

Supplementary Information

Straightforward Synthesis of Model Polystyrene-block-Poly(vinyl alcohol) Diblock Polymers

Ozcan Altintas,^a Joshua C. Speros,^b Frank S. Bates^c and Marc A. Hillmyer^{a*}

^aDepartment of Chemistry, ^cDepartment of Chemical Engineering and Materials Science,
University of Minnesota, Minneapolis, Minnesota 55455, United States

^bBASF Corporation, 339B Hildebrand Hall, Berkeley, California 94720, United States

*Corresponding author (e-mail: hillmyer@umn.edu)

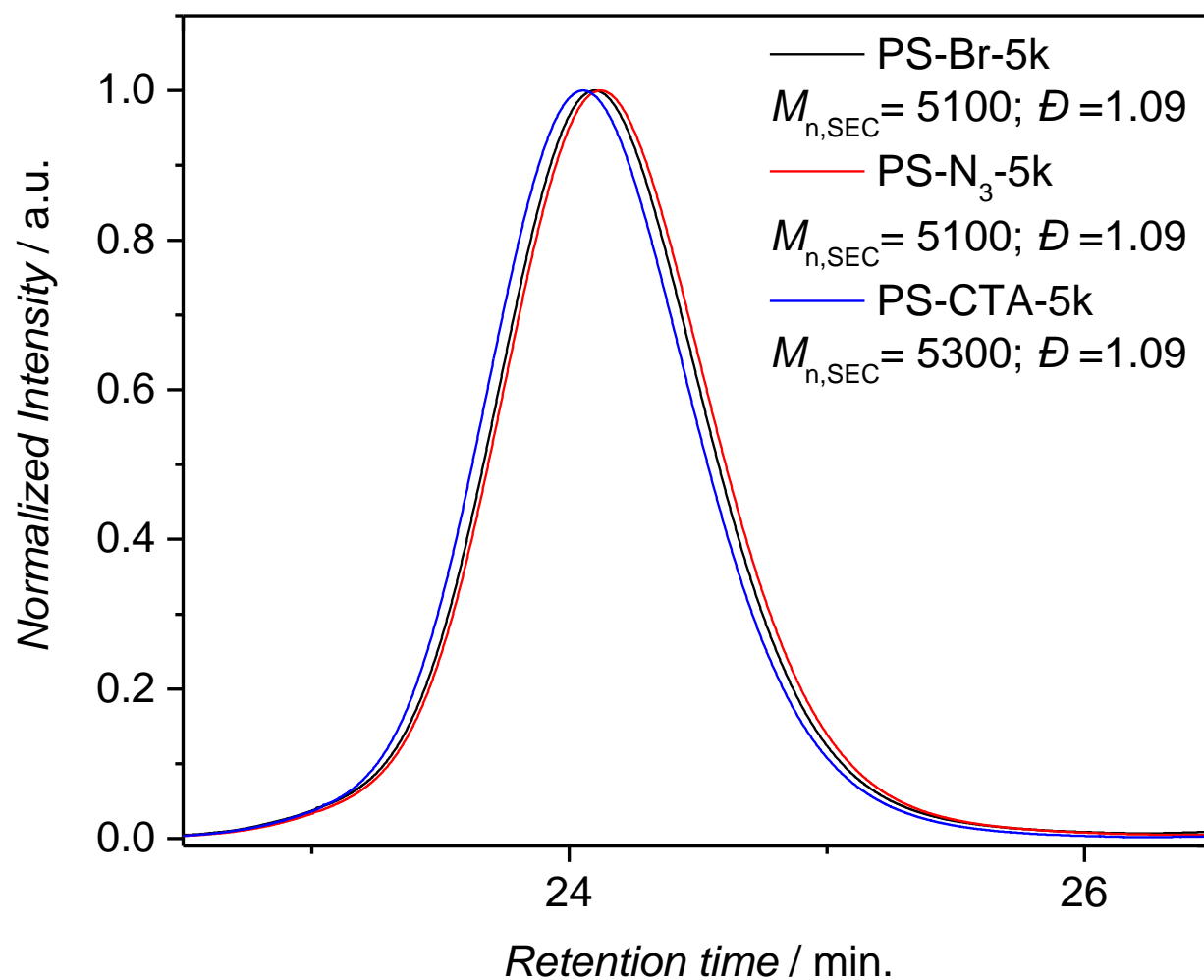


Figure S1. SEC traces of the precursor polymers (PS-Br-5k, PS-N₃-5k, PS-CTA-5k) using CHCl₃ as the eluent and calibrated with polystyrene standards.

