Electronic Supplementary Information (ESI)

Polymer Blend-Filled Nanoparticle Films via Monomer-Driven Infiltration of Polymers and Photopolymerization

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Spectroscopic Ellipsometry Data Fitting and Modeling

Step 1. The optical constants (A, B, and C) of pure PS film and pure SiO_2 NP film are measured using a spectroscopic ellipsometry under ambient conditions. The thickness of a SiO_2 NP/PS bilayer is determined using a two-layer Cauchy model with measured optical constants of the pure PS and SiO_2 NP films as inputs as shown in Figure S1. The refractive index (n) of each Cauchy layer as a function of wavelength (λ) is described by:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad \text{(S1)}$$

where A, B and C are optical constants of the Cauchy Model.

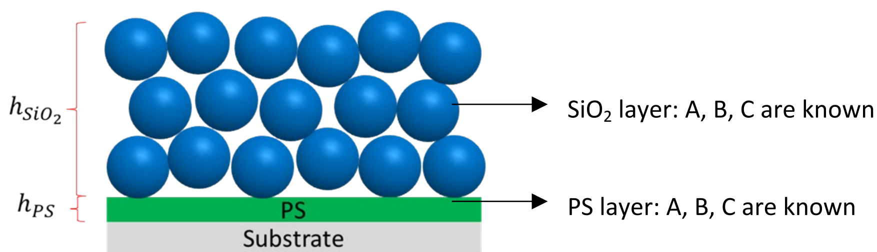

Figure S1 Measurement of the thickness of a bilayer consisting of a SiO_2 NP layer atop a PS layer, using a two-layer Cauchy model.

Step 2. We perform *in situ* spectroscopic ellipsometry to monitor PS infiltration into the SiO_2 NP packing and the photopolymerization of MMA. The bilayer sample is placed in an ellipsometry cell that have small aliquots of MMA and HMP. Then the cell is sealed and the collection of the change in amplitude ratio (ψ) and the phase difference (Δ) starts within a few seconds. To fit *in situ* data during solvent annealing and UV exposure, we use a two-layer Cauchy model with

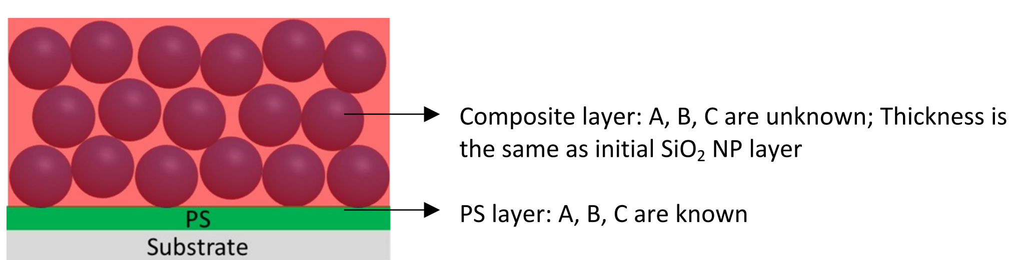

Figure S2 Fitting of the refractive index of composite layer and the thickness of PS layer undergoing monomer-driven infiltration of polymers and subsequent photopolymerization using a two-layer Cauchy model.

measured optical constants of the pure PS and the thickness of the SiO_2 NP film fixed. The optical constants of the composite layer and the thickness of PS layer are set as variables (Figure S2).

<u>Step 3</u>. To determine the refractive index of polymer blend-filled SiO_2 NP film and the thickness of residual PS layer, the film is measured with ellipsometry again after 12 hrs drying. With the optical constants of the pure PS layer and the thickness of the composite layer fixed, the data is fitted using a two-layer Cauchy model.

Calculating Volume Fraction of Each Component in Composite Films

Volume Fraction-Weighted Mixing Rule for Refractive Index[1-2]

1. SiO_2 NP layer (before annealing or photopolymerization):

$$n = \emptyset_{void} n_{void} + \emptyset_{SiO_2} n_{SiO_2} \quad \text{(S2)}$$

$$\emptyset_{void} + \emptyset_{SiO_2} = 1 \quad \text{(S3)}$$

$$\therefore\ \emptyset_{void} = \frac{n_{SiO_2} - n}{n_{SiO_2} - 1} \quad \text{(S4)}$$

