

## **Supporting Information**

### **Orientation Control of Block Copolymers using Surface Active, Phase-preferential Additives**

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## Experimental Details

**Synthesis of 5-Methyl-5-methoxycarbonyl-1,3-dioxan-2-one (MTC-Me) monomer.** 2,2-Bis(hydroxymethyl)propionic acid (20.0 g, 0.149 mol) and 300 ml of methanol were added to a 500 ml round bottom flask equipped with a magnetic stir bar and an overhead condenser. To this mixture, a few drops of concentrated sulfuric acid were added and the reaction was stirred under reflux for 72 hours. At this point, the reaction was cooled to room temperature and methanol was removed under vacuum. The crude product was distilled under high vacuum to obtain the pure methyl-2,2bis-(hydroxymethyl)propionate. Next, to a two liter round bottom flask equipped with a magnetic stir bar, purified 2,2bis-(hydroxymethyl)propionate (20.0 g, 0.135 mol) and anhydrous THF (1.35 L, 1 molar w.r.t. to the diol) were taken. The reaction was stirred over a nitrogen blanket and was cooled to 0 °C over 20 minutes. Ethyl chloroformate (32.2 g, 0.297 mol) was added to the cold reaction mixture while continued stirring. Finally, triethylamine (34.15 g, 0.337 mmol) was added dropwise to the reaction mixture. The reaction was stirred for 18 hours while slowly warming it up to room temperature. After 18 hours, the reaction was stopped and filtered to remove the salt. THF was evaporated under vacuum and the crude product was dissolved in approximately 200 ml of ethyl ether. This mixture was cooled to -20 °C to crystallize the 5-Methyl-5-methoxycarbonyl-1,3-dioxan-2-one (MTC-Me) monomer. Ethyl ether was decanted and the MTC-Me monomer was further crystallized three times to remove any ring opened diol or oligomeric impurities. To the purified monomer, approximately 5 ml of toluene was added and mixture was placed under high vacuum to remove any residual moisture. Finally the monomer was stored in a desiccator until it was used for polymerization. Yield 12.0g, ~ 51%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) δ: 1.34 –1.38 (3H, C-CH<sub>3</sub>), 3.80–3.82 (3H, O-CH<sub>3</sub>), 4.18–4.22, 4.66– 4.72 (4H, O-CH<sub>2</sub>-O-).

**Determination of Neutral Underlayers for PS-*b*-PMTC-Me BCP.** P(Sty-*r*-MMA)-OH brush polymer solutions in PGMEA, with various ratios of styrene and methyl methacrylate were spin coated at 2000 rpm on a silicon wafer. The coated wafer was baked at 250 °C for 2 minutes on a hot plate and

immediately cooled to room temperature. The resulting substrate was treated with a solvent (PGMEA) rinse step to remove any non-grafted brush polymer. Next, a 1.2 wt% solution of PS-*b*-PMTC-Me BCP was prepared by dissolving the BCP in PGMEA and filtering using a 0.2  $\mu\text{m}$  PTFE filter. The BCP solution was spin coated onto the P(Sty-*r*-MMA) underlayer modified silicon wafer obtained as described above. The BCP was annealed at 170 °C for 5 minutes and cooled to room temperature to enable phase-separation. The thin-film morphology was characterized by AFM to determine the step height of the islands and holes. The underlayer that showed the step height of 0.5 Lo ( $\sim 9.5$  nm) for the island/hole morphology was selected as the neutral underlayer for PS-*b*-PMTC-Me as observed by Bates and Willson previously.<sup>1</sup> Details are summarized in Table S1 below.

Table S1. Underlayers with various PMMA:PS ratios used to identify neutral conditions.