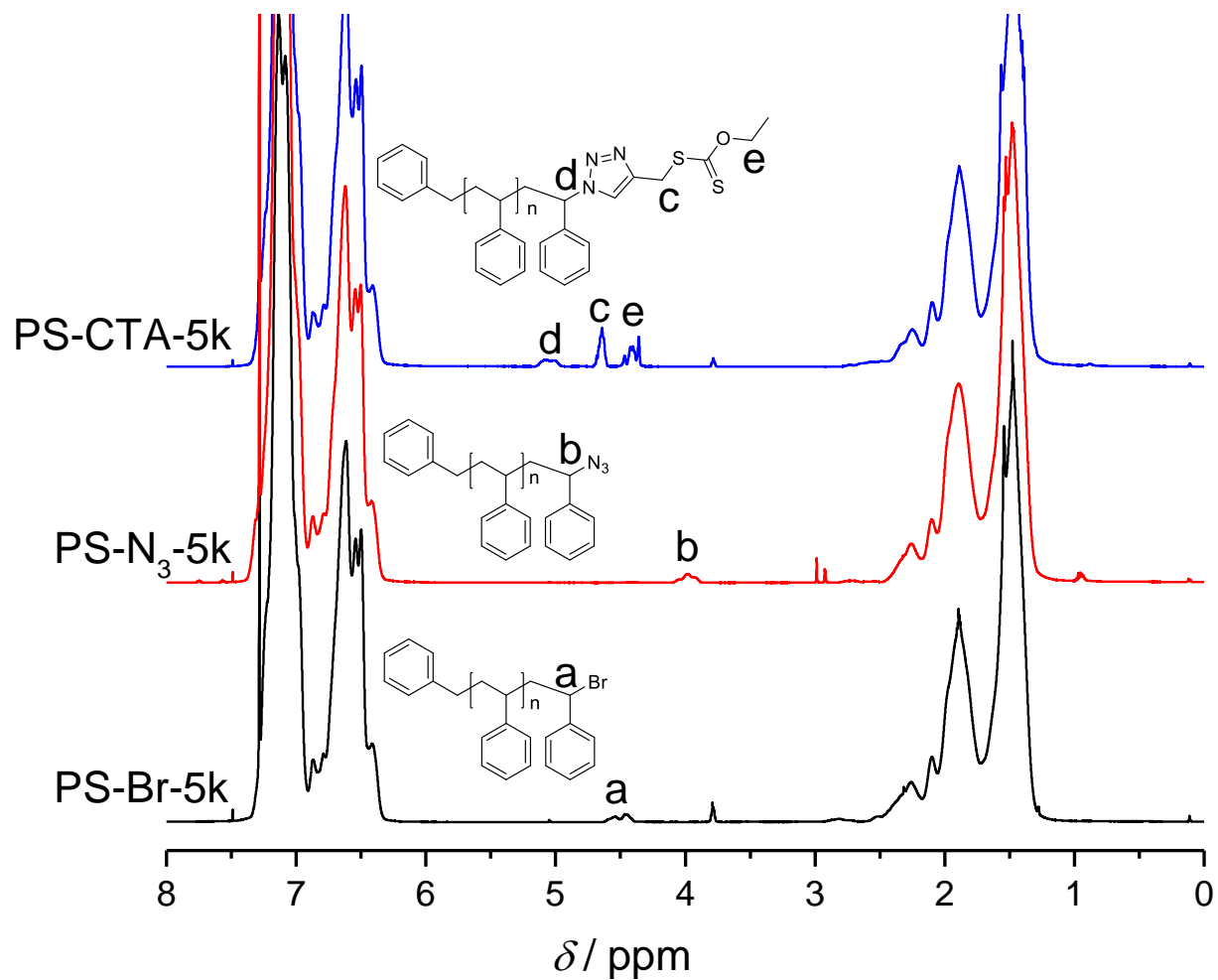


Figure S2. ^1H NMR spectra of the precursor polymers (PS-Br-5k, PS-N₃-5k, PS-CTA-5k) in CDCl_3 at the ambient temperature.

