Control of Interface Nanoscale Structure Created by Plasma Enhanced Chemical Vapor Deposition

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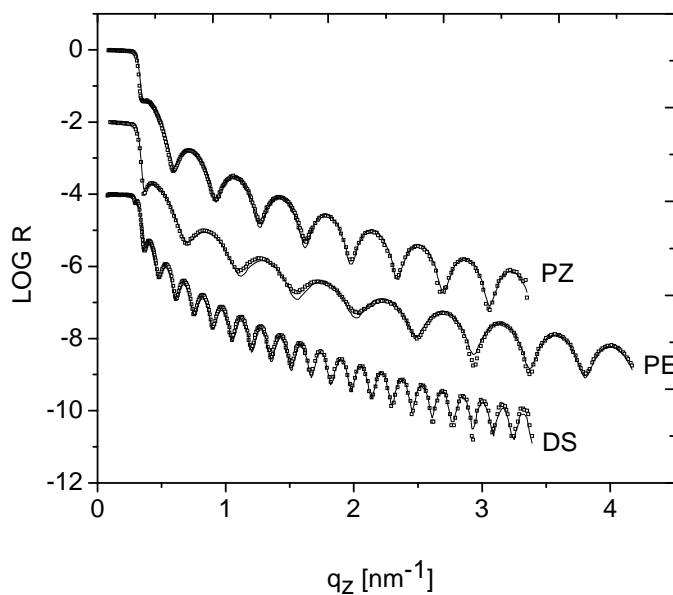
Supplementary Information

Figure S1: XR data (open squares) and best-fit curves (solid line) after swelling for PP-OFCB samples deposited using PZ, PE, or DS feed location. The curves for PE and DS have been shifted along the y-axis for clarity.
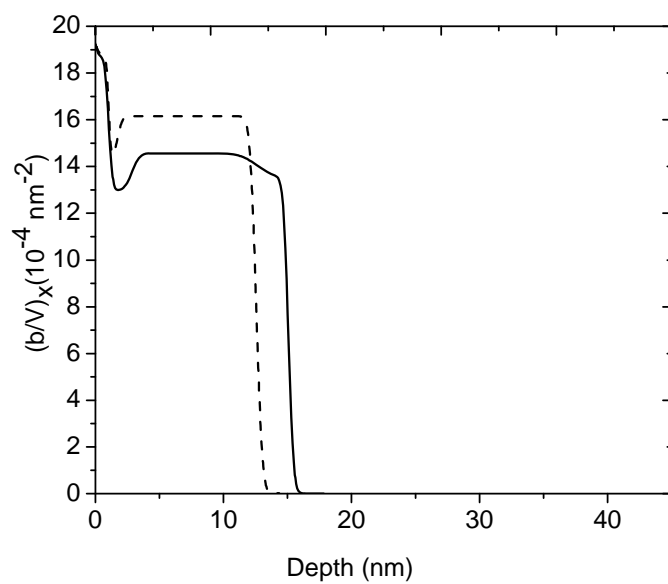
Figure S2: X-ray SLD profiles for as-deposited (dashed line) and swollen (solid line) sample deposited using the PE feed location and 30 W power.
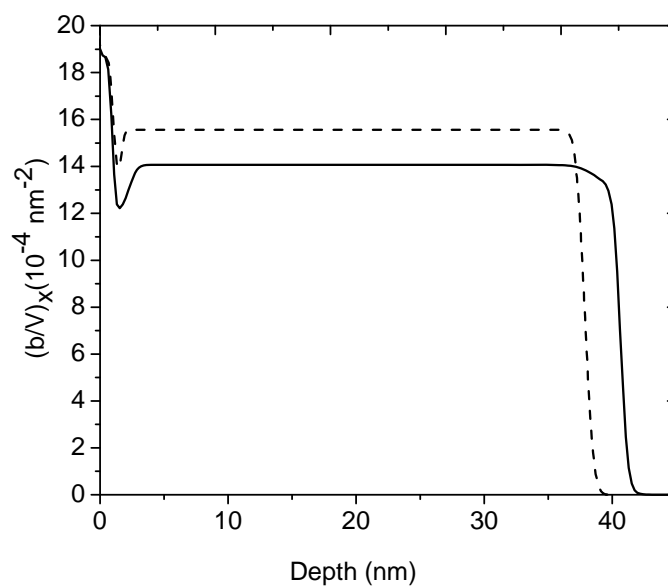

