Supporting Information

Morphological Study on an Azobenzene-containing Liquid Crystalline Diblock Copolymer

Liming Ding, Huiming Mao, Ji Xu, Jinbo He, Xuan Ding, and Thomas P. Russell*

Department of Polymer Science & Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Douglas R. Robello and Mark Mis

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Experimental Section

SEC was performed using differential refractive index and viscometry detection in uninhibited THF using three Polymer Laboratories Plgel mixed-C columns. Absolute molecular weights were calculated from the viscosity data and a universal calibration curve constructed from narrow-molecular weight distribution polystyrene standards between 162 (log M = 2.21) and 1,920,000 (log M = 6.28). Reverse phase HPLC analysis of the macroinitiator and diblock copolymer were performed using a Hamilton PRP-1 (4.1×150 mm) column with a solvent gradient of 70% aqueous 0.01 M ammonium

acetate (pH=6.8)/THF to 100% THF over 15 min, followed by a hold at 100% THF for 5 min. The flow rate was 1.0 mL/min, and the injection volume was 25 μL. Detection was made by evaporative light scattering using a SEDEX-55 instrument at 40 °C at 2.3 bar of nitrogen pressure. ^{1}H NMR spectra of the macroinitiator and the diblock copolymer were taken on Varian Unity Inova (500 MHz) and Bruker Avance DPX 300 (300 MHz) spectrometers, respectively. TGA and DSC thermograms were obtained on TGA 2950 Thermogravimetric Analyzer and Q200 Differential Scanning Calorimeter (TA Instruments), respectively. Film thicknesses were measured by using a FILMETRICS thin-film measurement system (Model F20). AFM images were obtained from Dimension^{TM} 3100 Atomic Force Microscope (Digital Instruments) using a tapping mode. SAXS samples were made by drop-casting the copolymer solution onto Kapton® polyimide films. The resulting films were annealed at 140 °C *in vacuo* for 1 day, then stained with RuO_4 vapor for 2 hr. SAXS measurements were performed *in vacuo* with exposure time of 4 hr, using an Osmic MaxFlux X-ray source with a wavelength of 1.54 Å.

The Si wafer coated with the annealed copolymer film was glued onto the sample stage. When heated to 110°C, a PDMS (polydimethylsiloxane) pad was pressed onto the sample by a weight. Then shearing started. The sample stage was driven by a stepper motor, rotating 0.0001° per step, which corresponds to about 87 nm per step in sample movement. The stepper motor was controlled to move 3000 step, taking about 25 min. Figure S8 shows the AFM image of the diblock copolymer film after shearing. The hexagonal packing of PEO nanocylinders can be clearly seen. It should be noted here that our shearing facility was built by referring Angelescu's shear-alignment setup.[1]

Thermal annealing procedure: put the spin-coating film in the oven; dry the film at 60 °C for 30 min in vacuo; gradually elevate the temperature to certain annealing temperature for example 180 °C; keep 180 °C for 1 day; then gradually lower the temperature to room temperature; take the sample out for AFM.

References and Notes

(1) Angelescu, D. E.; Waller, J. H.; Register, R. A.; Chaikin, P. M. *Adv. Mater.* **2005**, *17*, 1878.

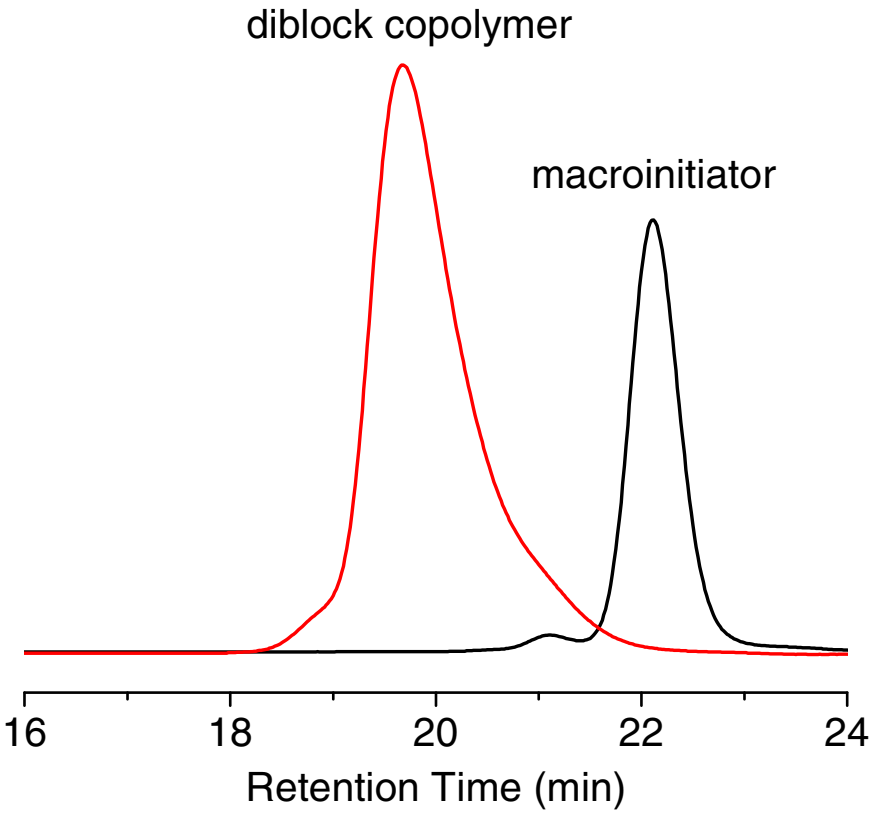


Figure S1. SEC curves for the macroinitiator and the diblock copolymer.