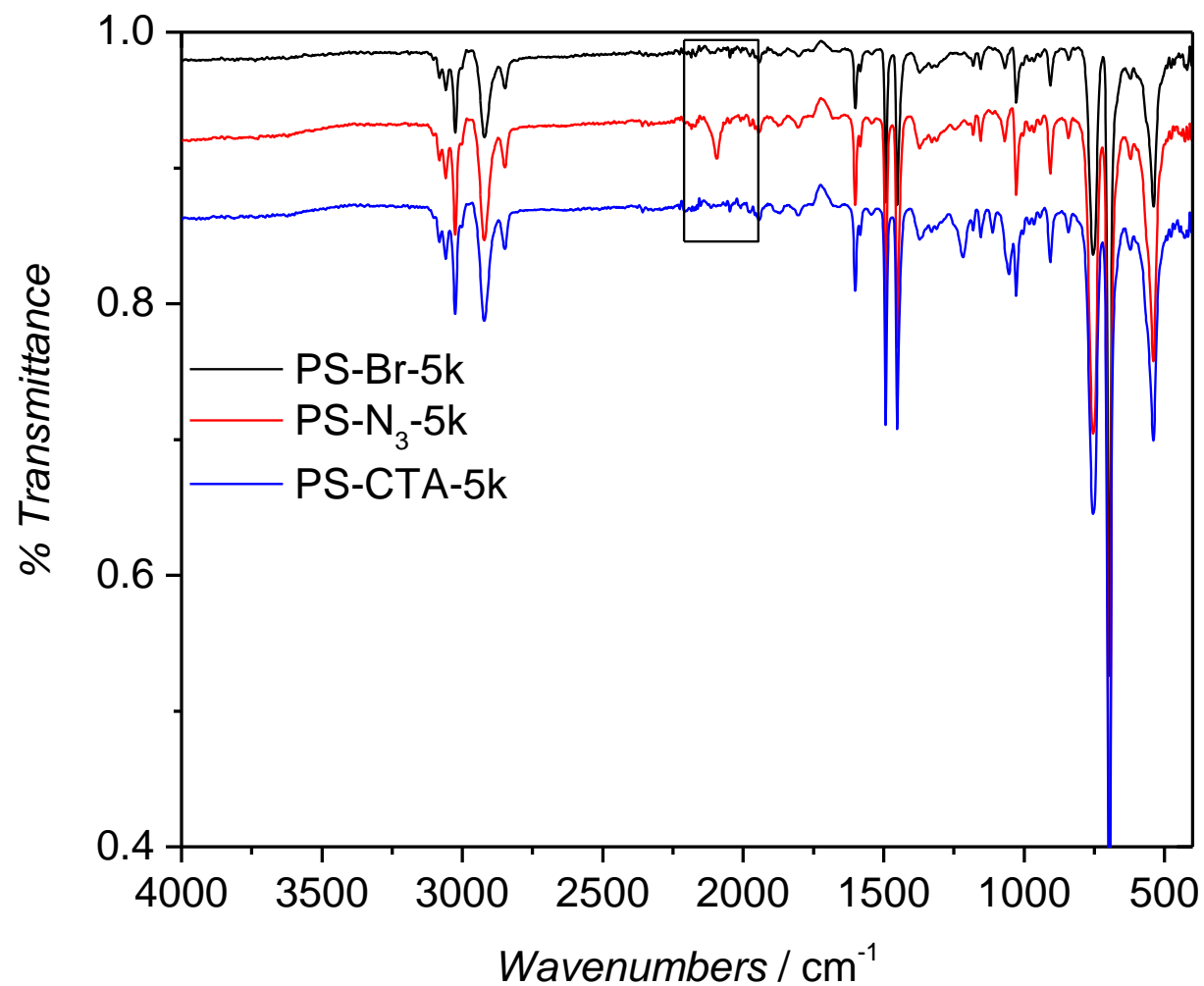


Figure S3. FT-IR spectra of the precursor polymers (PS-Br-5k, PS-N₃-5k, PS-CTA-5k).

