Temperature Tunable Micellization of Polystyrene-*block*-poly(2-vinylpyridine) at Si–Ionic Liquid Interface

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Supporting Information

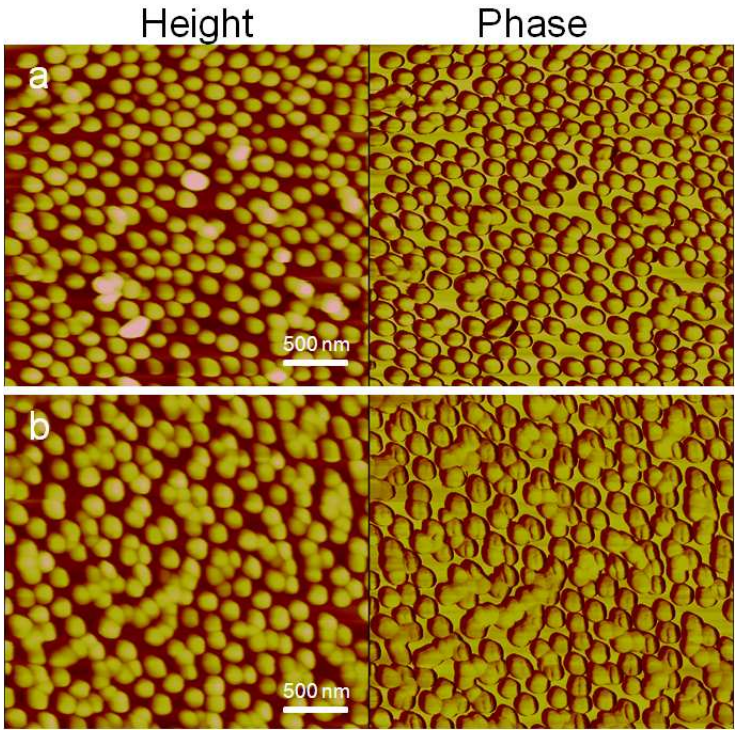
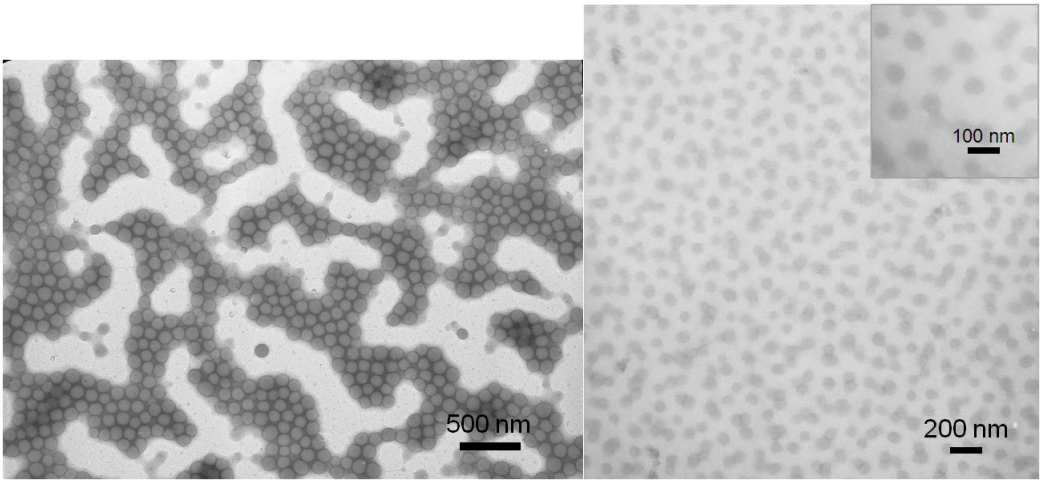


Figure S1. SFM images (height and phase mode) of PS-*b*-P2VP micelles formed from as-spun 30-nm-thick S2VP200K films annealed in the IL at 150 °C for 1 h followed by (a) quenching and (b) slow cooling.



(a) (b)

Figure S2. TEM images of PS-*b*-P2VP micelles formed from (a) as-spun and (b) pre-annealed 16-nm-thick S2VP200K films annealed in the IL at 150 °C for 1 h. The P2VP block was selectively stained with I_2 and appeared as dark spherical coronae.