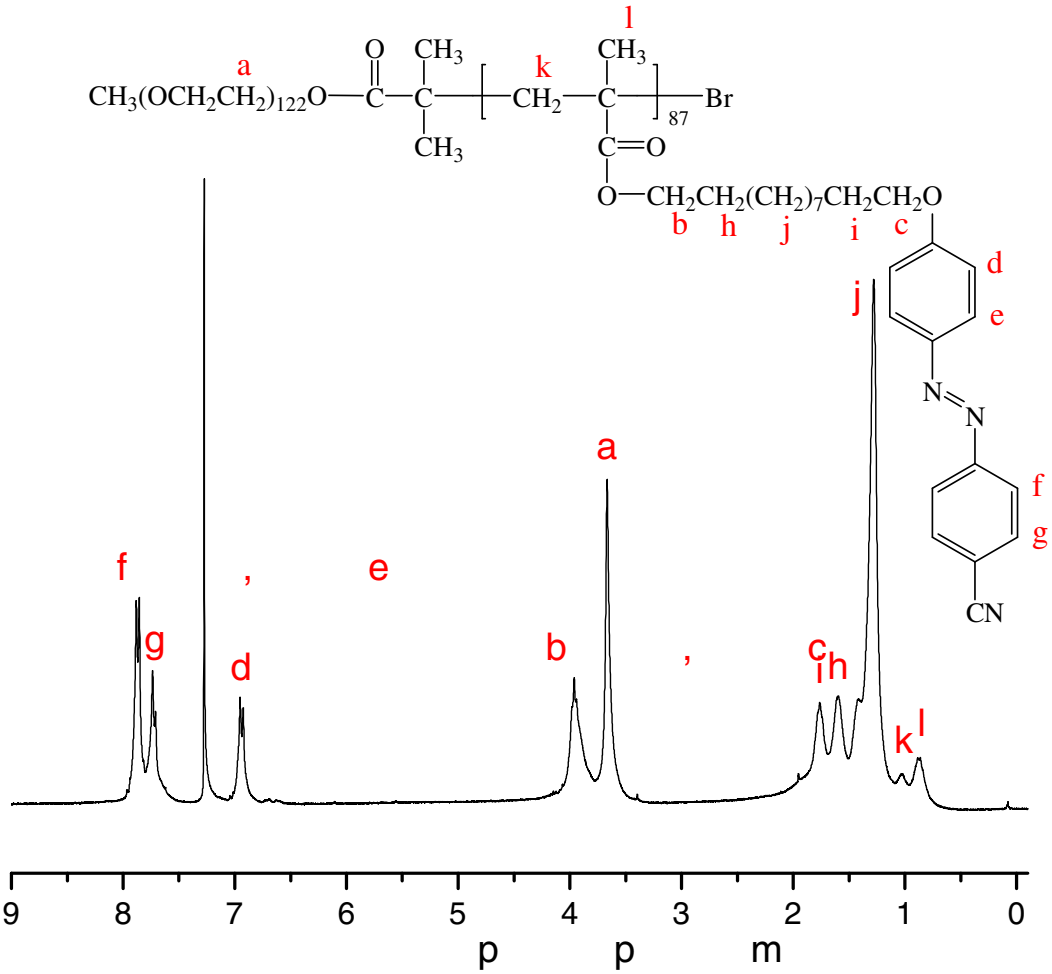


Figure S2. ^{1}H NMR spectrum of the diblock copolymer in $CDCl_3$.