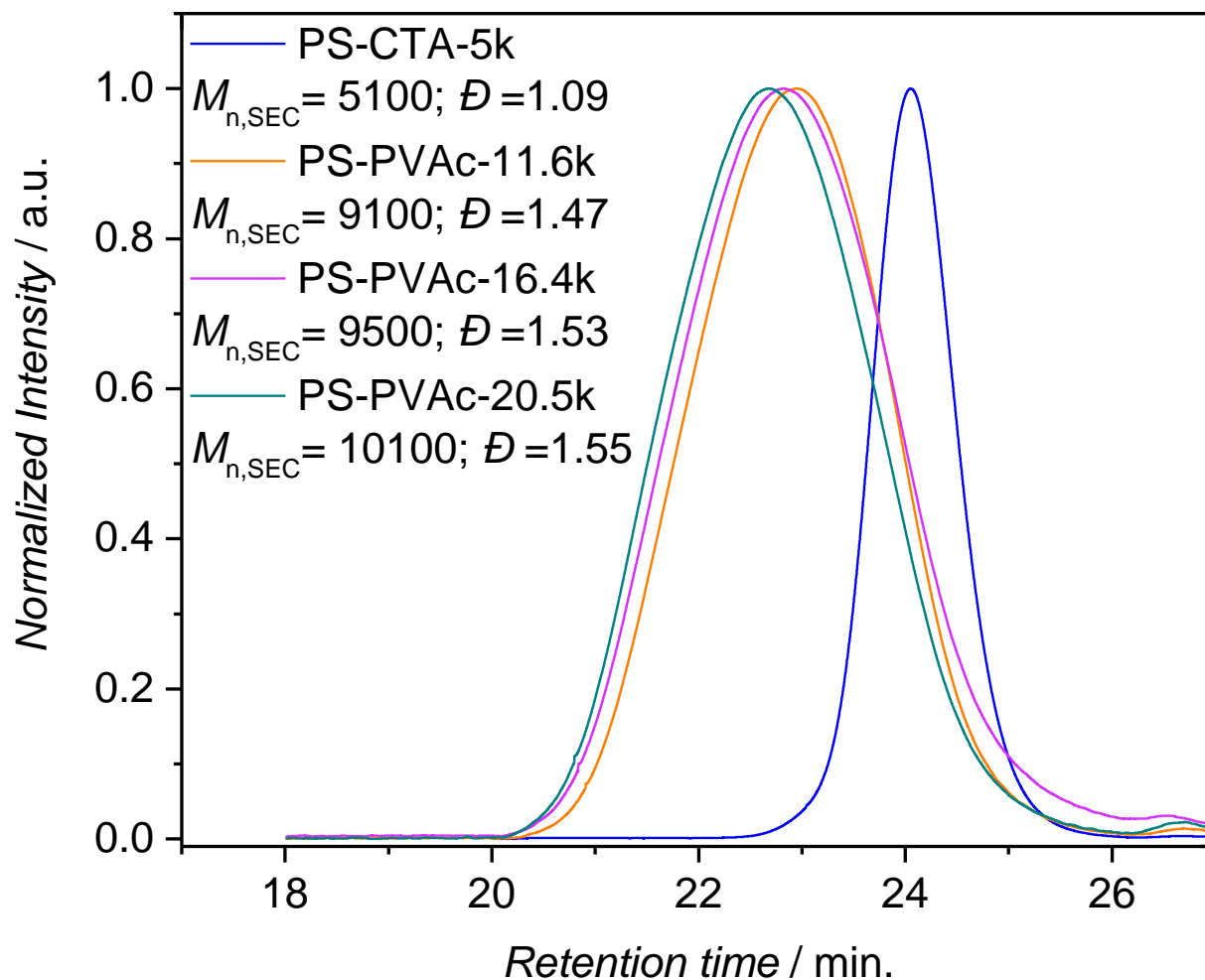


Figure S4. SEC traces of diblock block polymers (PS-PVAc-11.6k, PS-PVAc-16.4k, PS-PVAc-20.5k) and the precursor polymer (PS-CTA-5k) using CHCl_3 as the eluent and calibrated with polystyrene standards.