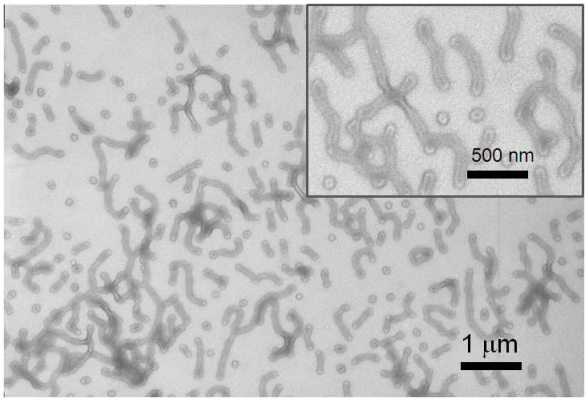


Figure S3. TEM images of PS-*b*-P2VP micelles formed by an as-spun 16-nm-thick S2VP200K film after being annealed in the IL at 110 °C for 1 h. The P2VP block was selectively stained with I_2 and appeared as dark spherical coronae.

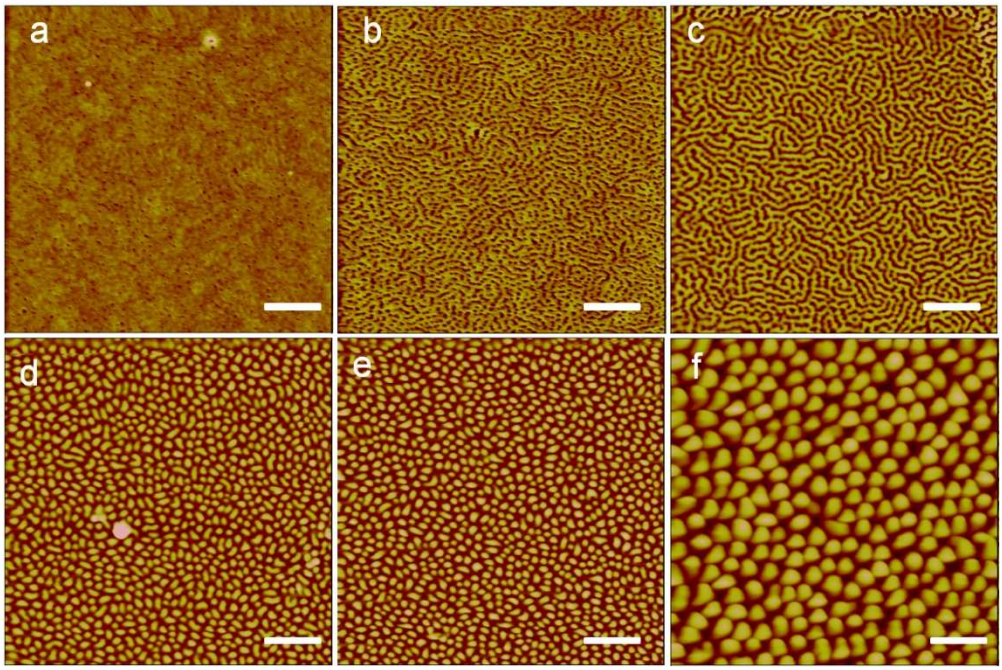


Figure S4. SFM images (height mode) of PS-*b*-P2VP micelles formed by pre-annealed 16-nm-thick (S2VP200K) films after annealing in the IL at different temperatures for 1 h: (a) 50 °C, (b) 70 °C, (c) 90 °C, (d) 110 °C, (e) 130 °C, and (f) 150 °C. Scale bar: 500 nm.

To check the solubility of P2VP blocks in the IL, the P2VP homopolymer (M_n = 97 kg/mol, from Polymer Source, Inc.) was dissolved into a certain amount of IL at room temperature, 70 °C, 110 °C, and 150 °C, respectively. After filtering with 0.45 μm PTFE syringe filters, the solutions were measured by UV-Vis absorbance spectroscopy (PerkinElmer, Lambda 25 UV/Vis). The results showed that at room temperature, P2VP was barely soluble in the IL over a 24 h period, while at 70 °C, 110 °C and 150 °C, the P2VP could dissolve in the IL and showed absorption at 300 nm, about 40 nm red shift compared with the absorption of P2VP in dichloromethane solvent (Figure S5). Dynamic light scattering results showed the hydrodynamic size of P2VP in the IL was 37 nm, much larger than the radius of gyration (R_g) of P2VP (~9 nm calculated based on the relationship between R_g and the molecular weight: $R_g = 0.0277\ M_w^{0.5}$), which might be due to the aggregation of P2VP molecules in the IL.

