Polystyrene-Poly(ethylene oxide) Diblock Copolymer: The Effect of Polystyrene and Spreading Concentration at the Air/Water Interface

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## **Supporting Information**

**Transfer Ratio.** During a Langmuir-Blodgett (LB) film transfer, the pressure is maintained at a designated value. As a film is pulled from the surface, the barriers compress further to compensate for the lost polymer. Ideally, the area of the substrate equals the area that the barriers must compress, resulting in a TR=1.0 (where TR = barrier compression area/ substrate area). Transfer ratios for LB films of the PS-PEO samples are provided in Table S1. Each film was prepared at a pressure of 2 mN/m and the indicated spreading solution (either 0.1, 1.0, or 5.0 mg/mL). In the case of the 216k, several films were transferred at a variety of concentrations ranging from 2-10 mg/mL.

Several general trends appear. First, polymers containing lower % PEO (12% and lower) result in lower transfer ratios (< 2) while higher % PEO (20.5% and higher) lead to transfer ratios > 2. Second, as spreading concentration increases, the resulting transfer ratios vary, depending on % PEO. PS-PEO containing 12% or less PEO exhibits a decrease in TR. Those polymers that have 20% or more PEO generally increase in TR with increasing concentration. A possible explanation for these trends is that as the PS chain length increases, transfer becomes more

difficult. This could be due to further entanglement in the PS chains at the air/water interface, impeding facile transfer to a vertically pulled substrate. The 216k (7.4% PEO) proved especially difficult to transfer as demonstrated by low TR and subsequent issues with finding polymer-covered areas of the LB film. A horizontal (Langmuir-Schaefer) transfer was also attempted of the 216k though this, too, led to poor coverage.

**Table S1.** Transfer ratios obtained for PS-PEO LB films ( $\pi = 2 \text{ mN/m}$ ) for various spreading concentrations. Averages and standard deviations are shown for several of the films.

PS-PEO	Transfer Ratios				
_	0.1 mg/mL	1.0 mg/mL	5.0 mg/mL		
216k (7.4% PEO)	1.5	$1.2 \pm 0.2$	0.6 (2 mg/mL) 0.5 ± 0.2 (5 mg/mL) 0.7 (10 mg/mL)		
148k (12.2% PEO)	1.3	$1.3 \pm 0.5$	0.7		
78k (20.5% PEO)	2.5	2.9	3.4		
49k (34.7% PEO)	2.7	$3.0 \pm 0.7$	4.8		
27.5k (65 5% PEO)	2.5	3.0	4.5		

The magnitude of these TR's are similar to those reported for star PS-PEO systems containing 29-61% PEO.<sup>1</sup> Similar to our own polymers of 20% PEO or higher, these polymers had TR's that were greater than the ideal value of TR = 1. Films pulled of PS-PEO containing very little PEO (2% PEO) and pure PS homopolymers led to TR's of <0.8.<sup>2</sup> These low TR's compare to our own for polymers of 12% or less PEO. These findings indicate an inherent difficulty in achieving adequate film coverage for polymers containing longer PS chains.

Isotherm Areas vs AFM Features. Our AFM images reflect PS-PEO aggregation at large areas, within the pancake region for the more hydrophilic polymers. Empirical data reported for PS-PEO in both our studies and others indicate that the PEO pancake occupies  $\sim 31 \text{ Å}^2/\text{EO}$  in the pancake region<sup>3</sup> while the PS requires 4.2  $Å^2/St$  unit.<sup>4</sup> Based on these measurements, the projected area of the PEO pancake is expected to equal that of the collapsed PS "blob" at 7 wt. %. The PEO pancake in the 216k (7.4% PEO) would thus be predicted to have the same area as the PS (Table S2). This ratio increases such that the PEO of the 49k (34.7%) occupies 9x more area than the PS while the 27.5k and 20.2k would be 33x and 81x more, respectively. (The actual ratio of  $A_p:A_0$  is 10x and 13x for the 27.5k and 20.2k, respectively, showing that our experimental  $A_0$  is indeed bigger than expected, as seen in Figure 2b in the actual article.) The more hydrophobic polymers (<20% PEO) do not show pancake or plateau regions within the isotherms (Figure 1 in the article), indicating that the projected PEO areas (1-5x the PS size) are still too small to adequately separate the PS aggregates. The PEO sits under the PS blobs, masking changes in PEO conformation as seen through isothermal analysis.<sup>5</sup> When the PEO is projected to occupy at least 9x the PS area, then a pancake region does indeed appear. A similar calculation involves determining  $N_{\rm PS}/N_{\rm PEO}$  where  $N_{\rm PS}$  and  $N_{\rm PEO}$  are the number of styrene and ethylene oxide units, respectively. The 216k, 148k, and 78k all have ratios of  $N_{\rm PS}/N_{\rm PEO} > 1$ which has been reported to lead to complex 2D morphologies while  $N_{PS}/N_{PEO} < 1$  (the 49k, 27.5k, and 20.2k) results in dots (Table S2).<sup>6</sup>

PS-PEO	wt. % PEO	Projected Ratio of $A_{\rm P}$ : $A_0^{\rm a}$	Experimental Ratio of $A_p: A_0^b$	$N_{\rm PS}/N_{\rm PEO}$	Primary AFM Features
216k	7.4	1		5.3	Continents, spaghetti, dots
148k	12.2	2		3.1	Spaghetti, dots
78k	20.5	5		1.6	Spaghetti, dots
49k	34.7	9	8	0.8	Dots
27.5k	65.5	33	10	0.2	Dots
20.2k	82.2	81	13	0.1	Dots

Table S2. Theoretical and experimental areas of PS-PEO with corresponding AFM features.

<sup>a</sup>The projected ratio of  $A_p$ :  $A_0$  is based on  $A_p = N_{PEO} \cdot 31 \text{ Å}^2/\text{EO}$  and  $A_0 = N_{PS} \cdot 4.2 \text{ Å}^2/\text{St}$ .

<sup>b</sup>An experimental  $A_p:A_0$  could only be calculated for polymers showing both pancake and brush regions.

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