Electronic Supplementary Information for

Worm-Globule Transition of Amphiphilic pH-Responsive Heterografted Bottlebrushes at Air-Water Interface

*Michael T. Kelly and Bin Zhao**

Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States

* Corresponding author. Email: bzhao@utk.edu (B.Z.)

Table S1. Structural Characteristics for Six Molecular Bottlebrush Polymers Used in this Work*

Molecular Bottlebrush Polymer	Grafting Density	Molar Ratio of P*n*BA-to-PDEAEMA Side Chains	M_n ($\times 10^6$ Da)
MBB-$B_{1.00}E_{0.00}$	94.5%	1:00 : 0:00	2.69
MBB-$B_{0.80}E_{0.20}$	87.3%	0.80 : 0.20	2.60
MBB-$B_{0.64}E_{0.36}$	88.6%	0.64 : 0.36	2.73
MBB-$B_{0.51}E_{0.49}$	86.8%	0.51 : 0.49	2.75
MBB-$B_{0.24}E_{0.76}$	86.7%	0.24 : 0.76	2.89
MBB-$B_{0.00}E_{1.00}$	88.8%	0.00 : 1.00	3.09

* The degree of polymerization (DP) of the backbone is 406. The DP is 51 for alkyne end-functionalized P*n*BA and 44 for alkyne-end-functionalized PDEAEMA side chains. The M_n values were calculated on the basis of the grafting density, the molar ratio of two side chain polymers, and the calculated molecular weights of P*n*BA and PDEAEMA from their DPs.

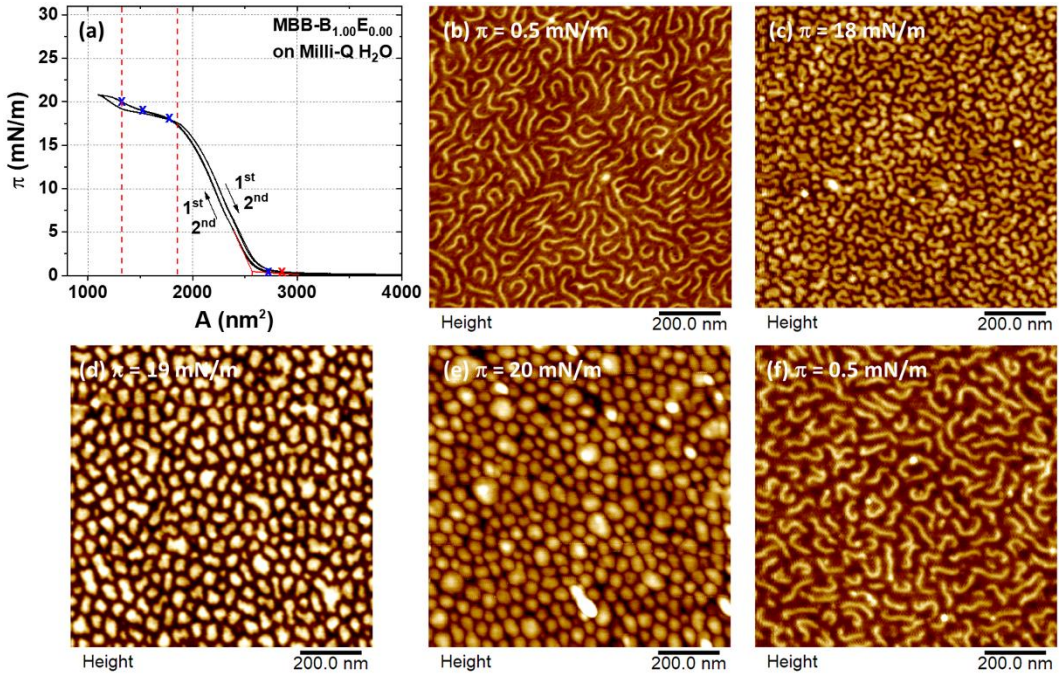

Figure S1. (a) Surface pressure (π)-mean area per brush (A) isotherms from two cycles of lateral compression and expansion for MBB-$B_{1.00}E_{0.00}$ on the Milli-Q water surface and AFM images at different surface pressures: (b) π = 0.5 mN/m, (c) π = 18 mN/m, (d) π = 19 mN/m, (e) π = 20 mN/m, and (f) π = 0.5 mN/m again.

