# **Supporting Information**

# Simultaneous in-film polymer synthesis and selfassembly for hierarchical nanopatterns

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#### **Experimental Procedures**

Polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) copolymers (Kraton D1164P and Kraton D1113P) were obtained from Kraton Polymer, containing 71 vol% and 84 vol% polyisoprene respectively. Molecular weights were estimated to be 124 kg/mol (D1164P, SIS-71) and 110 kg/mol (D1113P, SIS-84) from size exclusion chromatography in tetrahydrofuran using polystyrene standards. Toluene, styrene, isoprene, methyl methacrylate, 4-vinyl pyridine, anisole and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide were purchased from Sigma-Aldrich and used as received. Polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA, P8149-SMMA,  $M_n$ =52-142 kg/mol,  $M_w/M_n$ =1.2) and polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP, P9006A-S4VP,  $M_n$ =21-4 kg/mol,  $M_w/M_n$ =1.2) were purchased from Polymer Source. N<sub>2</sub> (purity >99.99%) was used throughout the entire study. Silicon wafers were obtained from University Wafer and used as substrates.

The silicon wafers were first cleaned with Piranha solution ( $H_2O_2:H_2SO_4 = 3:7 \text{ vol:vol}$ ) at 95°C for 2 h, rinsed with deionized water, and dried with compressed air prior to use. SIS-71 and SIS-84 were dissolved in toluene at 2 wt% solid concentration; PS-b-PMMA and PS-b-P4VP were dissolved in anisole at 5 wt% solid concentration. The photoinitiator (diphenyl(2,4,6trimethylbenzoyl)phosphine oxide) was dissolved in toluene (2 wt%) or anisole (5 wt%) first and then added into polymer solution. The initiator concentration relative to all solids was 2.4 wt% throughout the entire study. All the polymeric films were spun cast from the above photoinitiatorcontained solutions at 800 rpm for the first 9 s and then at 3500 rpm for 45 s. For the in-film photopolymerization process, the samples were placed in a chamber with a quartz top (for UVtransmittance), and vapors were introduced by bubbling N2 through liquid monomers at flow rates regulated by two mass flow controllers (Alicat, MCS-100SCCM-D), responsible for saturated monomer vapor and dry N2 gas separately. The films were first exposed to monomer vapor and N2 at 100 sccm for 90 min to remove the oxygen from the liquid reservoir, sample chamber, and polymer thin films. A UV lamp (Black-Ray, high intensity UV lamp, 365 nm wavelength) was then turned on for irradiating the photoinitiator with a lamp-sample distance of 10 cm. Thermal annealing of BCP films after in-film polymerization was performed by heating at 140 °C for 24 h. The control experiment of solvent vapor annealing of SIS-71 films under UV irradiation was performed under toluene vapor at  $p/p_0=0.85$  for 2 h. UV fused silica metallic ND filters (OD=0.1,

0.2 and 0.3, ThorLabs) were used for manipulating the power intensity, which was measured by a power meter (ThorLabs, PM100A). The in-film photopolymerization proceeded with exposure to the UV (5 min to 800 min). After the reactions, the films were dried with neat N<sub>2</sub> at 50 sccm for 1 h. The control experiments of PS-*b*-PMMA and PS-*b*-P4VP (both containing photoinitiators) were annealed in styrene vapor at  $p/p_0=0.85$  with no UV irradiation, where p is the partial pressure of styrene and p<sub>0</sub> is the vapor pressure of styrene at room temperature.

Photomasks with circular patterns and square patterns were directly placed on the as-cast SIS-71 and SIS-84 films, respectively, during in-film photopolymerization. SIS-71 and SIS-84 thin films were exposed to styrene vapor and isoprene vapor at  $p/p_0=0.75$  with UV irradiation for 30 min. Post shear aligning of the SIS-84 film was performed by toluene vapor annealing with a PDMS cap (Sylgard 184, crosslink ratio=10:1, m<sub>base</sub> : m<sub>curing agent</sub>) on the top of BCP/homopolymer blends for 1 h at  $p/p_0=0.85$ .

The BCP films were characterized using variable angle spectroscopic ellipsometry (VASE, J.A. Woollam Co., M-2000D) to determine the film thickness using a wavelength range from 420 nm to 1600 nm with incident angles of 55°, 60° and 65°. The data were fit using a model consisting of the silicon substrate, a SiO<sub>2</sub> layer and a Cauchy layer for describing the thickness and optical constants of polymer films before and after photopolymerization. Atomic force microscopy (SPID Bruker Fastscan AFM) in tapping mode was used to investigate the surface nanostructures of polymer films. A custom quartz crystal microbalance (QCM, Advanced Wave Sensors, Valencia, Spain) with a N2PK impedance analyzer (Thornhill Canada) was used to determine the in-situ mass changes of films with time during in-film photopolymerization using the same experimental setup. The films were spun from the same solution with identical spin coating conditions onto 1 in. quartz crystals with Au electrodes (Inficon, East Syracuse, NY). The QCM provides changes in resonance frequency and dissipation of the piezoelectric quartz crystal at the 1<sup>st</sup>, 3<sup>rd</sup> and 5<sup>th</sup> harmonic of the fundamental frequency (5 MHz), which fit by a Lorentzian peak to the conductance and susceptibility in the frequency domain. The areal mass of the film ( $\Delta M_A$ ) was then determined using Sauerbrey equation:

$$\Delta f_n = \frac{-2n {f_1}^2}{Z_q} \Delta M_A$$

where  $f_1$  is the resonance frequency of quartz (5MHz),  $Z_q$  is the acoustic impedance of quartz (8.84  $\times 10^6$  kg/m<sup>2</sup>·s), n is the order of the measured harmonic. The grazing-incidence X-ray small angle scattering (GISAXS) experiments were performed at the 8-ID-E beamline at the Advanced Photon Source, Argonne National Lab. The beamline operates at an energy of 7.35 keV and the GISAXS patterns were collected at the incident angle of 0.14° by a Pilatus 1M-F area detector. The beam size is approximately 100 µm  $\times$  50 µm with a sample-to-detector distance (SDD) of 2165 mm. Domain-spacing of BCP films was determined using d=2 $\pi$ /q<sup>\*</sup>, where q<sup>\*</sup> is the primary peak position. A Keck-II 3D optical profilometer was used to characterize surface topology of SIS films after photopolymerization with photomasks.