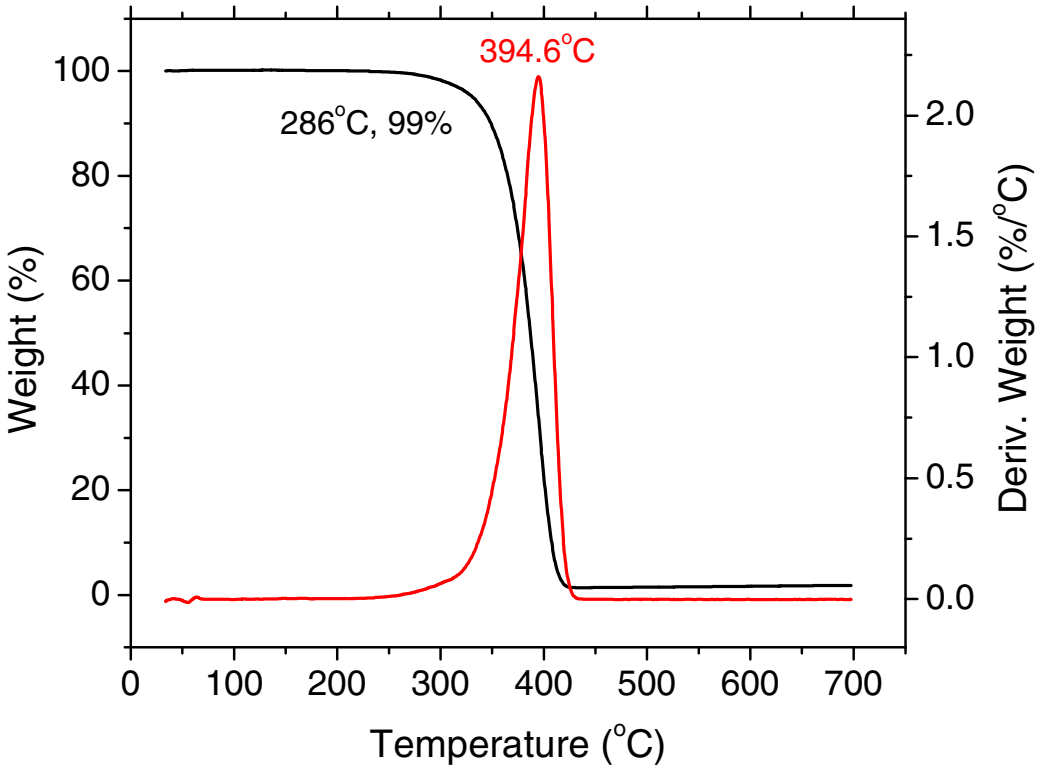


Figure S3. TGA curves of the PEO macroinitiator in N_2.

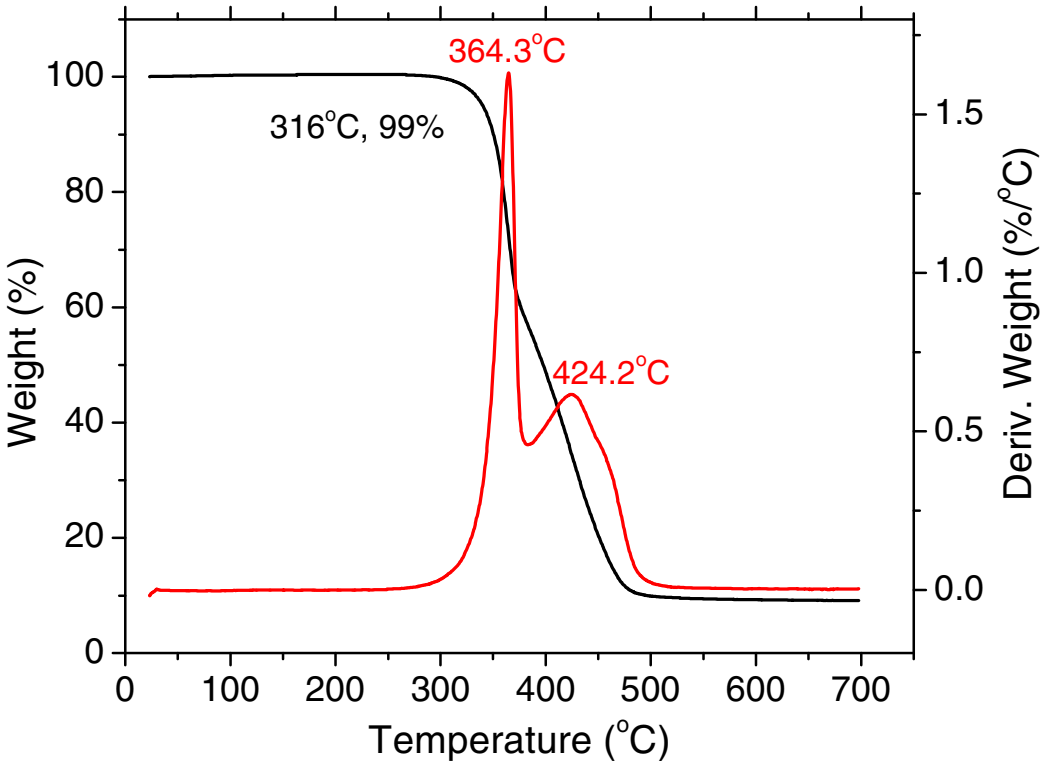


Figure S4. TGA curves of the diblock copolymer in N_2.