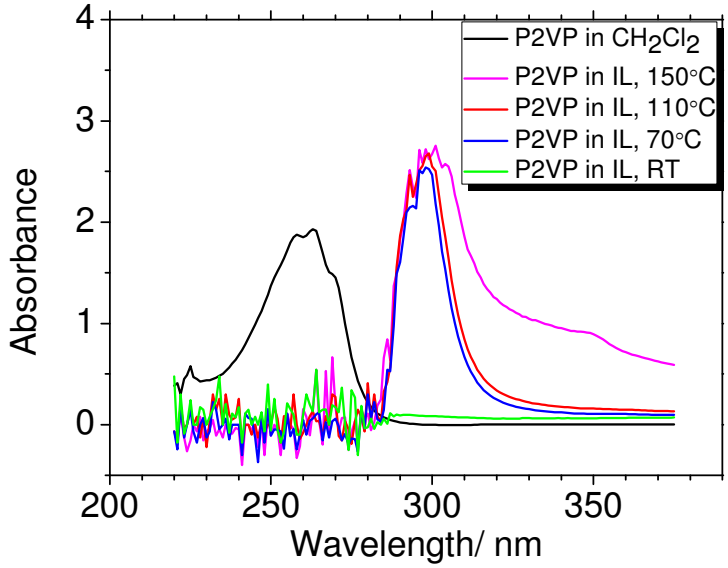


Figure S5. UV–Vis absorption spectra of P2VP (M_n = 97 kg/mol) solubilized in dichloromethane and in the IL at different temperatures.

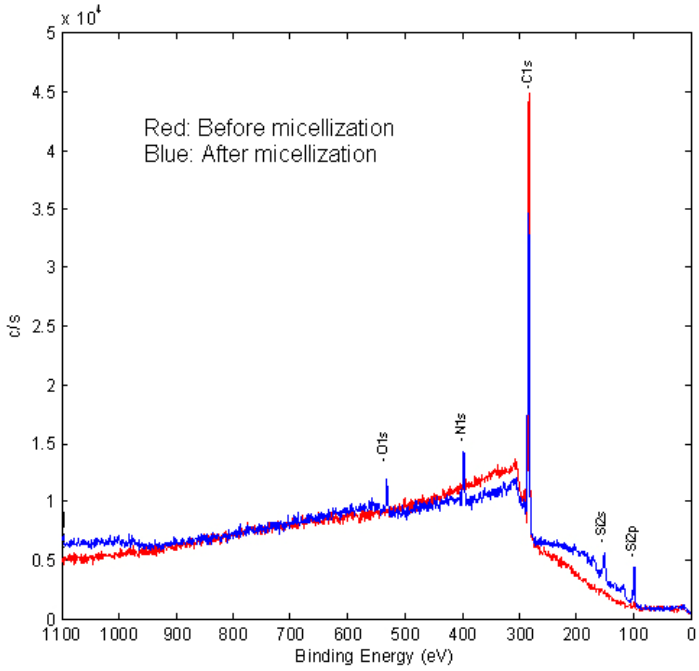


Figure S6. X-ray photoelectron spectra of a 16-nm-thick pre-annealed S2VP200K film before (red line) and after (blue line) annealing in the IL at 150 °C for 1 h. Only C1s peak was dominant on the spectrum of the pre-annealed PS-*b*-P2VP film, indicating that the film surface was PS. After annealing in the IL, the ratio for the relative amounts of different elements is C1s: N1s: Si2p: O1s = 7:1:0.8:0.5, which not only demonstrated that the surface composition was mainly P2VP, but also indicated the exposure of the bare Si substrate.