#### Estimates of $\chi N$ of SIS during in-film photopolymerization

The degree swelling of the SIS has been determined from in-situ QCM to be approximately 40 %; due to pinning by the substrate, this swelling can be considered to be identical to the volume

fraction of solvent in the film at equilibrium. In order to estimate if the copolymer is ordered or disordered under the solvent annealing conditions,  $\chi N$  is estimated for the neat copolymer and the swollen state. For the neat block copolymer, we estimate  $\chi N$  to be 260 ( $\chi = 71.4/T-0.0857 = 0.154$  at 298K)<sup>1</sup> and the molecular weight of 124,000 Da from GPC. Based on the scaling of  $\chi$  with solvent swelling ( $\chi_{eff} = \chi (1-\phi_{solvent})^{1.6}=0.068$  at 298 K),<sup>2</sup> the effective  $\chi N$  in the styrene vapor swollen state is approximately 120, which is well-above ( $\chi N$ )<sub>ODT</sub> (20-30) for SIS copolymer. Thus, the SIS remains in an ordered state throughout the whole process.

#### Estimates molar ratio of monomer : initiator for SIS films with styrene and isoprene vapor

The degree of swelling (f) in BCP films by monomer vapor is determined by QCM measurements. With a known mass ratio of photoinitiator: BCP (2.4 wt%) in the films, we can estimate molar ratio of monomer to initiator by following equation and the result are listed in Table S1.

$$\frac{n_{monomer}}{n_{initiator}} \frac{\frac{f}{M_{monomer}}}{\frac{2.4 \times 10^{-2}}{M_{initiator}}}$$

	Styrene vapor at p/p <sub>0</sub> =0.85	Isoprene vapor at p/p <sub>0</sub> =1
SIS-71	55:1	40:1
SIS-84	55:1	40:1

**Table S1.** The estimated molar ratio of monomer to initiator of SIS films with in-film photopolymerization of styrene and isoprene vapor

#### **Supplemental Figures**



**Figure S1.** The derived mass gain and film thickness increases of SIS-71 film as a function of photopolymerzation time. In-film photopolymerzation was performed with presence of styrene vapor at  $p/p_0=0.85$  and UV power intensity of 0.5 mW/cm<sup>2</sup>.



Figure S2. AFM phase images of as-cast (a) SIS-71 and (b) SIS-84 thin films. Scale bar: 500 nm



**Figure S3.** (a) AFM height images of SIS-71 films after photopolymerization in presence of styrene with homo-polystyrene content of 19 vol%, corresponding with Figure 2(c) and (b) its line-cut height step profile. The scale bar is  $6 \mu m$ .



**Figure S4.** AFM phase images of SIS-71 films after in-film photopolymerization with the added homo-polystyrene content of (a) 10 vol%, (b) 23 vol%, (c) 25 vol%, and with the added homo-polyisoprene of (d) 5 vol%, (e) 11 vol% and (f) 13 vol% in the film. AFM phase images of SIS-84 films after photopolymerization in the presence of styrene, with (g) 6 vol%, (h) 9 vol% and (i) 19 vol% polystyrene content. The scale bar is 500 nm except for (b) and (c) where it is 6  $\mu$ m.



Figure S5. AFM height image of films (a) SIS-71 blending with 19 vol% PS, with characteristic island and hole features, representing lamellar morphology of SIS/homo-PS blends film (Scale bar: 6  $\mu$ m) and (b) AFM phase image of SIS-84 blending with 14 vol% PI (Scale bar: 500 nm) after thermal annealing of films after in-film photopolymerization (Figure 2c and Figure 2h, respectively) at 140 °C for 24h.



**Figure S6.** AFM phase image of SIS-71 film annealed in toluene vapor at  $p/p_0=0.85$  with UV irradiation (intensity: 0.5 mW/m<sup>2</sup>) for 2 h. Scale bar: 500 nm



**Figure S7.** BCP nanostructures as a function of polyisoprene content (in the BCP + synthesized) of the film corresponding to the AFM images.



**Figure S8.** 2D GISAXS patterns of an SIS-84 film after in-film photopolymerization of styrene vapor at  $p/p_0=0.85$  for 1 h with UV power intensity of (a)  $0.5 \text{ mW/cm}^2$ , (b)  $0.4 \text{ mW/cm}^2$ , (c)  $0.32 \text{ mW/cm}^2$  and (d)  $0.25 \text{ mW/cm}^2$ 



**Figure S9**. Unaltered AFM phase images that were stitched together to generate Figure 5d. The figure in the main text was generated from images (a) and (c) here. These images were flattened by subtracting a 2D spline function derived from the flat areas of both images. In the stitched image, the overlap region between the two images is a linear combination of the two flattened images. Scale bar: 1  $\mu$ m

## **References**

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