Figure S3: X-ray SLD profiles for as-deposited (dashed line) and swollen (solid line) sample deposited using DS feed location and 30 W power.
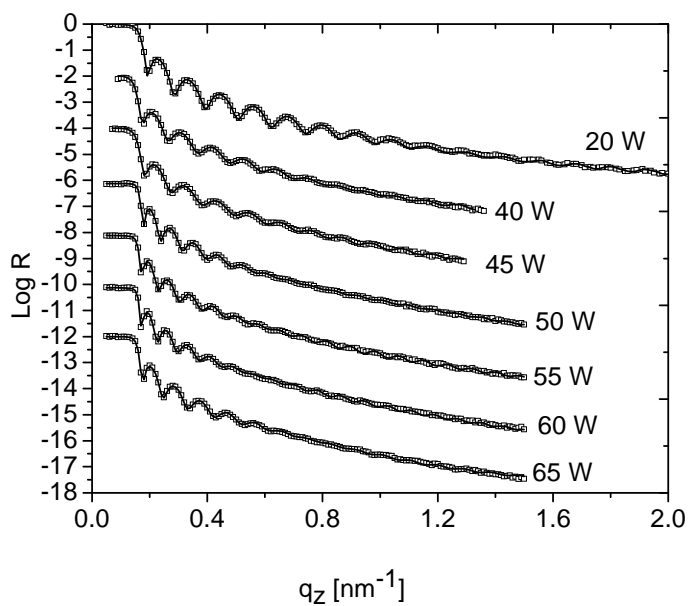
Figure S4: NR data (symbols) and best-fit curves (solid lines) for feed location in PZ and processing power of 40, 45, 50, 55, 60 and 65 W. The pairs of curves for 45, 45, 50, 55, 60 and 65 W have been shifted along the y-axis for clarity.
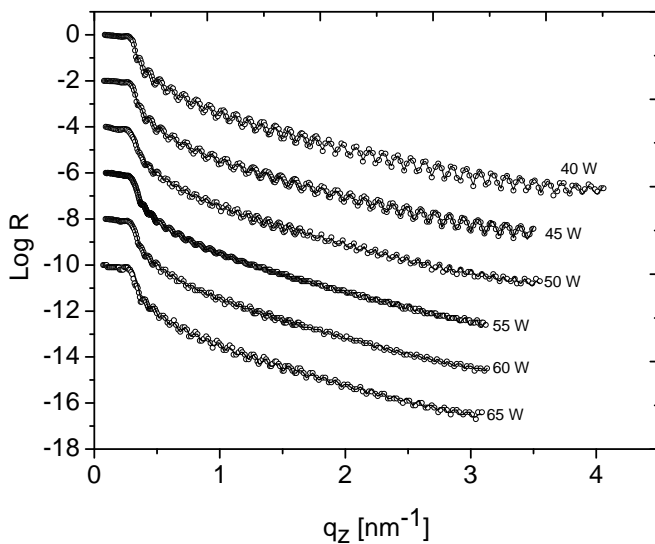