Sample	Underlayer Name	MMA % , Sty %	Morphology	Step height (nm)	Underlayer Neutral Yes/No
1	AZEMBLY™ NLD-303	100, 0	Holes	19.5, 1Lo	No
2	AZEMBLY™ NLD-328J	80, 20	Holes	9.5, 0.5Lo	Yes
3	AZEMBLY™ NLD-320	70, 30	Islands	19.5, 1Lo	No

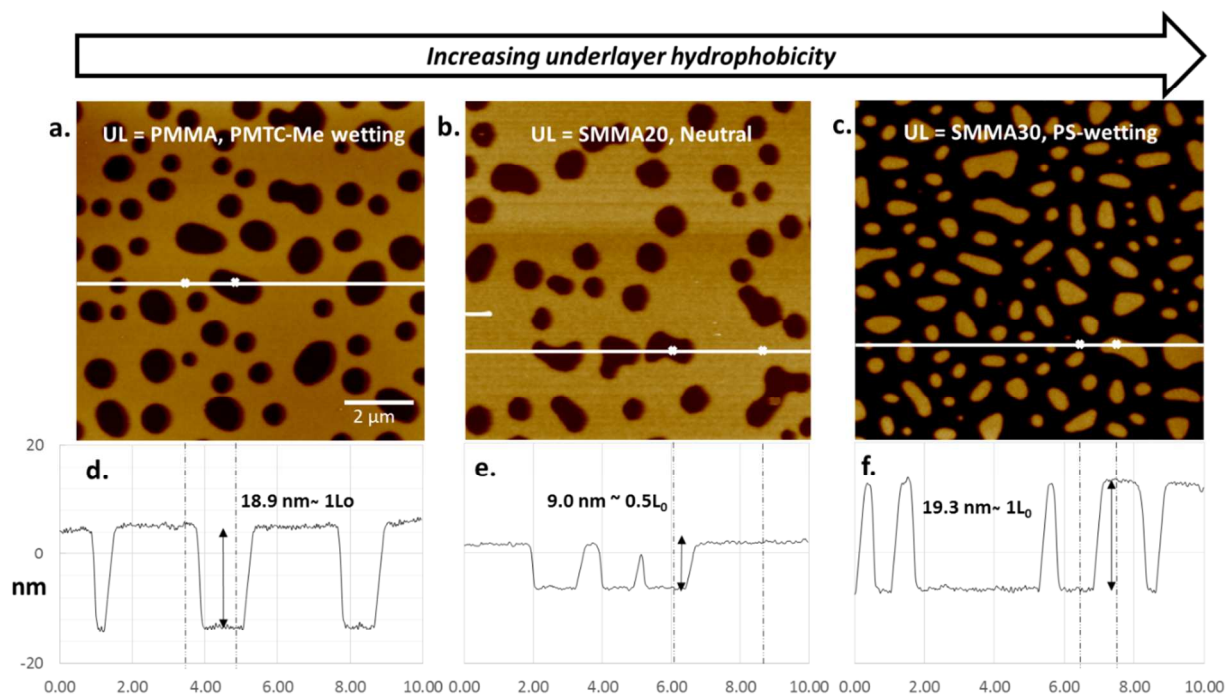


Figure S1. AFM height images and height profile data of PS-*b*-PMTC-Me BCP on various P(S-*r*-MMA) underlayer modified substrates to determine underlayer neutrality. (a,d) PMMA underlayer with PMTC-Me block wetting and 1 $L_0$  holes, (b,e) P(S-*r*-MMA) having 20% styrene with both PS and PMTC-Me wetting (neutral UL) and 0.5  $L_0$  holes, and (c,f) P(S-*r*-MMA) having 30% styrene with PS wetting and 1  $L_0$  islands.