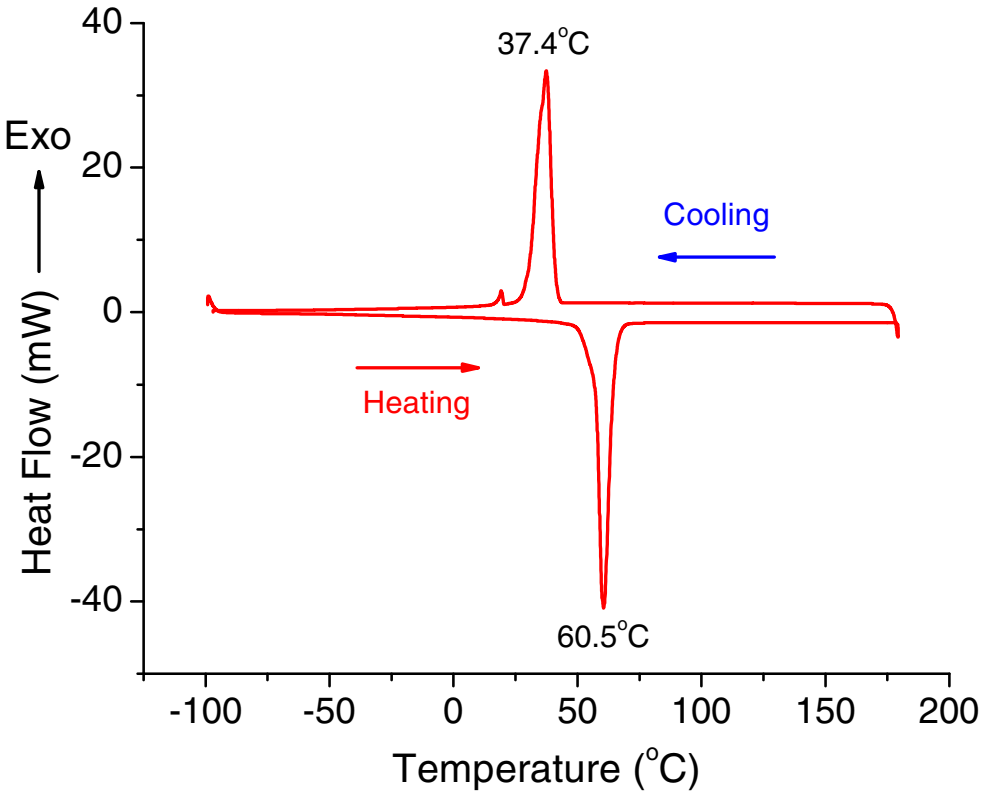


Figure S5. DSC curves of the PEO macroinitiator (10 °C/min, the second heating-cooling cycle).

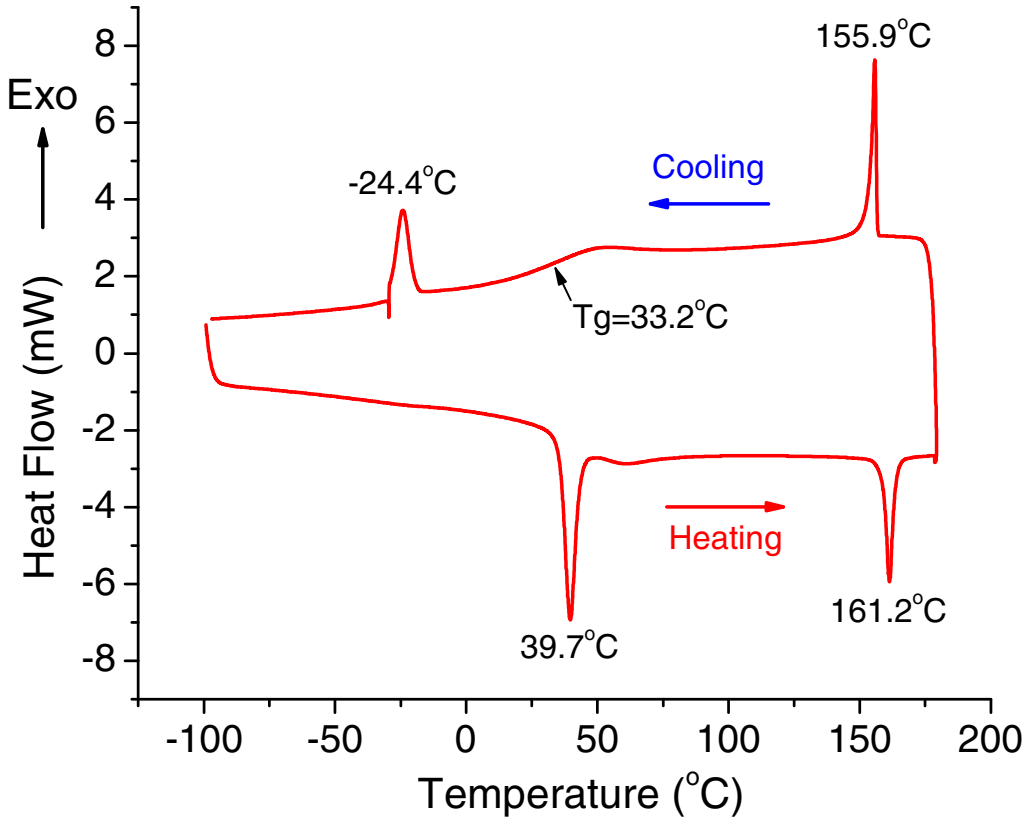


Figure S6. DSC curves of the diblock copolymer (10°C/min, the second heating-cooling cycle).