Figure S5: XR data (symbols) and best-fit curves (solid lines) for films deposited with PZ feed location and processing power of 40, 45, 50, 55, 60 and 65 W. The pairs of curves for 45, 45, 50, 55, 60 and 65 W have been shifted along the y-axis for clarity.
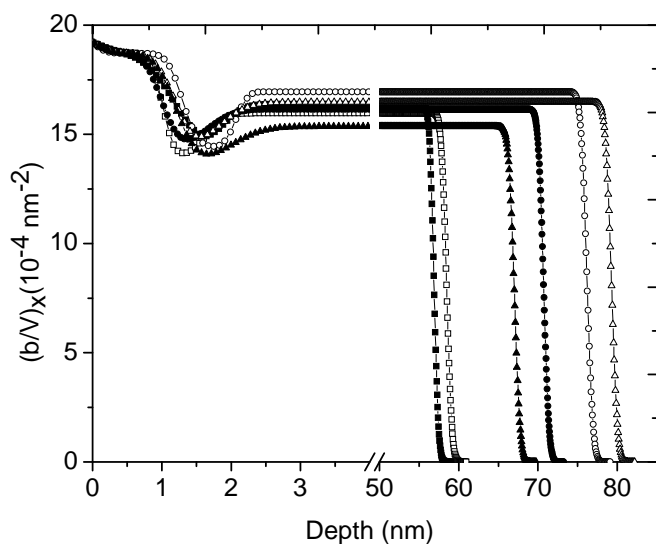
Figure S6: X-ray SLD profiles for samples deposited at 40 W (open squares), 45 W (filled squares) and 50 W (open circles), 55 W (filled circles), 60 W (open triangles) and 65 W (filled triangles) using the PZ feed location.
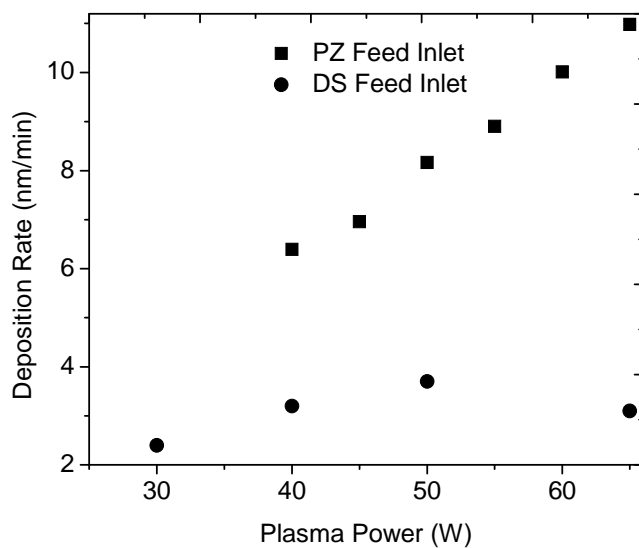

Figure S7: Deposition rate as a function of power for the DS and PZ feed locations.

