

Supporting Information

Application of Scanning Angle Raman Spectroscopy for Determining the Location of Buried Polymer Interfaces with Tens of Nanometer Precision

Craig A. Damin^{ab†}, Vy H. T. Nguyen^{ab†}, Auguste S. Niyibizi^a and Emily A. Smith^{ab*}

^a Ames Laboratory, U.S. Department of Energy, Ames, IA 50011-3111, USA

^b Department of Chemistry, Iowa State University, Ames, IA 50011-3111, USA

†These authors contributed equally to the work.

*Author to whom correspondence should be sent: esmith1@iastate.edu

Table S1. Best-fit functions for the curves shown in Fig. 4 when fitting the full range of $Thick_{PS}$
 $Thick_{PC}$.

$$\frac{Int_{PS}}{Int_{PC}} = \left(\frac{Int_{PS}}{Int_{PC}} \right)^0 + A \left(\frac{Thick_{PS}}{Thick_{PC}} \right)^B$$

$$\left(\frac{Thick_{PS}}{Thick_{PC}} \right) \text{ between } 0.067 \text{ and } 15$$

Total thickness (nm)	$\left(\frac{Int_{PS}}{Int_{PC}} \right)^0$	A	B	RMSR ^a
1200	-0.07	3.34	1.55	0.76
1300	-0.69	3.24	1.59	0.80
1400	-1.12	3.69	1.56	1.64
1500	-0.66	3.14	1.66	0.94
1600	-0.66	3.11	1.70	1.12
1700	-0.86	3.39	1.67	1.28
1800	-0.75	3.25	1.72	1.26
1900	-0.42	2.88	1.79	0.79
2000	-0.35	2.92	1.81	0.61
2100	-0.37	2.98	1.80	0.57
2200	-0.41	3.04	1.82	0.89
2300	-0.07	2.75	1.88	0.41
2400	-0.02	2.78	1.90	0.40
2500	-0.04	2.90	1.88	0.37
2600	-0.06	2.93	1.90	0.68
2700	0.35	2.63	1.96	0.50
2800	0.44	2.69	1.96	0.46
2900	0.59	2.63	1.98	0.63
3000	0.56	2.79	1.96	0.60
3200	1.07	2.60	2.02	1.24
3400	0.93	2.96	1.98	1.04
3600	1.68	2.56	2.07	1.83

^a Root mean square residual (RMSR) is the mean absolute value of the residuals (r), in which a smaller RMSR indicates a better fit. n is the number of data points.

$$RMSR = \sqrt{\frac{\sum r^2}{n}}$$

Table S2. Localized fit functions for plots of total bilayer thickness vs. $\text{Thick}_{\text{PS}}/\text{Thick}_{\text{PC}}$ constructed by applying experimental $\Delta\theta$ to calibration plots of $\Delta\theta$ vs. total bilayer thickness^a (Fig. 3, Table 1).

	Polystyrene^b			Polycarbonate^b		
	y₀	A	power	y₀	A	power
Sample 1	3412	-98.71	-2.87	-439.0	3707	0.087
Sample 2	2745	-389.0	-0.32	2388	102.8	3.48
Sample 3	-878.6	2936	0.04	1949	-234.4	2.20
Sample 4	1078	436.7	0.51	-0.039	1389	0.0025

^a Unless limited by graph, localized fits included two points on each side of the intersection point.

^b The selected data points were fit to power functions of the form: $y = y_0 + Ax^{\text{power}}$, where y = total bilayer thickness (nm) and $x = \text{Thick}_{\text{PS}}/\text{Thick}_{\text{PC}}$.

Table S3. Localized fit functions for plots of total bilayer thickness vs. $\text{Thick}_{\text{PS}}/\text{Thick}_{\text{PC}}$ constructed by applying experimental $\text{Int}_{\text{PS}}/\text{Int}_{\text{PC}}$ to calibration plots of $\text{SSEF}_{\text{PS}}/\text{SSEF}_{\text{PC}}$ vs. $\text{Thick}_{\text{PS}}/\text{Thick}_{\text{PC}}$ ^a (Fig. 4, Table 2).

	Polystyrene ^b		Polycarbonate ^b	
	a	b	a	b
Sample 1	7647	-3389	7647	-3389
Sample 2	7685	-6857	7469	-6567
Sample 3	-874.7	11136	1463	1897
Sample 4	140.0	5194	140.0	5194

^a Unless limited by graph, localized fits included two points on each side of the intersection point.

^b The selected data points were fit to linear functions of the form: $y = \mathbf{a} + \mathbf{b}x$, where y = total bilayer thickness (nm) and x = $\text{Thick}_{\text{PS}}/\text{Thick}_{\text{PC}}$.

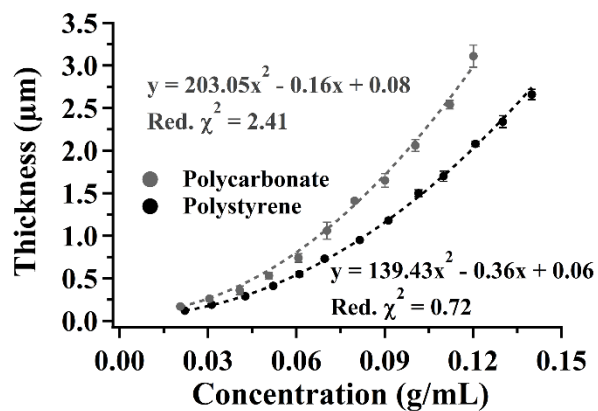


Fig. S1. Calibration curves of PS and PC thicknesses (μm) measured by optical profilometry as a function of concentration when spin coated onto a glass substrate. The error bars represent the standard deviation associated with six thickness determinations for each thin film sample.

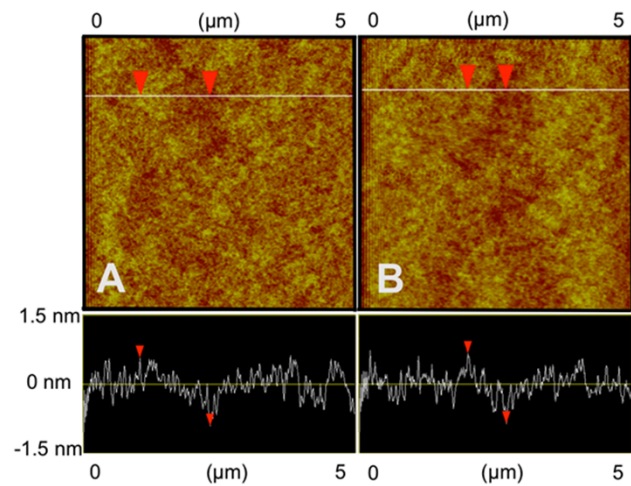


Fig. S2. AFM images of **(A)** an 1800-nm PS film spin coated on a glass substrate and **(B)** a 2500-nm bilayer (1800-nm PS/700-nm PC) film on a glass substrate after “lift-off” transfer of the PC film onto the PS film.