**Effect of Annealing Time and Temperature on Thin Film Self-assembly of PS-*b*-PMTc-Me BCP with 3 wt. % SAP Additive**

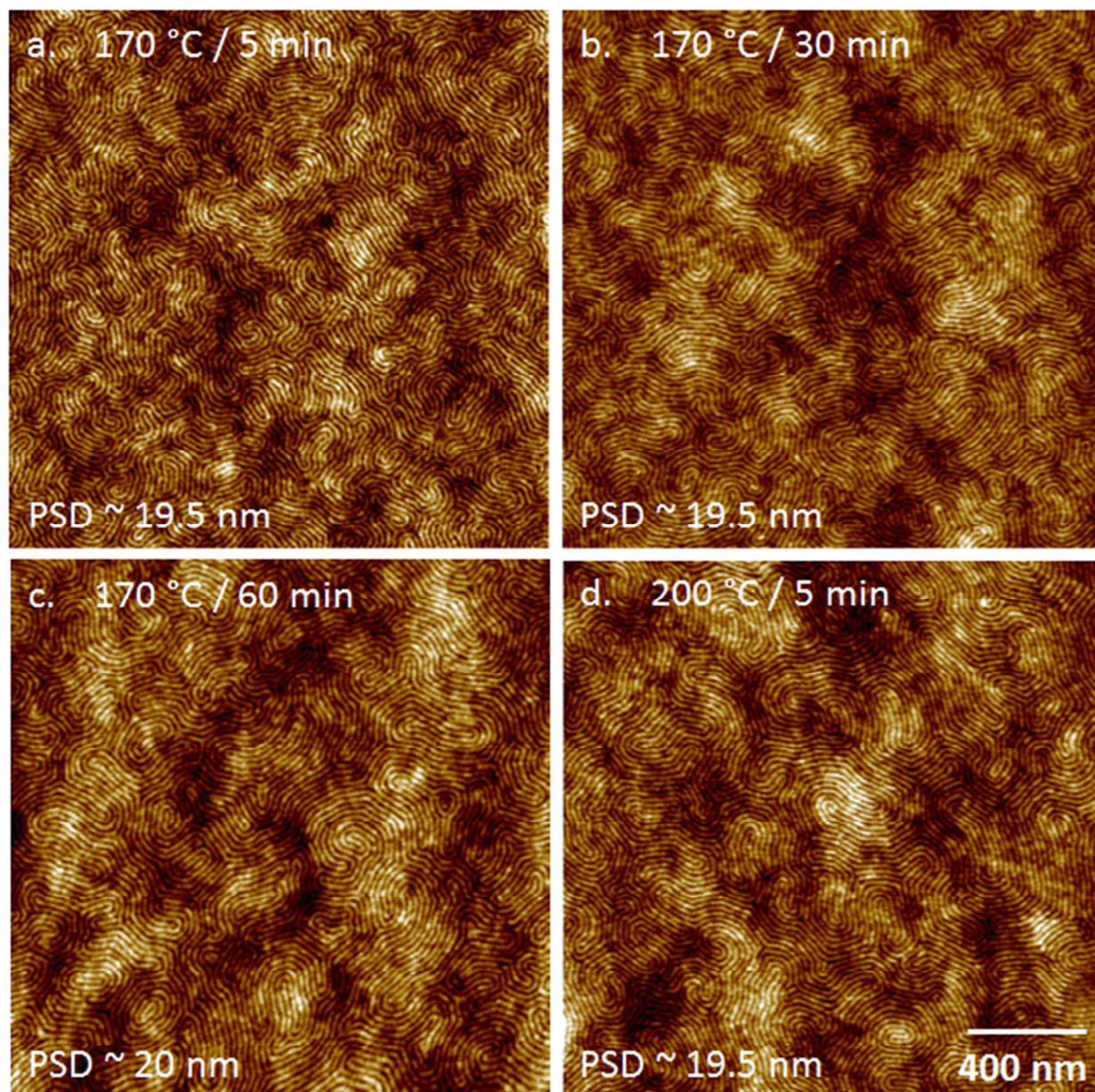


Figure S2. AFM height images of PS-*b*-PMTc-Me BCP (27 nm) on neutral underlayer modified substrate as a function of annealing time and temperature. (a) 170 °C for 5 minutes, (b) 170 °C for 30 minutes, (c) 170 °C for 60 minutes, and (d) 200 °C for 5 minutes.