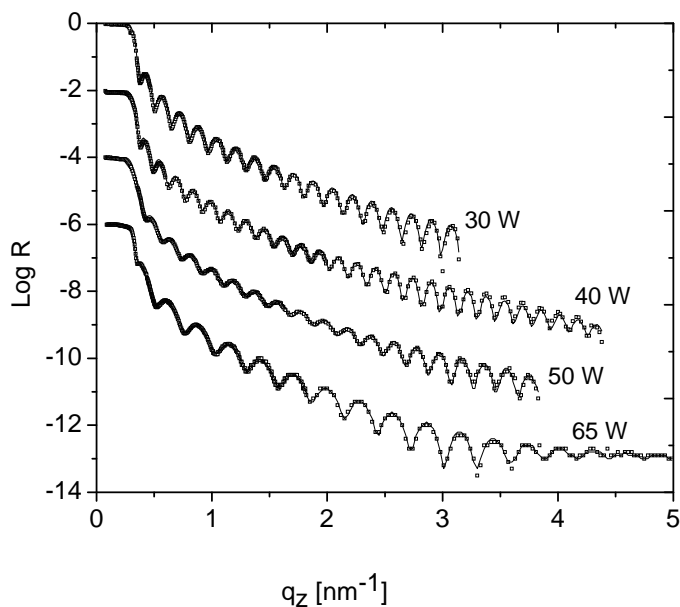Figure S8: XR data (symbols) and best-fit curves (solid lines) for PP-OFCB films deposited with DS feed and power of 30, 40, 50 and 65 W. The pairs of curves for 40, 50 and 65 W have been shifted along the y-axis for clarity.
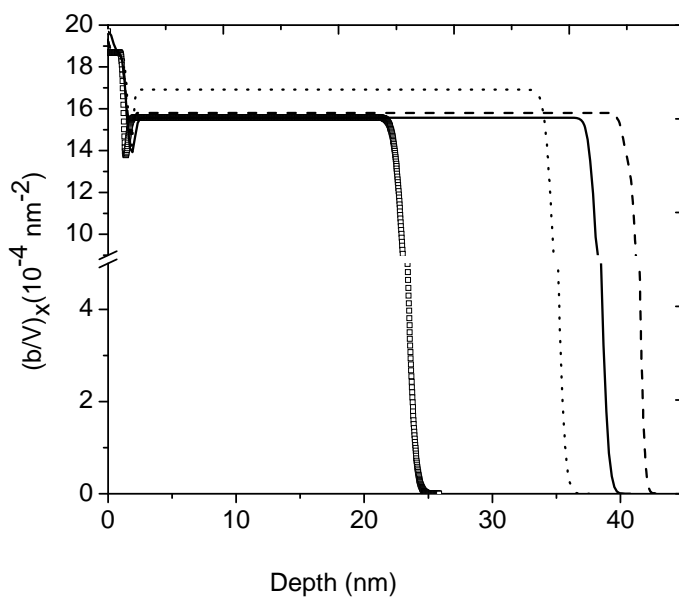
Figure S9: X-ray scattering length density profiles for samples deposited at 30 W (solid line), 40 W (dashed line), 50 W (dotted line), and 65 W (open squares) using the DS feed location.
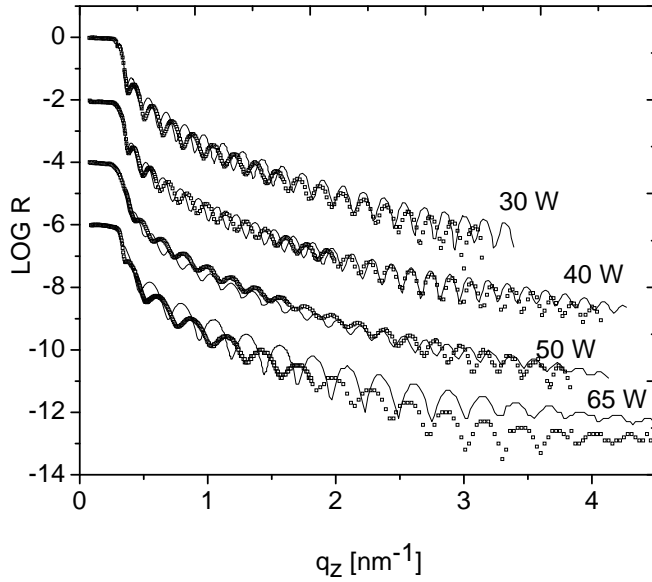
Figure S10: XR data for PP-OFCB films as-deposited (open squares) and after swelling (solid line) for samples deposited using 30, 40, 50 or 65 W plasma power. The pairs of curves for 40, 50 and 65 W have been shifted along the y-axis for clarity.