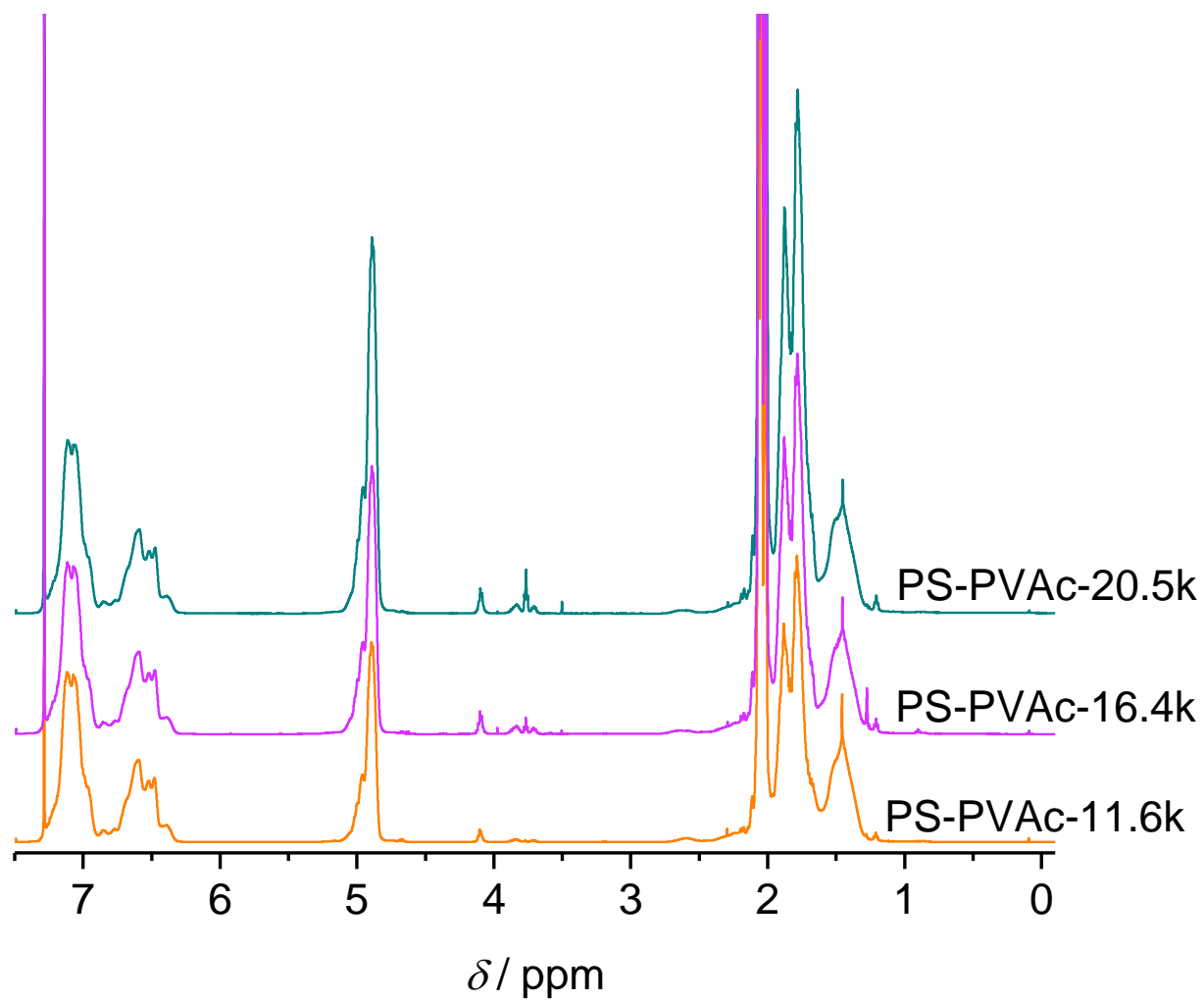


Figure S5. ^1H NMR spectra of diblock block polymers (PS-PVAc-11.6k, PS-PVAc-16.4k, PS-PVAc-20.5k) in CDCl_3 at the ambient temperature.