Effect of Film Thickness on Thin Film Self-assembly of PS-*b*-PMTC-Me BCP with 3 wt. % SAP Additive

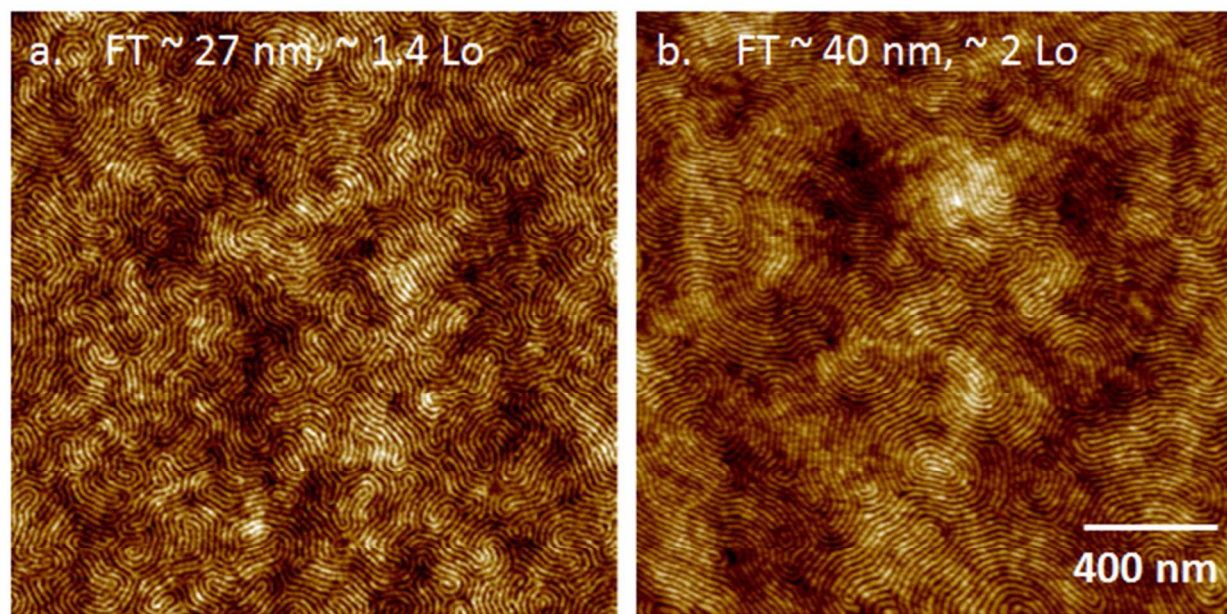
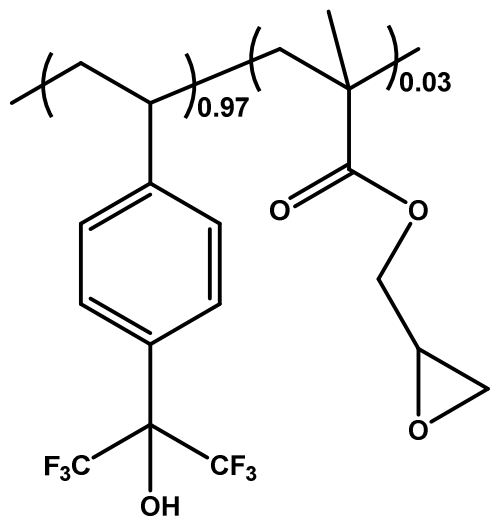


Figure S3. AFM height images of PS-*b*-PMTC-Me BCP thin films annealed at 170 °C for 5 minutes on neutral underlayer modified substrate as a function of film thickness. (a) 27 nm thick film (1.4 Lo) and (b) 40 nm thick film (2 Lo).

## Experiments to determine that SAP Additive is Phase-preferential and Non-neutral

*Synthesis of Poly(Hexafluoroalcohol styrene-r-glycidyl methacrylate) copolymer for underlayer based on HFA-Styrene.*



Scheme S1. Poly(Hexafluoroalcohol styrene-r-glycidyl methacrylate) copolymer as an underlayer to determine that SAP additive is phase-preferential.