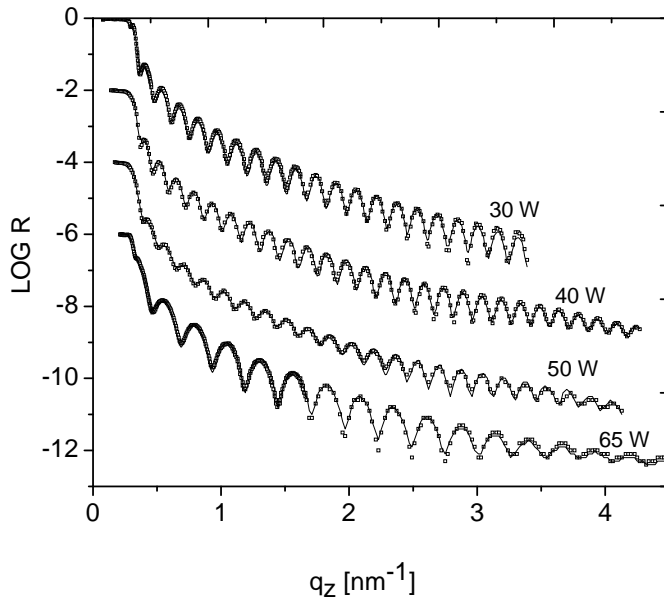
Figure S11: XR data (symbols) and best-fit curves (solid lines) after swelling for PP-OFCB samples deposited using 30, 40, 50 and 65 W plasma powers. The pairs of curves for 40, 50 and 65 W have been shifted along the y-axis for clarity.
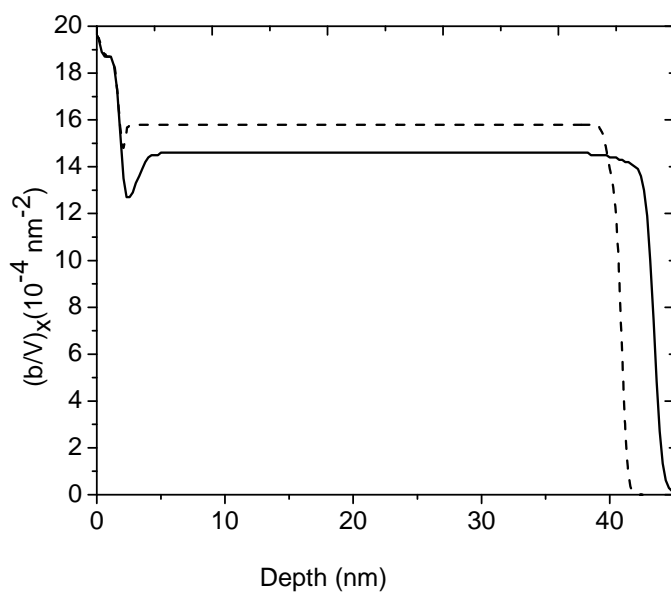
Figure S12: X-ray SLD profiles for as-deposited PP- OFCB sample (dashed line) and sample swollen with vapor (solid line) for deposition using DS feed and 40 W plasma power.
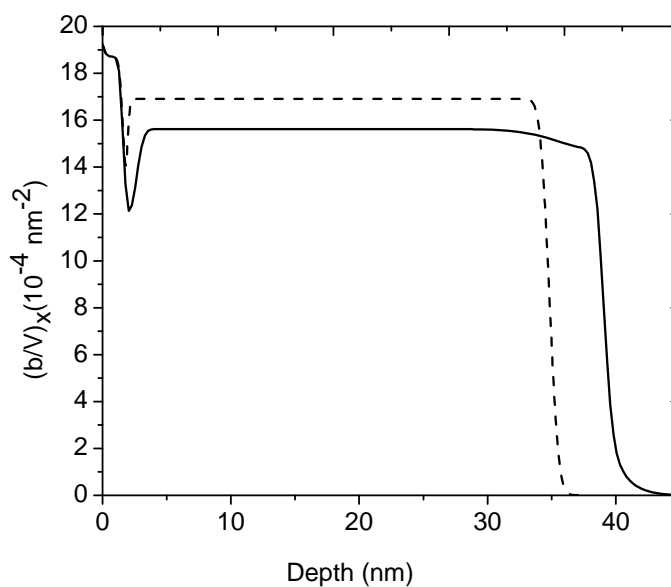
Figure S13: X-ray SLD profiles for as-deposited PP-OFCB sample (dashed line) and sample swollen with vapor (solid line) for deposition using DS feed and 50 W power.