2. Top layer of SiO_2 NP/PS bilayer after monomer-driven infiltration of polymers and drying

$$n_{comp} = \emptyset_{void}' n_{void} + \emptyset_{SiO_2} n_{SiO_2} + \emptyset_{PS} n_{PS} \quad \text{(S5)}$$

$$\emptyset_{void}' + \emptyset_{SiO_2} + \emptyset_{PS} = 1 \quad \text{(S6)}$$

$$\emptyset_{void}' + \emptyset_{PS} = \emptyset_{void} \quad \text{(S7)}$$

$$\emptyset_{PS} = \frac{\Delta h_{PS}}{h_{SiO_2}} \quad \text{(S8)}$$

3. SiO_2 NP film after MMA condensation, photopolymerization and drying

$$n_{comp} = \emptyset_{void}' n_{void} + \emptyset_{SiO_2} n_{SiO_2} + \emptyset_{PMMA} n_{PMMA} \quad \text{(S9)}$$

$$\emptyset_{void}' + \emptyset_{SiO_2} + \emptyset_{PMMA} = 1 \quad \text{(S10)}$$

$$\emptyset_{void}' + \emptyset_{PMMA} = \emptyset_{void} \quad \text{(S11)}$$

4. PS/PMMA/SiO_2 NP Composite Film:

$$n_{comp} = \emptyset_{void}' n_{void} + \emptyset_{SiO_2} n_{SiO_2} + \emptyset_{PS} n_{PS} + \emptyset_{PMMA} n_{PMMA} \quad \text{(S12)}$$

$$\emptyset_{void}' + \emptyset_{SiO_2} + \emptyset_{PMMA} + \emptyset_{PS} = 1 \quad \text{(S13)}$$

$$\emptyset_{void}' + \emptyset_{PMMA} + \emptyset_{PS} = \emptyset_{void} \quad \text{(S14)}$$

$$\emptyset_{PS} = \frac{\Delta h_{PS}}{h_{SiO_2}} \quad \text{(S15)}$$

where n_{comp}, n_{void}, n_{SiO_2}, n_{PS} and n_{PMMA} refer to the refractive indices of the polymer filled composite, void (air), SiO_2, PS, PMMA respectively, whereas $\emptyset_{void}'$, $\emptyset_{SiO_2}$, $\emptyset_{PS}$ and $\emptyset_{PMMA}$ refer to the volume fraction of each component. The values for n_{void} and n_{SiO_2} are taken as 1 and 1.45, respectively.[3]

$\emptyset_{void}$ which refers to the original void fraction of densely-packed SiO_2 NP film prepared by spin-coating can be determined by Equations S3 where n is obtained by characterizing the SiO_2 NP layer (pure SiO_2 NP film or SiO_2 NP/PS bilayer before annealing) with spectroscopic elliposometry. Thus, $\emptyset_{SiO_2}$ can be calculated based on Equation S3.

$\emptyset_{PS}$ can be calculated from Equation S15 where Δh_{PS} is the change in the thickness of the PS layer and h_{SiO_2} is the thickness of the SiO_2 NP layer before annealing (see Figure. S1).

To obtain $\emptyset_{PMMA}$ and $\emptyset_{void}'$ by combining Equations S12-S15, it is important to determine n_{PS} and n_{PMMA} in the interstices of NP packing. It has been well established that the refractive index of one polymer is the result of several factors, including polarization, chain flexibility, orientation in the backbone, etc.[4] Large shifts in the refractive index of a polymer from its bulk value are known to occur when polymer chains are mechanically rubbered.[5] Confinement in the interstices could result in a shift in polymer's refractive index from its bulk value.

Thus, to determine the refractive indices of PS and PMMA in the interstices, we prepare SiO_2 NP/PS and SiO_2 NP/PMMA bilayers by first spin-coating polymer solution (in toluene) on Si wafer at a rotation speed of 2250 rpm for 1.5 min, followed by coating NP layer on the polymer layer at a rotation speed of 2500 rpm for 2 min. Then the bilayers are annealed with MMA in ellipsometry cell for a certain period. Take the PS/SiO_2 NP bilayer as an example, as the thickness change of the polymer layer reflects the actual amount of polymer that infiltrates into the NP packing, $\emptyset_{PS}$ can be calculated according to Equation S8. Then n_{PS} can be derived from Equation S5-S6. n_{PMMA} can be determined similarly using SiO_2 NP/PMMA bilayers. The value of

n_{PS} is determined to be 1.74±0.06 by averaging the values calculated from 5 SiO_2 NP/PS bilayers while values of n_{PMMA} is determined to be 1.50±0.04 by averaging 4 SiO_2 NP/PMMA bilayers.

(1) L. Zimmermann, M. Weibel, W. Caseri, U. W. Suter, P. Walther, *Polym. Adv. Technol.*, 1993, **4**, 1–7.

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(5) X. Hu, K. Shin, M. Rafailovich, J. Sokolov, R. Stein, Y. Chan, K. Williams, W. Wu and R. Kolb, *High Perform. Polym.*, 2000, **12**, 621-629.