Hexafluoroalcohol styrene (HFAS, 1.0 g, 3.70 mmol), glycidyl methacrylate (GMA, 0.016 g, 0.114 mmol) THF (5 g), and azobisisobutyronitrile (AIBN, 0.025 g, 0.1524 mmol, 4 mol% based on total moles of vinyl monomers) were combined in a 100 mL round bottom flask (RBF) equipped with a magnetic stir-bar and an overhead condenser. The reaction mixture was stirred at 70° C for 18 hours and was stopped by cooling the reaction to room temperature. The resulting polymer was isolated by two precipitations in cold hexanes, and was dried under vacuum at 50° C for 24 hours.

### *Grafting of P(HFAS-r-GMA) underlayer and PS-b-PMTC-Me BCP coating*

95 mg of P(HFAS-r-GMA) copolymer obtained above and 5 mg of pNBT PAG were dissolved in 900 mg of PGMEA solvent to obtain a 1 wt. % solution. The resulting solution was filtered through a 0.2 μm PTFE

filter and was coated on a silicon coupon at 2000 rpm for 30 sec. The coated wafer was baked at 200 °C for 3 minutes on a hot plate and immediately cooled to room temperature. The resulting substrate was treated with a solvent (PGMEA) rinse step to remove any non-grafted brush polymer. Next, a 1.2 wt% solution of PS-*b*-PMTC-Me BCP was prepared by dissolving the BCP in PGMEA and filtering using a 0.2 μm PTFE filter was spin coated onto the underlayer modified silicon wafer obtained as described above. The BCP was annealed at 170 °C for 5 minutes and cooled to room temperature to enable phase-separation.