Figure S14: Swelling ratio with dry depth for samples deposited at 80 Pa pressure and DS feed location for 30 W (dashed line), 40 W (dotted line), and 50 W (solid line).

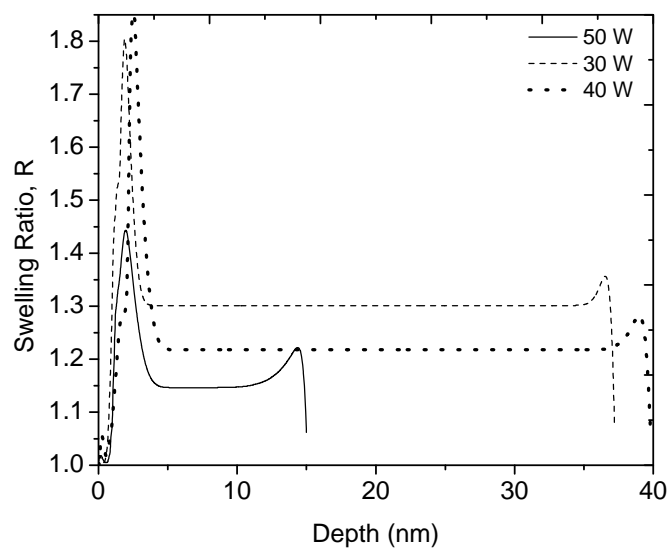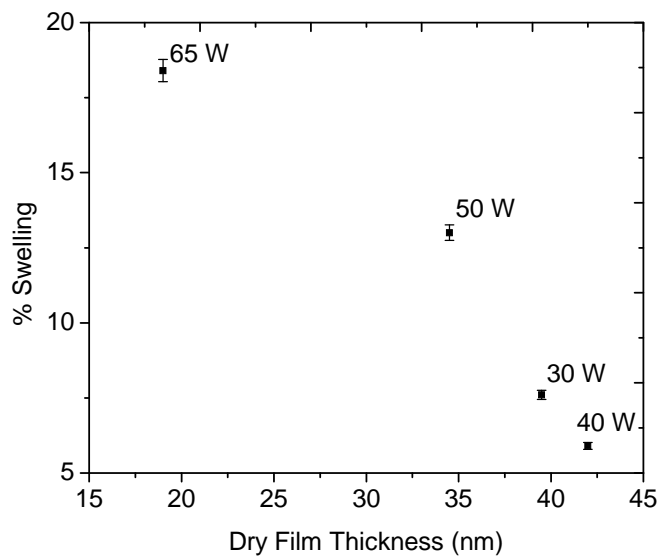Figure S15: Film swelling as a function of film thickness for films deposited with DS feed using the powers shown.
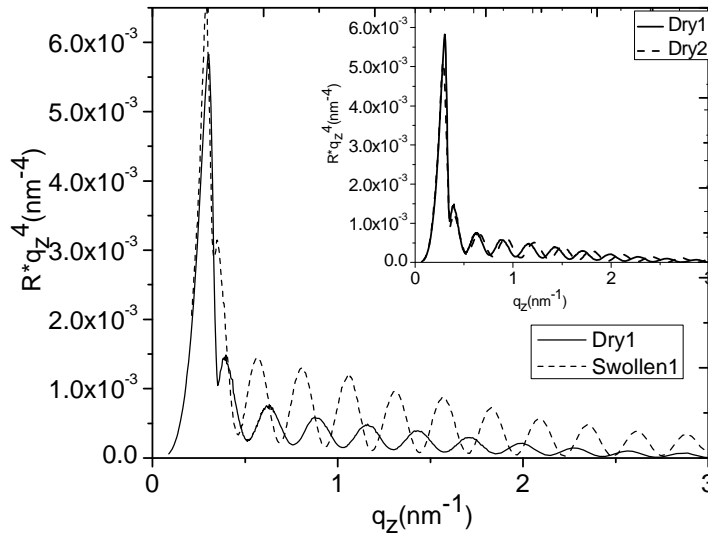
Figure **S**16**:** XR curves (plotted as $R \cdot q_z^4$ to highlight differences in thickness) for the PP-OFCB sample deposited using DS feed and 65 W power dry (solid line) and after swelling (dashed line). Inset (a) compares the XR curves for the as-deposited sample (solid line, Dry1) and the sample after drying following its first swelling (dashed line, Dry2).

Table S1: Summary of neutron SLD model structure parameters for samples deposited using the PZ feed location

Power (W)	d(nm)[a]			b/V*10^{-4} (nm^{-2})[b]			σ(nm)[a]		
	T[c]	B[c]	S[c]	T[c]	B[c]	S[c]	T[c]	B[c]	S[c]
40	2.6	48.7	5.1	2.7	3.6	4.3	2.2	2.1	0.3
45	3.4	46.8	4.1	2.9	3.9	4.7	2.3	2.4	0.5
50	4.4	63.7	4.0	3.0	4.6	5.6	1.7	3.8	0.6
55	4.4	64.2	5.2	2.9	4.4	4.8	1.6	2.7	0.6
60	4.8	66.2	5.2	3.0	4.5	5.0	2.2	2.3	0.6
65	4.1	55.6	5.1	3.0	4.1	4.6	1.6	1.0	0.4

[a] Uncertainty in d is ±0.2 nm and that of σ inferred from the fitting process is 10-15 %.
[b] Uncertainty in (b/V) is ±0.1 x 10^{-4} nm^{-2}.
[c] "T" = transition layer, "B" = bulk layer, "S" = surface layer.

Table S2: Summary of X-ray SLD model structure parameters for films deposited using the PZ feed location

Power (W)	d(nm)[a]		b/V*10⁻⁴ (nm⁻²)[b]		σ(nm)[a]	
	T[c]	B[c]	T[c]	B[c]	T[c]	B[c]
40	0.6	56.8	13.9	15.9	0.2	0.5
45	0.6	55.1	14.0	16.4	0.4	0.6
50	0.6	72.9	14.4	16.9	0.2	0.6
55	0.6	60.0	13.5	16.2	0.2	0.4
60	0.4	77.8	14.7	16.5	0.3	0.6
65	0.7	65.0	13.5	15.3	0.4	0.6

[a] Uncertainty in d is ±0.2 nm and that in σ inferred from the fitting process is 10-15 %.
[b] Uncertainty in (b/V) is ±0.1 x 10⁻⁴ nm⁻².
[c] "T" = transition layer, "B" = bulk layer.