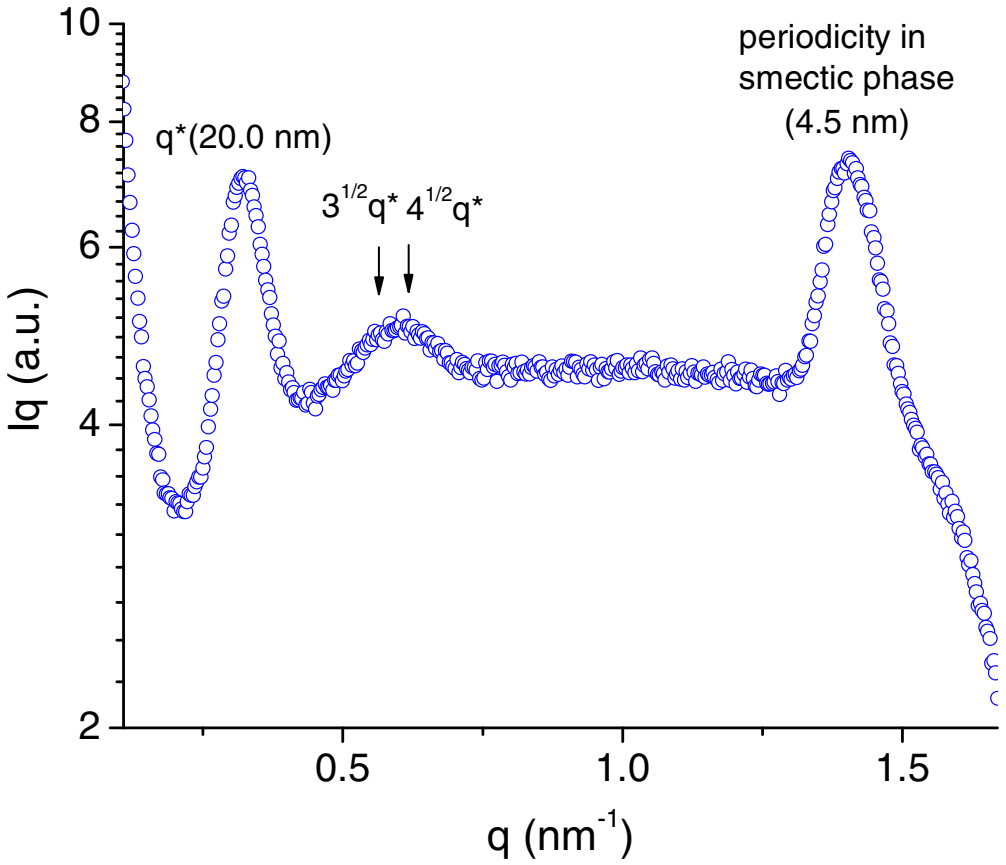


Figure S7. SAXS profile of annealed diblock copolymer film (stained with RuO_4).