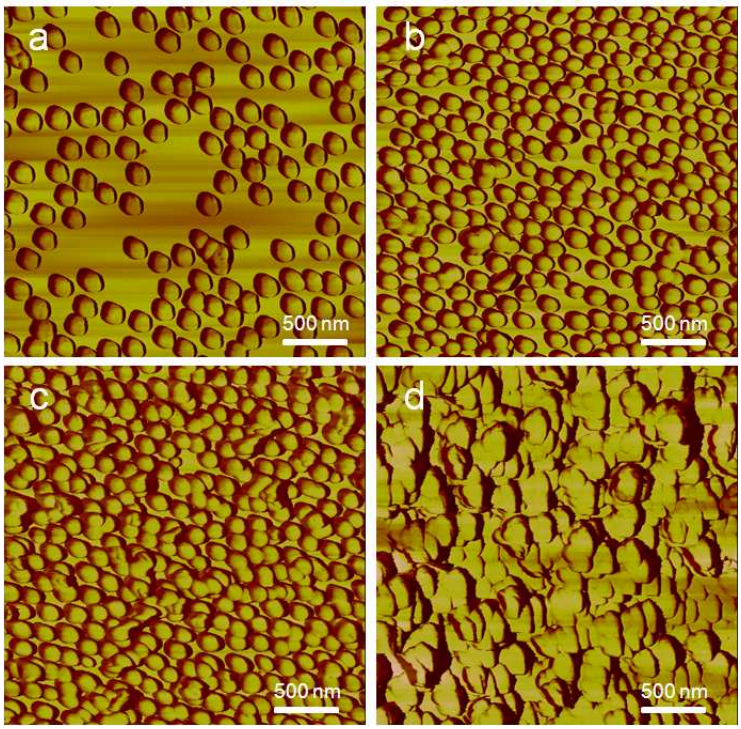


Figure S7. SFM images (phase mode) of PS-*b*-P2VP micelles formed from as-spun S2VP200K films with different initial thicknesses annealed in the IL at 150 °C for 1 h: (a) 16 nm, (b) 30 nm, (c) 40 nm, and (d) 78 nm.

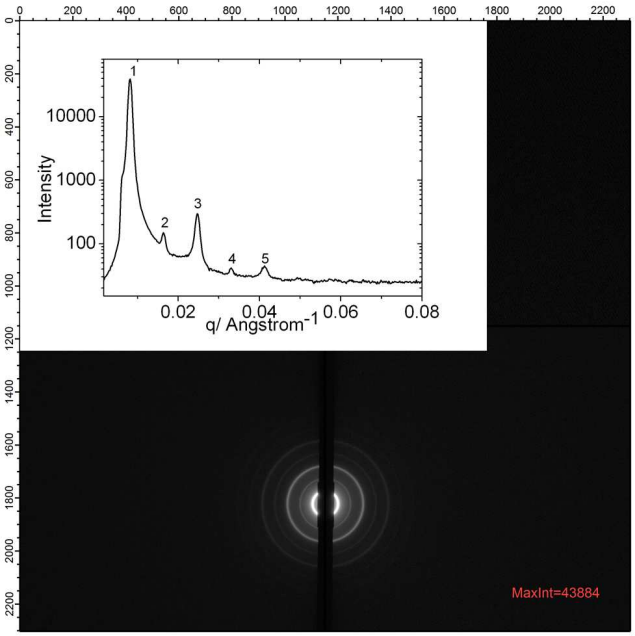


Figure S8. Small-angle X-ray scattering (SAXS) pattern and the line profile of the scattering as a function of scattering vector for the S2VP200K bulk sample which was annealed in high vacuum oven at 180 °C overnight. SAXS measurements were performed in Advanced Light Source, Berkeley National Laboratory, Berkeley, CA.

