

Supporting Information (SI) for

**Surface Mechanical and Rheological Behaviors of Biocompatible Poly((D,L-lactic acid-*ran*-glycolic acid)-*block*-ethylene glycol) (PLGA-PEG) and Poly((D,L-lactic acid-*ran*-glycolic acid-*ran*- $\epsilon$ -caprolactone)-*block*-ethylene glycol) (PLGACL-PEG) Block Copolymers at the Air-Water Interface**

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## S1. Box-Model Analysis of the X-ray Reflectivity Data

To convert the X-ray reflectivity (XR) profiles to real-space electron density profile, the so-called box-model analysis method was used. The raw XR data were first shifted horizontally by adding an offset ( $q_{z,\text{offset}}$ ), and then vertically by multiplying the reflectivity data ( $R(q_z)$ ) by a constant ( $R_{\text{shift}}$ ).

$$q_z = q_{z,\text{original}} + q_{z,\text{offset}}; \quad (\text{S1})$$

$$R(q_z) = R_{\text{original}}(q_z) \times R_{\text{shift}}. \quad (\text{S2})$$

This corrected reflectivity profile was then normalized by the theoretical Fresnel reflectivity profile:

$$R_F(q_z) = \left| \frac{q_z - \sqrt{q_z^2 - q_c^2 - 4ik\mu}}{q_z + \sqrt{q_z^2 - q_c^2 - 4ik\mu}} \right|^2. \quad (\text{S3})$$

The box-model fitting analysis was performed on this normalized data ( $R(q_z)/R_F(q_z)$ ). We assumed that the monolayer is composed of four sublayers (i.e., “boxes”) of variable thickness ( $\mathbf{d_1, d_2, d_3, d_4}$ ) and electron density ( $\rho_{e,1}, \rho_{e,2}, \rho_{e,3}, \rho_{e,4}$ ), each bounded by error function-type interfaces of variable roughness ( $\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5$ ):

$$\begin{aligned} \rho_e(z) = & \frac{(\rho_{e,1} - \rho_{e,\text{air}})}{2} \left( 1 + \operatorname{erf} \left( \frac{z}{\sqrt{2\sigma_1^2}} \right) \right) + \frac{(\rho_{e,2} - \rho_{e,1})}{2} \left( 1 + \operatorname{erf} \left( \frac{z - d_1}{\sqrt{2\sigma_2^2}} \right) \right) + \frac{(\rho_{e,3} - \rho_{e,2})}{2} \left( 1 + \operatorname{erf} \left( \frac{z - (d_1 + d_2)}{\sqrt{2\sigma_3^2}} \right) \right) + \frac{(\rho_{e,4} - \rho_{e,3})}{2} \left( 1 + \right. \\ & \left. \operatorname{erf} \left( \frac{z - (d_1 + d_2 + d_3)}{\sqrt{2\sigma_4^2}} \right) \right) + \frac{(\rho_{e,\text{sub}} - \rho_{e,4})}{2} \left( 1 + \operatorname{erf} \left( \frac{z - (d_1 + d_2 + d_3 + d_4)}{\sqrt{2\sigma_5^2}} \right) \right). \end{aligned} \quad (\text{S4})$$

The assumed electron density profile calculated using Equation (S4) was converted through the first Born approximation to an expected XR profile. Then this predicted XR profile was compared with the experimental data. This process was repeated to find the thickness, electron density and roughness values that minimize the sum of the magnitudes of the differences between the measured and calculated XR values at all the data points:

$$\varepsilon = \sum_{i=1}^N \left( \frac{|R_{\text{experiment},i}(q_z) - R_{\text{calculation},i}(q_z)|}{R_{F,i}(q_z)} \right). \quad (\text{S5})$$

A more detailed discussion of this procedure is given in Lee et al., *Soft Matter*, 10(21), 3771 (2014).