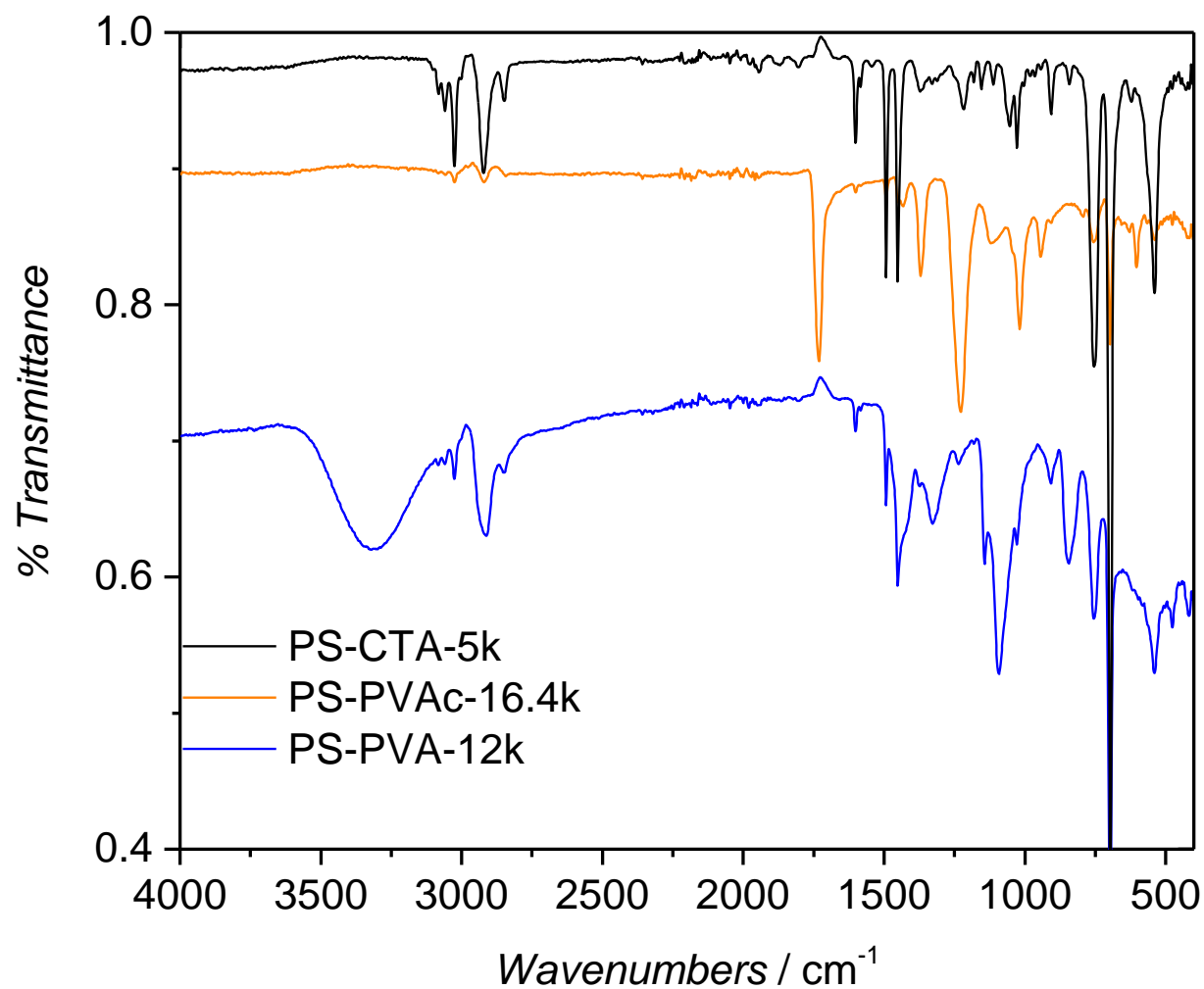


Figure S6. FT-IR spectra of the diblock block polymers (PS-PVA-12k and PS-PVAc-16.4k) and the precursor polymer (PS-CTA-5k).