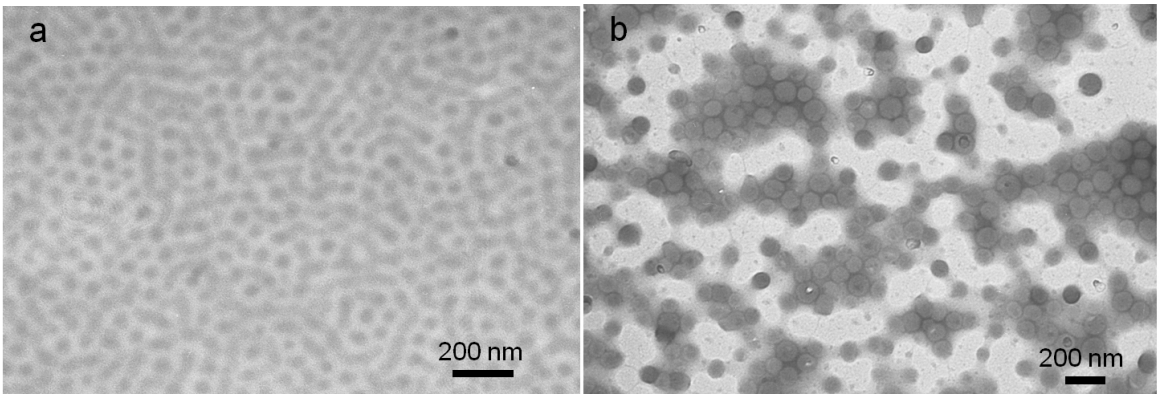


Figure S9. TEM images of an 18-nm-thick S2VP200K film (a) as-spun from toluene solutions and (b) after being annealed in the IL at 150 °C for 1 h. The P2VP block was selectively stained with I_2 and appeared as dark spherical (a) core and (b) shell.

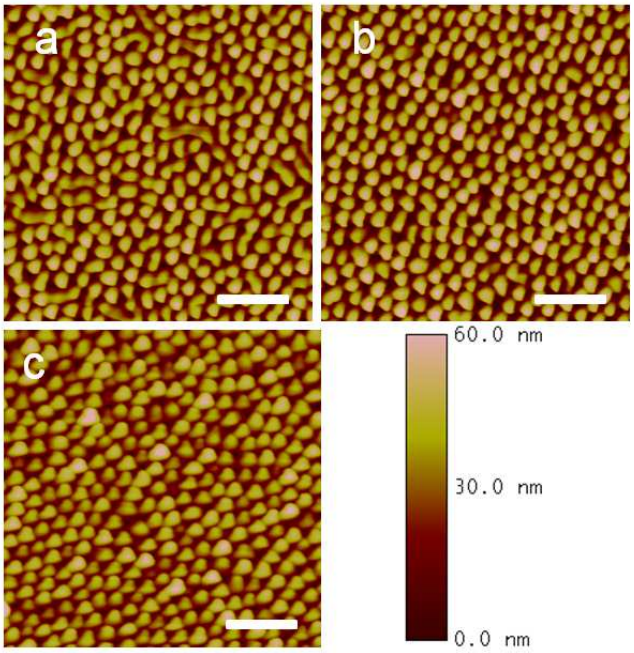


Figure S10. SFM images (height mode) of S2VP80K (51 kg/mol-*b*-29 kg/mol) micelles formed by a pre-annealed 27-nm-thick film after annealing in the IL at different temperatures for 1 h: (a) 110 °C, (b) 130 °C, and (c) 150 °C. Scale bar: 500 nm.

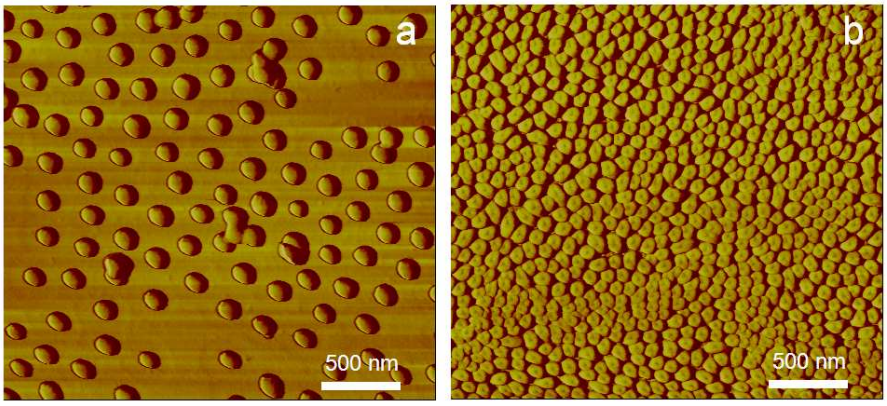


Figure S11. SFM images (phase mode) of PS-*b*-P2VP micellar structures after exposure to 5% HF solution for 10 min. The micelles were formed from (a) as-spun and (b) pre-annealed 16-nm-thick S2VP200K films annealed in the IL at 150 °C for 1 h.