pH- and Thermo-Responsive

Diblock Copolymer Side Chains

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Figure S1. (A) Size exclusion chromatography (SEC) trace and ¹H NMR spectrum in CDCl₃ of the purified PTEGN₃MA with a degree of polymerization of 707.



Figure S2. SEC traces of PDEAEMA macroinitiator ($M_{n,SEC} = 6.5$ kDa, PDI = 1.17) and PDEAEMA-*b*-PTEGMA side chain polymer ($M_{n,SEC} = 14.1$ kDa, PDI = 1.21).



Figure S3. ¹H NMR spectra of (A) PDEAEMA macroinitiator and (B) PDEAEMA-*b*-PTEGMA side chain polymer in CDCl₃.



Figure S4. ¹H NMR spectrum of the reaction mixture at (A) t = 0 and (B) at the end of the click reaction in CDCl₃, showing the decrease in the integral of the alkyne peak at 4.62 ppm. (C) ¹H NMR spectrum of the purified PDEAEMA molecular brushes MBB-H in CDCl₃, and (D) shows the enlarged portion from 3.8 to 5.0 ppm; no alkyne peak left, indicating the removal of unreacted PDEAEMA side chains.



Figure S5. AFM height image (A) with sizes of $5 \times 5 \mu m$ and (B) with sizes of $2 \times 2 \mu m$ of MBB-H brush molecules spin cast onto bare mica from a 0.05 mg/g aqueous solution with pH of 5.00.



Figure S6. Apparent hydrodynamic size distributions of MBB-B molecular brushes at concentrations of 0.5 mg/g and 1.0 mg/g in aqueous 10 mM phosphate buffer with (A) pH of 6.00 and (B) pH of 8.50.



Figure S7. (A) Apparent average hydrodynamic size (D_h) of MBB-B in 10 mM phosphate buffer at a concentration of 0.5 mg/g as function of pH, adjusted using 0.1 M NaOH and 0.1 M HCl, in the process of increasing pH. (B) Hydrodynamic size distributions of 0.5 mg/g MBB-B in 10 mM buffer at pH = 6.00 and 8.50 under ambient conditions.



Figure S8. Optical photos of a 2.0 mg/g solution of PDEAEMA (a-d) and a 1.0 mg/g solution of MBB-H (e-h) in 10 mM phosphate buffer with a pH value of 7.10 at various temperatures. The onset temperature of clouding transition was 40 °C for PDEAEMA and 48 °C for MBB-H. Note that the PDEAEMA solution at pH = 6.13 and the MBB-H solution at pH = 6.00 remained clear in the entire temperature range of 0 to 100 °C. We could not determine if PDEAEMA exhibits a LCST transition at pH = 8.50 because the polymer becomes insoluble and precipitates in water at this pH.



Figure S9. Apparent hydrodynamic size distributions of MBB-B molecular brushes at concentrations of 0.2 mg/g in aqueous 10 mM phosphate buffer with pH of 8.50 at 25 °C and 70 °C from the first and second heating processes. At each selected temperature, the sample was equilibrated for at least 5 min before the measurement. After the first heating was completed, the solution was cooled back to 25 °C and allowed to equilibrate at that temperature for 30 min before the second heating began.



Figure S10. Additional AFM height image (A) with sizes of $2 \times 2 \mu m$ and (B) with sizes of $1 \times 1 \mu m$ of MBB-B molecular brushes with dually responsive PDEAEMA-*b*-PTEGMA side chains spin cast onto PMMA-coated mica at 3000 rpm from a 2.5 mM aqueous phosphate buffer solution with a polymer concentration of 0.05 mg/g at a pH of 5.00 and room temperature.



Figure S11. Additional AFM height image (A) with sizes of $2 \times 2 \mu m$ and (B) with sizes of $1.1 \times 1.1 \mu m$ of MBB-B molecular brushes spin cast onto PMMA-coated mica at room temperature from a 2.5 mM aqueous phosphate buffer solution at a pH of 9.56 with a polymer concetration of 0.05 mg/g diluted from 0.1 mg/g.



Figure S12. AFM height image (A) with sizes of $4 \times 4 \mu m$ and (B) with sizes of $1 \times 1 \mu m$ of MBB-B molecule brushes spin cast onto PMMA-coated mica from a 0.1 mg/g solution of MBB-B in 2.5 mM phosphate buffer with a pH of 9.54 after being heated to and equilibrated at 65 °C.



Figure S13. Additional AFM height image (A) with sizes of $3 \times 3 \mu m$ and (B) with sizes of $1 \times 1 \mu m$ of MBB-B molecular brushes spin cast onto PMMA-coated mica from a 0.1 mg/g aqueous solution of MBB-B that was diluted at 65 °C from a 1.0 mg/g aqueous solution of MBB-B in 2.5 mM buffer with a pH of 9.57. The 1.0 mg/g solution was heated to 65 °C before the dilution.