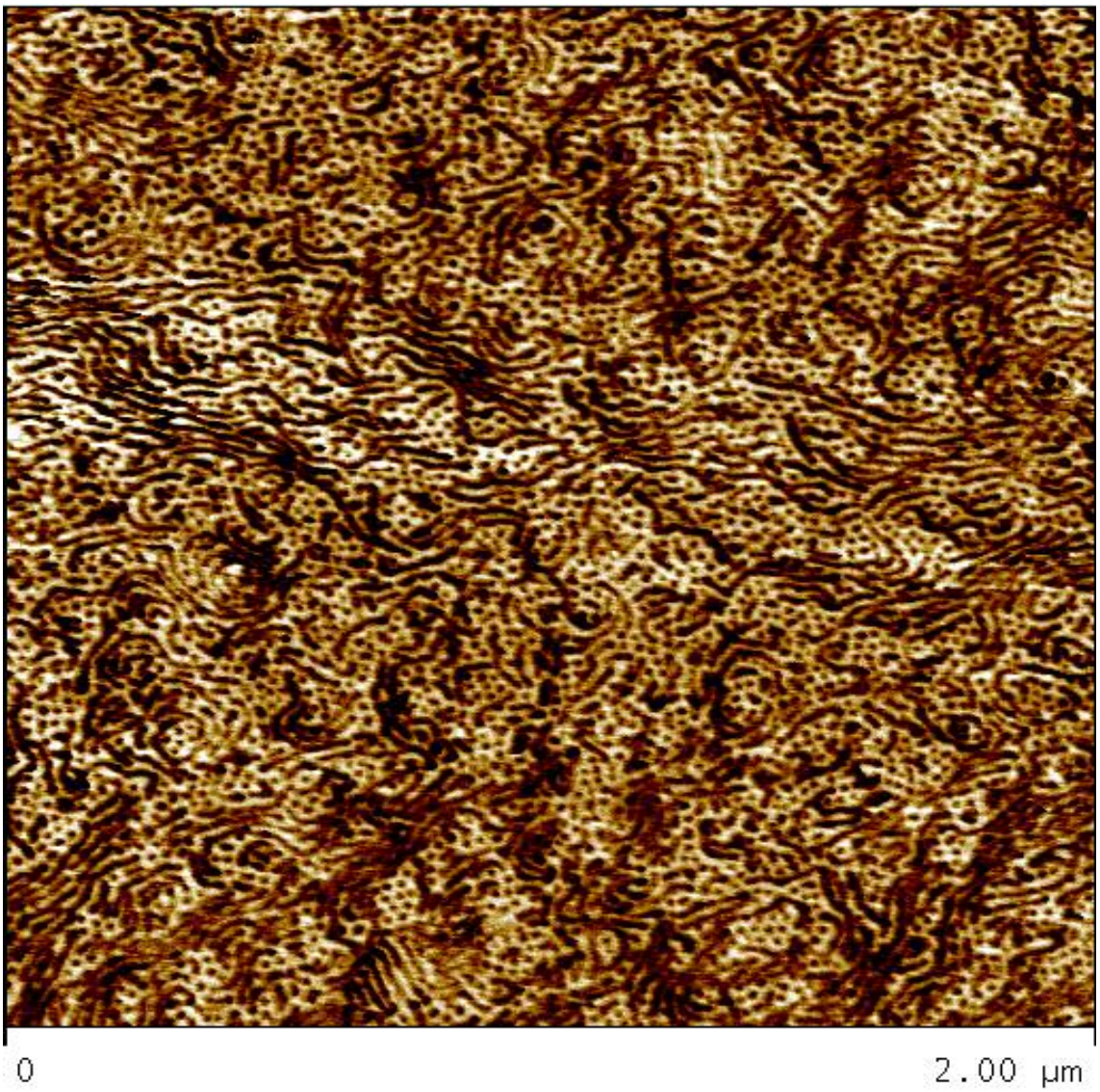


Figure S8. AFM image of diblock copolymer film after shearing.

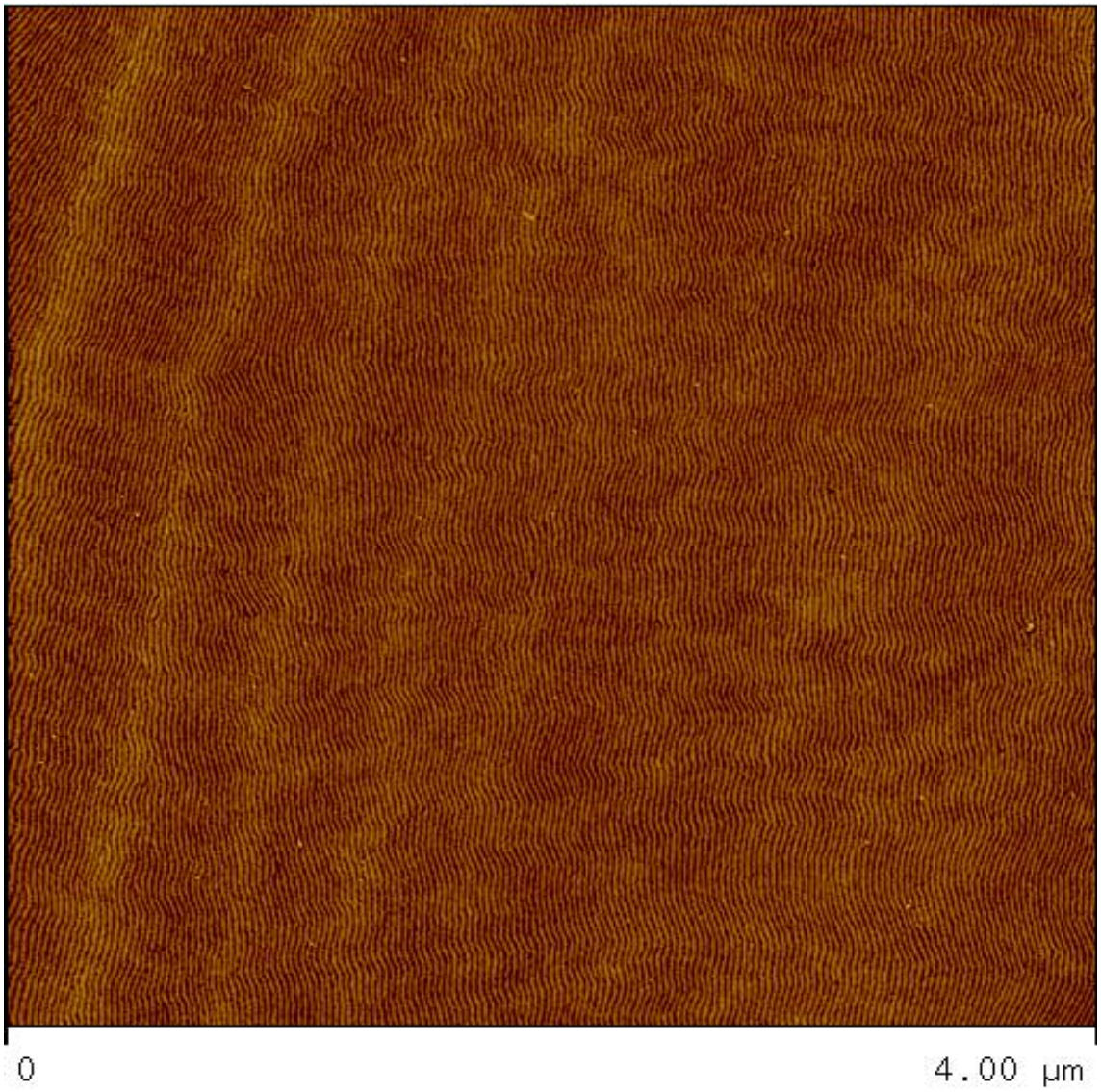


Figure S9. AFM phase image for the copolymer film annealed at 180°C for 1 day (4µm×4µm).