**Control Examples for Thin Film Self-assembly of PS-*b*-PMTC-Me BCP with Small Molecule Hydrogen-bonding Additives**

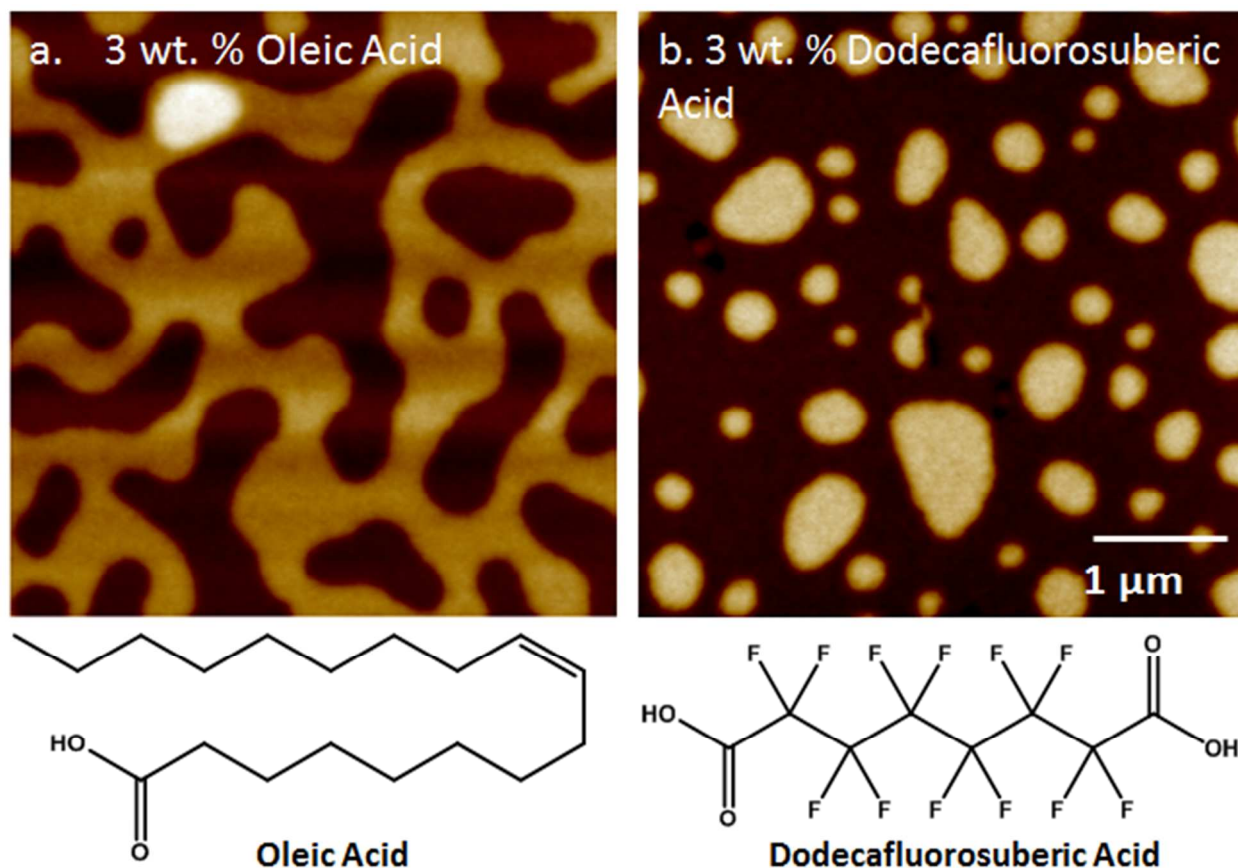


Figure S4. AFM height images of PS-*b*-PMTC-Me BCP thin films annealed at 170 °C for 5 minutes on neutral underlayer modified substrate with small molecule hydrogen-bonding additives. (a) 3 wt. % oleic acid, and (b) 3 wt. % dodecafluorosuberic acid. Both samples showed 0.5 Lo features.

**Graphoepitaxy Prepattern Substrate Preparation.** AZEMBLY™ NLD-328J was spin coated at 2000 rpm for 30 seconds on a silicon wafer substrate stack comprised of a silicon wafer bottom layer coated with ~30 nm thick amorphous carbon layer and 10 nm thick silicon nitride (SiN<sub>x</sub>) layer. After forming the thin film, the coated wafer was baked at 250° C for 2 minutes and cooled to room temperature. The underlayer was then given a solvent rinse by casting PGMEA on top of the coated wafer, letting the

solvent puddle for 30 seconds, and spin drying the treated wafer at 2000 rpm for 30 seconds. The final film thickness of the underlayer was 10 nm after the solvent rinse. Next, a 60 nm thick layer of a commercial 193 nm negative-tone photoresist (JSR ARF7210JN-8) was disposed on this underlayer coated substrate followed by post application bake at 80° C for 60 seconds. The photoresist layer was then exposed using a 193 nm immersion interference tool (IBM NEMO) with fixed dose of 4.67 mJ, baked at 95° C for 60 sec, and developed for 60 seconds with 2-heptanone developer. The resulting 200 nm pitch patterned photoresist layer was then hard baked at 200° C for 3 min prior to coating a block copolymer formulation.

**Graphoepitaxy DSA of PS-*b*-PMTc-Me BCP + 3 wt. % SAP Additive.** PS-*b*-PMTc-Me BCP (0.01 g) was dissolved in PGMEA (1.24 g, 10,000 parts by weight) to form a 0.8 wt. % stock solution of the block copolymer based on total weight of the solution. The solution was passed through a 0.2 micrometer polytetrafluoroethylene (PTFE) filter. A separate stock solution was prepared by dissolving a selected SAP additive (0.1 g) in PGMEA (12.4 g) at 0.8 wt. % SAP based on total weight of the solution. The SAP solution was passed through a 0.2 micrometer PTFE filter. A desired amount of SAP stock solution was added to the block copolymer solution and the mixture was stirred well to form a homogenous solution. The resulting solution containing block copolymer and SAP was spin coated on the patterned photoresist substrate described above. After spin coating, the coated wafer was baked at a 200 °C for 5 minutes and immediately cooled to room temperature. The self-assembled domains of the block copolymer inside the guiding prepattern trenches were analyzed with top down and cross section SEM.