Refractive Index Profile of a SiO_2 NP film exposing to HMP

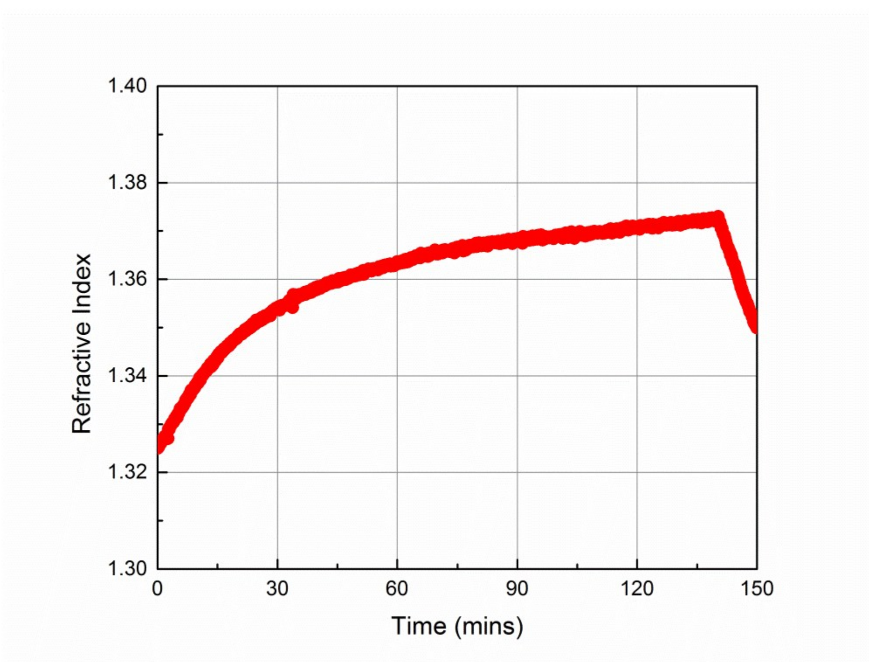

Figure S3 Refractive index profile of a 264 nm SiO_2 NP film as a function of annealing time, obtained using *in situ* spectroscopic ellipsometry. The SiO_2 NP film is annealed with HMP for 140 mins and then exposed to air for 10 mins.

Solvent	RI of NP layer before annealing	RI of NP layer after 30mins	$\emptyset_{void}$	$\emptyset_{MMA}$
Methyl methacrylate (MMA)	1.308	1.439	0.318	0.316

Table S1 The refractive index of a SiO_2 NP film before exposing to MMA and after exposing to MMA for 30 mins

This result shows that the interstices of the NP packing are completely flooded with MMA after 30 mins exposure to MMA vapour.

Solvent	PS layer thickness before annealing (nm)	PS layer thickness after annealing (nm)	SiO_2 NPs thickness (nm)	Annealing time (mins)	$\emptyset_{PS}$
Methyl methacrylate (MMA)	222.4	173.7	246.8	40	0.197
	226.1	175.2	252.2	120	0.202
	220.7	168.5	233.6	150	0.224

Table S2 Volume Fractions of PS in the nanoparticle layer after annealing a SiO_2 NP/PS bilayer with MMA

$\emptyset_{PS}$ in this table is calculated according to equation S7.

Table S3 Volume fraction of PS, PMMA and void in composite films which are fabricated by being exposed to UV light for 30 mins

UV exposure duration (mins)	$\frac{h_{PS}}{h_{SiO_2}}$ **Average**	$\emptyset_{PS}$	$\emptyset_{PMMA}$	$\emptyset_{void}'$
30	0.079	0.065±0.002	0.059±0.018	0.213±0.011
	0.121	0.108±0.006	0.071±0.030	0.149±0.022
	0.195	0.179±0.002	0.057±0.005	0.094±0.003
	0.240	0.205±0.018	0.047±0.032	0.075±0.008

Table S4 Volume fraction of PS, PMMA and void in composite films which are fabricated by being exposed to UV for different duration

$\frac{h_{PS}}{h_{SiO_2}}$ **Average**	**UV exposure duration (mins)**	$\emptyset_{PS}$	$\emptyset_{PMMA}$	$\emptyset_{void}'$
0.123	0	0.105±0.001	0.009±0.0004	0.209±0.001
0.128	10	0.109±0.005	0.032±0.017	0.181±0.014
0.121	30	0.108±0.006	0.071±0.030	0.149±0.022
0.134	50	0.119±0.002	0.091±0.007	0.118±0.009