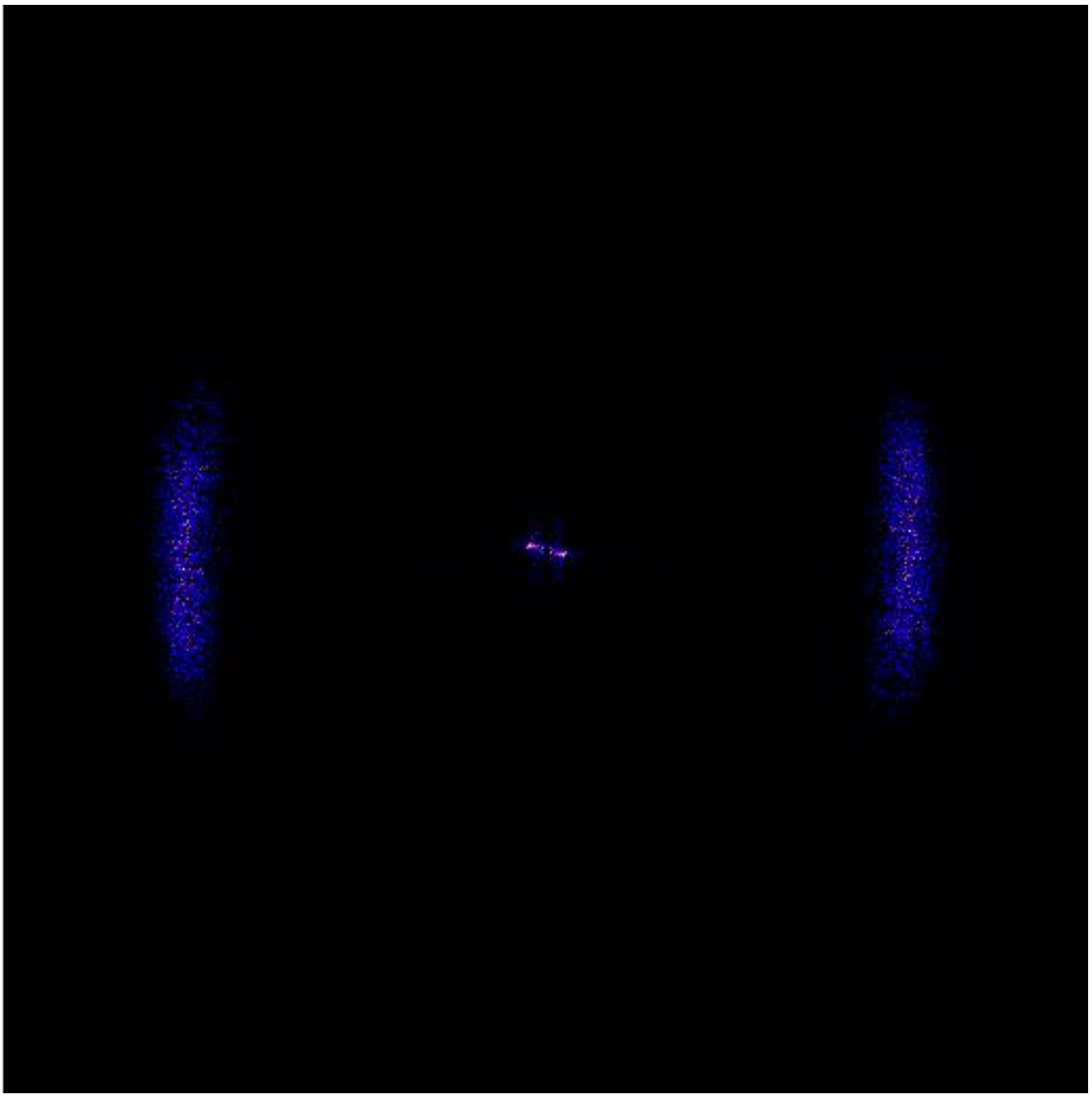
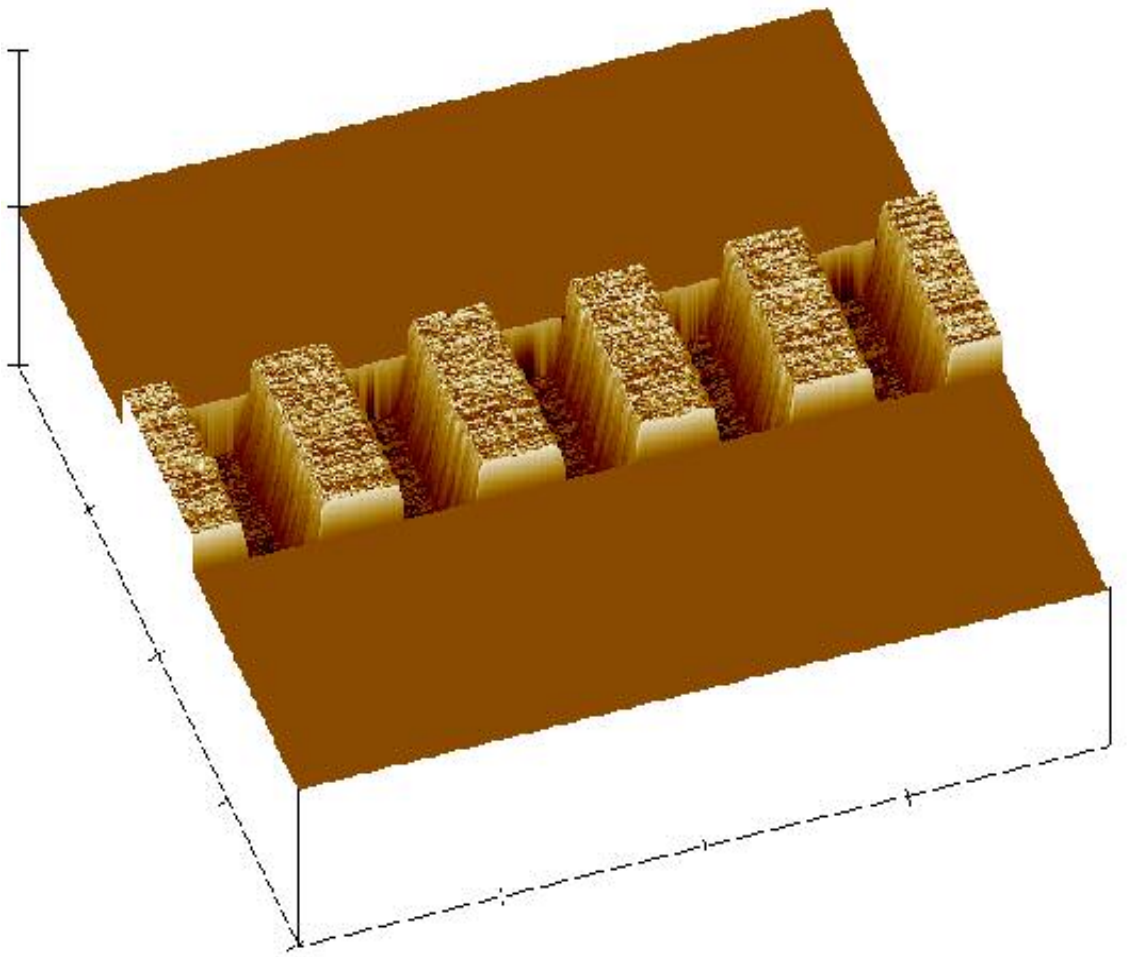
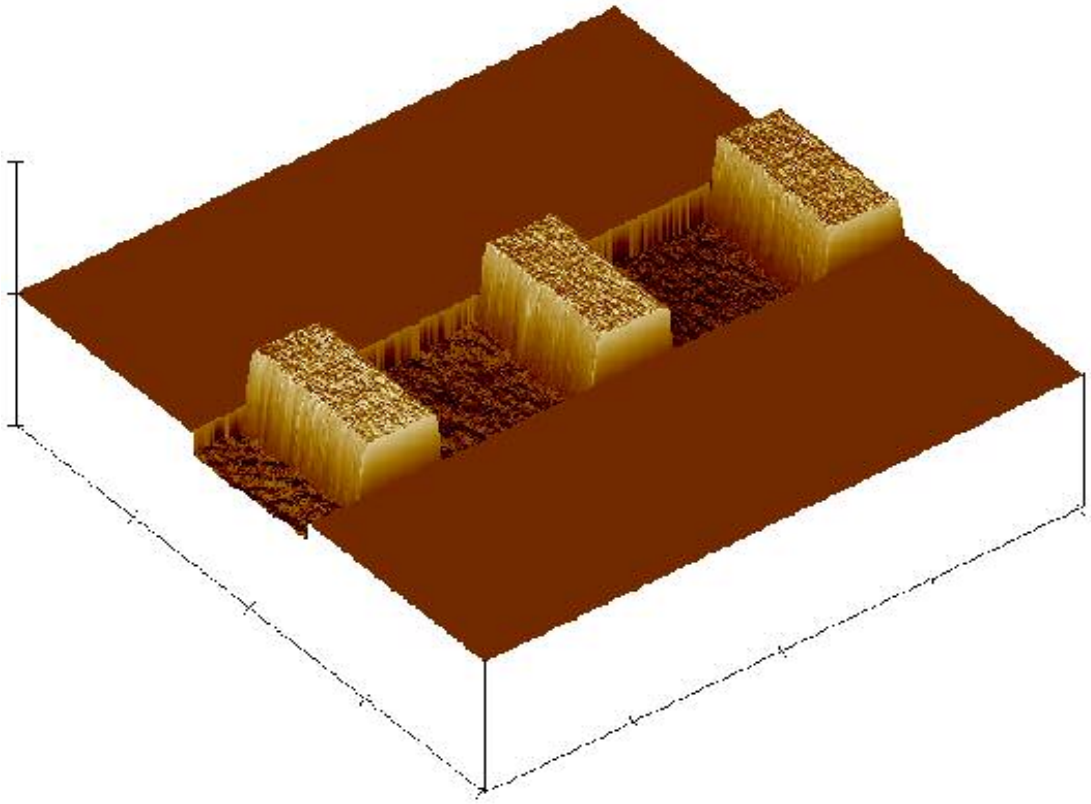


Figure S10. 2D FFT pattern of the image shown in Figure S9.



Scan size: 2μm×2μm; Z axis: 100 nm/div
Top width: 207 nm; Bottom width: 105 nm; Depth: 55 nm

Figure S11. 207 nm wide trench.



Scan size: 2μm×2μm; Z axis: 100 nm/div
Top width: 582 nm; Bottom width: 461 nm; Depth: 60 nm

Figure S12. 582 nm wide trench.