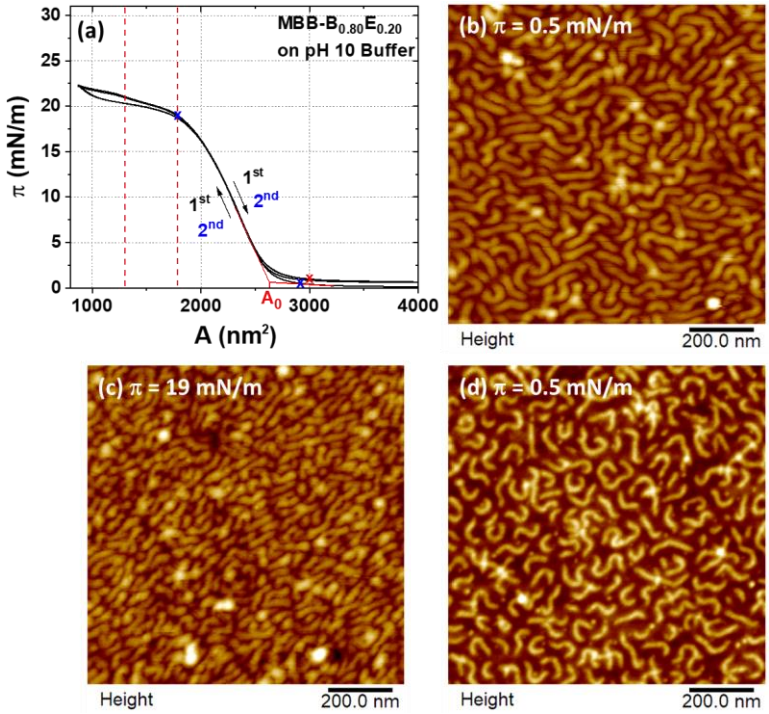

Figure S2. (a) Surface pressure (π)-mean area per brush (A) isotherms from two cycles of compression and expansion for MBB-$B_{0.80}E_{0.20}$ on the surface of a 1.0 mM phosphate buffer with a pH of 10.0 and AFM images of MBB-$B_{0.80}E_{0.20}$ bottlebrushes at different surface pressures: (b) π = 0.5 mN/m, (c) π = 19 mN/m, and (d) π = 0.5 mN/m. The isotherms are the same as in Figure 6a and are reproduced here to show where on the isotherms the AFM samples were prepared.

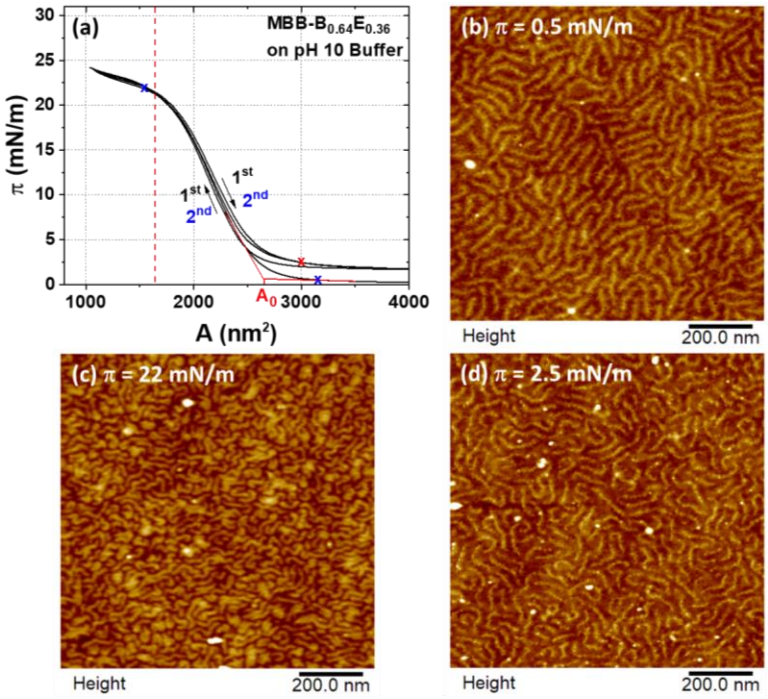

Figure S3. (a) Surface pressure (π)-mean area per brush (A) isotherms from two cycles of compression and expansion for MBB-$B_{0.64}E_{0.36}$ on the surface of a 1.0 mM phosphate buffer with a pH of 10.0 and AFM images of MBB-$B_{0.64}E_{0.36}$ bottlebrushes at different surface pressures: (b) π = 0.5 mN/m, (c) π = 22 mN/m, and (d) π = 2.5 mN/m. The isotherms are the same as in Figure 6c and are reproduced here to show where on the isotherms the AFM samples were prepared.