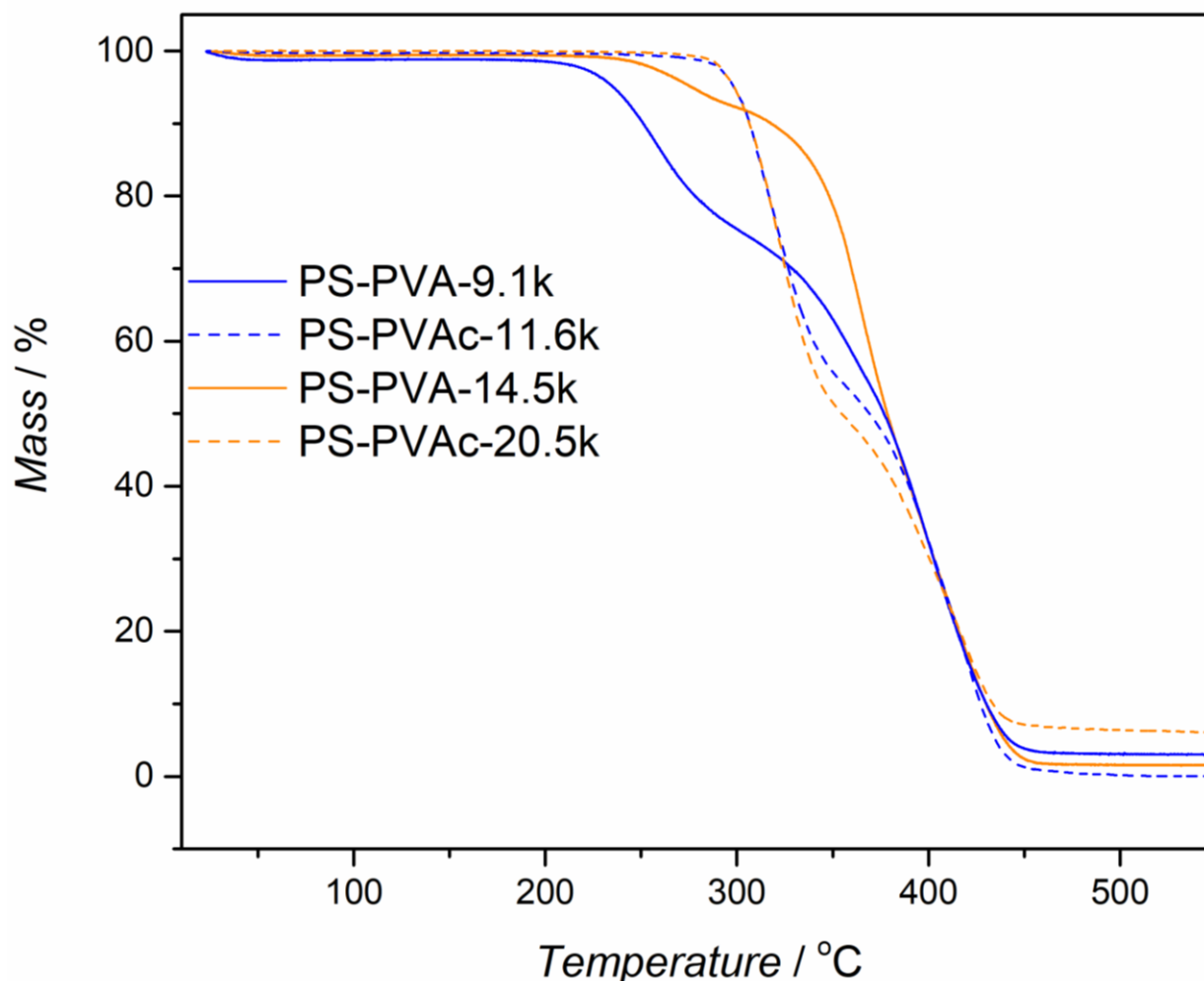


Figure S7. Thermogravimetric overlay of the diblock polymer and corresponding precursor diblock polymer heated at a rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere.

Atomic force microscopy (AFM) was utilized to investigate the surface structures of spin coated PS-PVA films. As a representative sample, the thin film assembly of the PS-PVA-12k block polymer was examined. A solution of the PS-PVA-12k block polymer was prepared with concentration of $25\text{ mg}\cdot\text{mL}^{-1}$ in dimethylacetamide at $85\text{ }^{\circ}\text{C}$. Thin films of the PS-PVA-12k sample were prepared on a silicon wafer with a native oxide layer by spin-coating from the hot solution. The thickness of the polymer film was around 35 nm as estimated by ellipsometry.

After keeping the sample at 230 °C for 1 min under nitrogen atmosphere above the melting temperatures of the PVA chains, the thin film was annealed under nitrogen atmosphere at 180 °C for 16 h above the recrystallization temperatures of the PVA chains (Figure S8). The AFM images of a $1\ \mu\text{m} \times 1\ \mu\text{m}$ scan area of the substrate coated with the PS-PVA-12k block polymer do not reveal clear morphology patterns (Figure S9).

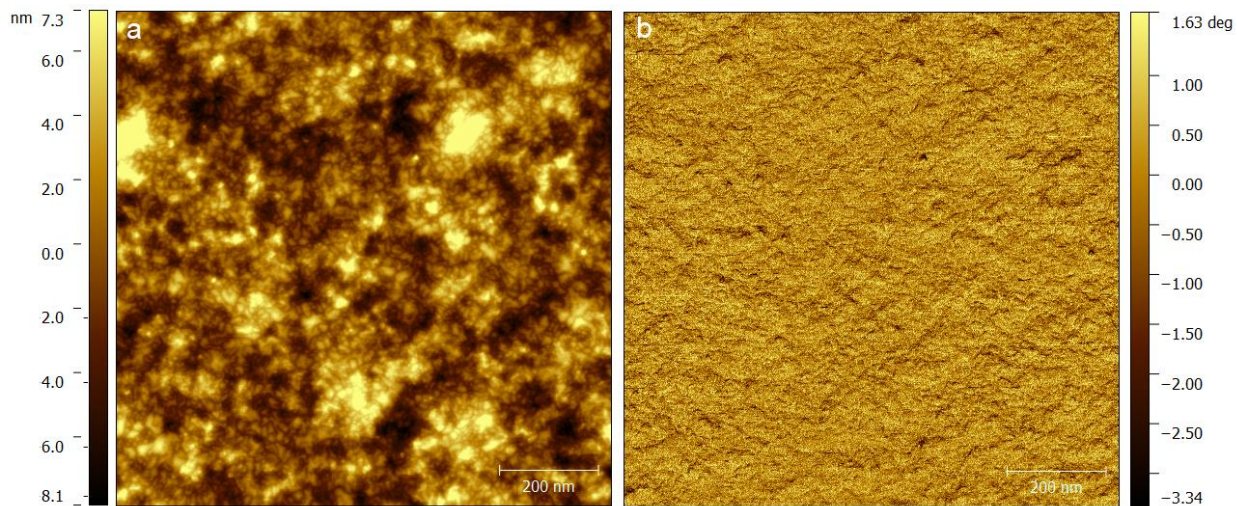


Figure S8. AFM height (a) and phase (b) images obtained in tapping mode of PS-PVA-12k, $T_o = 34\ \text{nm}$, thin film using Bruker's Peak Force tapping mode. T_o is the thickness as measured by ellipsometer. The thin film on the bare silicon wafer was melted at 230 °C for 1 min and then annealed at 180 °C for 16 h.