Table S3: XR Model parameters for the film structures deposited at different plasma powers using the DS feed location

Power (W)	d(nm)[a]		b/V*10⁻⁴ (nm⁻²)[b]		σ(nm)[a]	
	T[c]	B[c]	T[c]	B[c]	T[c]	B[c]
30	0. 6	36.3	13.2	15.7	0.2	0.5
40	0.5	38.6	13.5	15.9	0.2	0.5
50	0.6	32.3	14.8	16.4	0.2	0.5
65	0.4	21.6	12.8	15.6	0.2	0.4

[a] Uncertainty in d is ±0.2 nm and that in σ inferred from the fitting process is 10-15 %.
[b] Uncertainty in (b/V) is ±0.2 x 10⁻⁴ nm⁻².
[c] "T" = transition layer, "B" = bulk laye

Table S4: Overall degrees of swelling with vapor for films deposited using the DS location and at various plasma powers

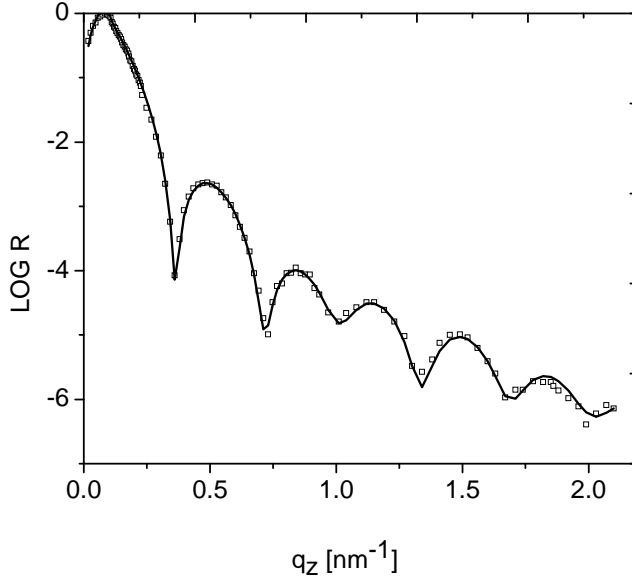| Sample Name	total film thickness dry (nm) ±.2 nm	total film thickness swollen (nm) ±.2 nm	% increase
30DS	39.5	42.5	7.6
40DS	42.0	44.5	5.9
50DS	34.5	39.0	13.0
65DS	24.0	28.5	18.7

Bilayer film:

Figure S17: NR data (open squares) and best-fit curve (solid lines) for bilayer film deposited using DS feed location for DB and PZ feed location for OFCB.

Calculation of Swelling Ratio (R)

Two main assumptions were used to estimate the swelling ratio as a function of depth and map the depth in the swollen film that corresponds to each depth in the dry film. First, we assumed that the swelling was highly anisotropic, and ignored swelling in the in-plane directions, since covalent bonds with the substrate hinder expansion laterally at the interface with the substrate. Secondly, we neglected accounting explicitly for the possible presence of air or voids in the film and assumed only two components; polymer and solvent, were present, so that

$$\left(\frac{b}{V}\right)_{i,swollen} = \left(1 - \phi_{solvent,i}\right) * \left(\frac{b}{V}\right)_{i,dry} + \left(\phi_{solvent,i}\right) * \left(\frac{b}{V}\right)_{solvent} , \qquad (S1)$$

where the subscript i denotes the ith differential slice of the structure at depth z_i, from a reference plane. We begin the calculation at the silicon oxide surface (z=0), since the position of the first differential slice of film there does not move, and calculate what the solvent concentration is. Then using this solvent concentration we calculate R_i, the swelling ratio in layer i,

$$\phi_{solvent,i} = 1 - \left(\frac{1}{R_i}\right), \qquad (S2)$$

and the thickness $\Delta z_{i,swollen}$, to which the differential slice of film swells,

$$\Delta z_{i,swollen} = \Delta z_{i,dry} * R_i \; . \tag{S3}$$

The depths in the swollen film corresponding to depths in the dry film are then calculated by working our way up to the top of the film, making sure that equations S1-S3 are satisfied self-consistently all through the depth profile.