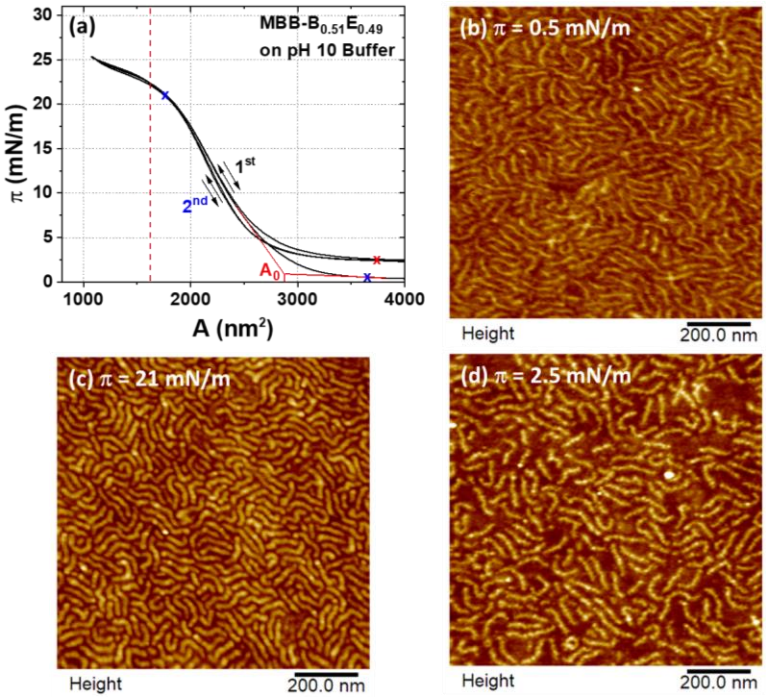

Figure S4. (a) Surface pressure (π)-mean area per brush (A) isotherms from two cycles of compression and expansion for MBB-$B_{0.51}E_{0.49}$ on the surface of a 1.0 mM aqueous phosphate solution with a pH of 10.0 and AFM images of MBB-$B_{0.51}E_{0.49}$ bottlebrushes at different surface pressures: (b) π = 0.5 mN/m, (c) π = 21 mN/m, and (d) π = 2.5 mN/m. The isotherms are the same as in Figure 6e and are reproduced here to show where on the isotherms the AFM samples were prepared.

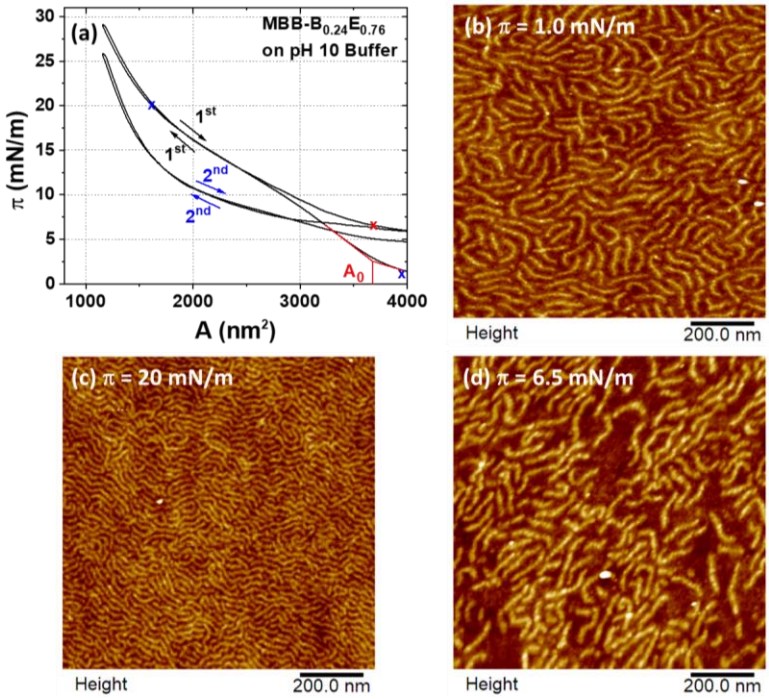

Figure S5. (a) Surface pressure (π)-mean area per brush (A) isotherms from two cycles of compression and expansion for MBB-$B_{0.24}E_{0.76}$ on the surface of a 1.0 mM aqueous phosphate solution with a pH of 10.0 and AFM images of MBB-$B_{0.24}E_{0.76}$ bottlebrushes at different surface pressures: (b) π = 1.0 mN/m, (c) π = 20 mN/m, and (d) π = 6.5 mN/m. The isotherms are the same as in Figure 6g and are reproduced here to show where on the isotherms the AFM samples were prepared.