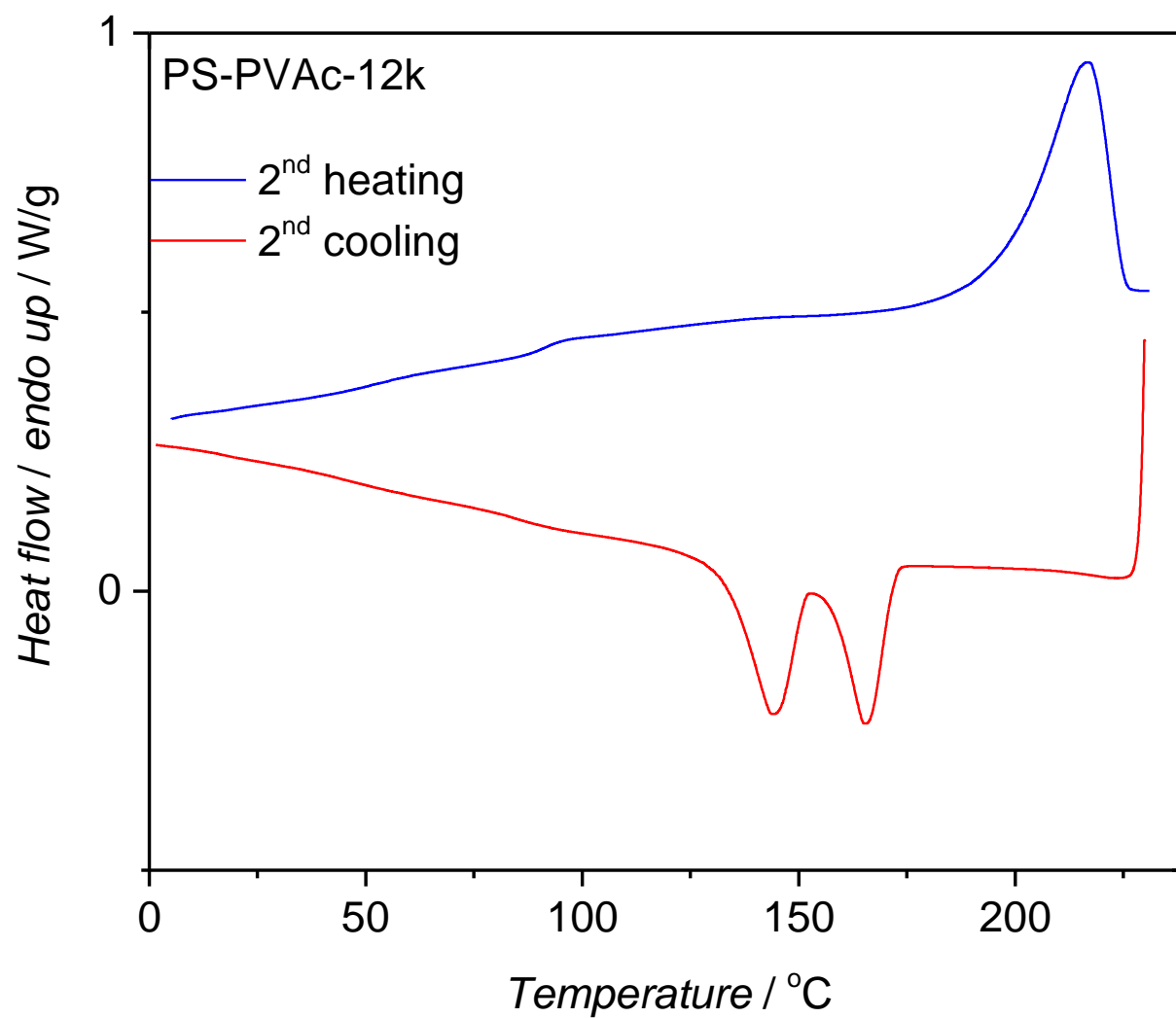


Figure S9. DSC thermograms for PS-*b*-PVA block polymer (PS-PVA-12k). Each thermal scan was taken at a rate of 10 °C·min⁻¹ upon a second heating as well as cooling.