**Determination of Polymer Density by X-ray Reflectivity.** The polymer density was determined to  $\rho = 1.28$  by specular x-ray reflectivity (XRR) using a diffractometer (X'Pert Pro MRD, Panalytical, Westborough, MA) equipped with a ceramic X-ray tube (wavelength = 0.154 nm) and high-resolution horizontal goniometer (reproducibility  $\pm 0.0001^\circ$ ). The XRR scans (x-ray counts versus incidence angle)

were fitted using the X'Pert Reflectivity software. A single layer model with the average composition  $C_6O_5H_{10}$  was used as shown in Figure S5.

### XRR of PMTC-Me Homopolymer

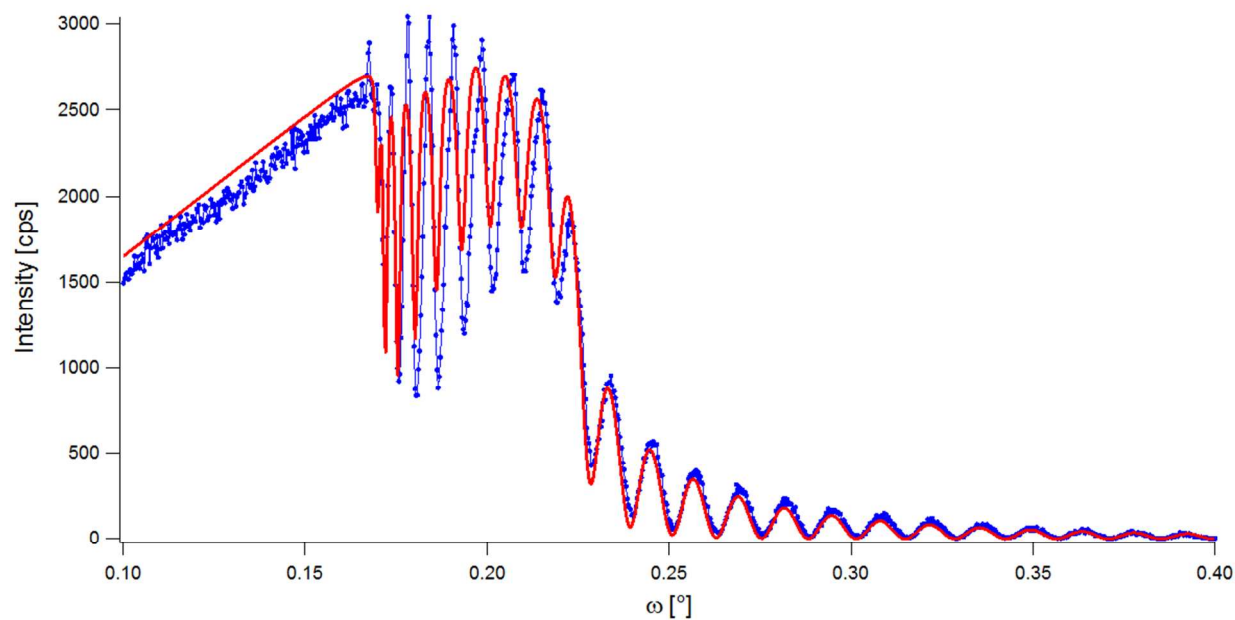


Figure S5: X-ray reflectivity data of a 27 nm thick film of PS-*b*-PTMC-Me on silicon. Data is shown in blue and the fit to a single layer is shown in red.

### References

- (1) Kim, S.; Bates, C. M.; Thio, A.; Cushen, J. D.; Ellison, C. J.; Willson, C. G.; Bates, F. S. Consequences of Surface Neutralization in Diblock Copolymer Thin Films. *ACS Nano* **2013**, 7 (11), 9905–9919.