## S2. Self-Consistent Field Polymer Brush Theory

Below we provide a very brief description of the self-consistent field (SCF) theory and the computational procedure used in this study. The polymer segment probability distribution functions satisfy the modified diffusion equation

$$\frac{\partial q(\mathbf{r}, s)}{\partial s} = \frac{b^2}{6} \nabla^2 q(\mathbf{r}, s) - \omega_p(\mathbf{r}) q(\mathbf{r}, s) \quad (\text{S6})$$

$$\frac{\partial q^*(\mathbf{r}, t)}{\partial t} = \frac{b^2}{6} \nabla^2 q^*(\mathbf{r}, t) - \omega_p(\mathbf{r}) q^*(\mathbf{r}, t) \quad (\text{S7})$$

where  $q(\mathbf{r}, s)$  represents the probability of finding the  $s$ -th segment counted from one end of a chain at position  $\mathbf{r}$ ,  $q^*(\mathbf{r}, s)$ , where  $t = N - s$ , represents the same quantity calculated using the other end of the chain as the initial point,  $N$  is the number of segments per polymer chain, and  $b$  is the size of the polymer segment. The conjugate field  $\omega_i(\mathbf{r})$  is obtained from the macroscopic density for each species  $i$  ( $i$  = polymer (P) or solvent (S))  $\rho_i(\mathbf{r})$

$$\omega_p(\mathbf{r}) = \eta(\mathbf{r})v_p + \rho_s(\mathbf{r})\chi_{ps}v_{ps} \quad (\text{S8})$$

$$\omega_s(\mathbf{r}) = \eta(\mathbf{r})v_s + \rho_p(\mathbf{r})\chi_{ps}v_{ps}. \quad (\text{S9})$$

Here  $v_{ps}$  is given by

$$v_{ps} = \sqrt{v_p v_s}, \quad (\text{S10})$$

and  $\rho_p(\mathbf{r})$  and  $\rho_s(\mathbf{r})$  can be self-consistently calculated by

$$\rho_p(\mathbf{r}) = n_p \int_0^N ds q(\mathbf{r}, s) q^*(\mathbf{r}, t) / \int d\mathbf{r} q(\mathbf{r}, N) \quad (\text{S11})$$

$$\rho_s(\mathbf{r}) = \rho_s^{\text{bulk}} \exp(-\omega_s(\mathbf{r})) \quad (\text{S12})$$

$$1 = v_p \rho_p(\mathbf{r}) + v_s \rho_s(\mathbf{r}) \quad (\text{S13})$$

where  $n_p$  is the number of polymer chains.

The system free energy can be calculated by

$$F = - \int d\mathbf{r} \left[ v_{ps} \rho_p(\mathbf{r}) \chi_{ps} \rho_s(\mathbf{r}) - \eta(\mathbf{r}) + \rho_s \right] - n_p \ln \frac{Q_p}{n_p} - n_p \quad (\text{S14})$$

where  $Q_p$  is the single chain partition function

$$Q_p = \frac{1}{V} \int d\mathbf{r} q(\mathbf{r}, N). \quad (\text{S15})$$

By an initial guess for  $\omega_p(\mathbf{r})$ , the diffusion equations are solved using a Crank-Nicholson scheme with the initial conditions

$$q(\mathbf{r}, 0) = \begin{cases} 1 & \text{if } \mathbf{r} \in \{\mathbf{r}_{\text{surface}}\} \\ 0 & \text{if } \mathbf{r} \notin \{\mathbf{r}_{\text{surface}}\} \end{cases} \quad (\text{S16})$$

$$q^*(\mathbf{r}, 0) = 1 \text{ for all } \mathbf{r} \quad (\text{S17})$$

The first condition defines that one end of the chain (at  $s = 0$ ) is fixed at the surface, while the second condition defines that the other end (at  $t = 0$ ) is free. Both  $q$ -functions are subject to the boundary conditions

$$\nabla q(\mathbf{r}, s > 0) = 0, \nabla q^*(\mathbf{r}, t > 0) = 0, \text{ if } \mathbf{r} \in \{\mathbf{r}_{\text{surface}}\} \quad (\text{S18})$$

$$q(\mathbf{r}, s > 0) = 0, q^*(\mathbf{r}, t > 0) = 0, \text{ if } \min(|\mathbf{r} - \mathbf{r}_{\text{surface}}|) \geq Nb \quad (\text{S19})$$

The first condition assumes an indifferent surface, and the second condition accounts for the finite extensibility of the chains. The grand potential ( $\varphi$ ) is calculated from the free energy by  $\varphi = -F - \int d\mathbf{r} \rho_S(\mathbf{r})$ .<sup>1</sup> Then the lateral pressure of the end-grafted polymer chains is calculated by

$$\pi = \left( \frac{\partial \varphi}{\partial A} \right)_{n_p, n_s, T} \quad (\text{S20})$$

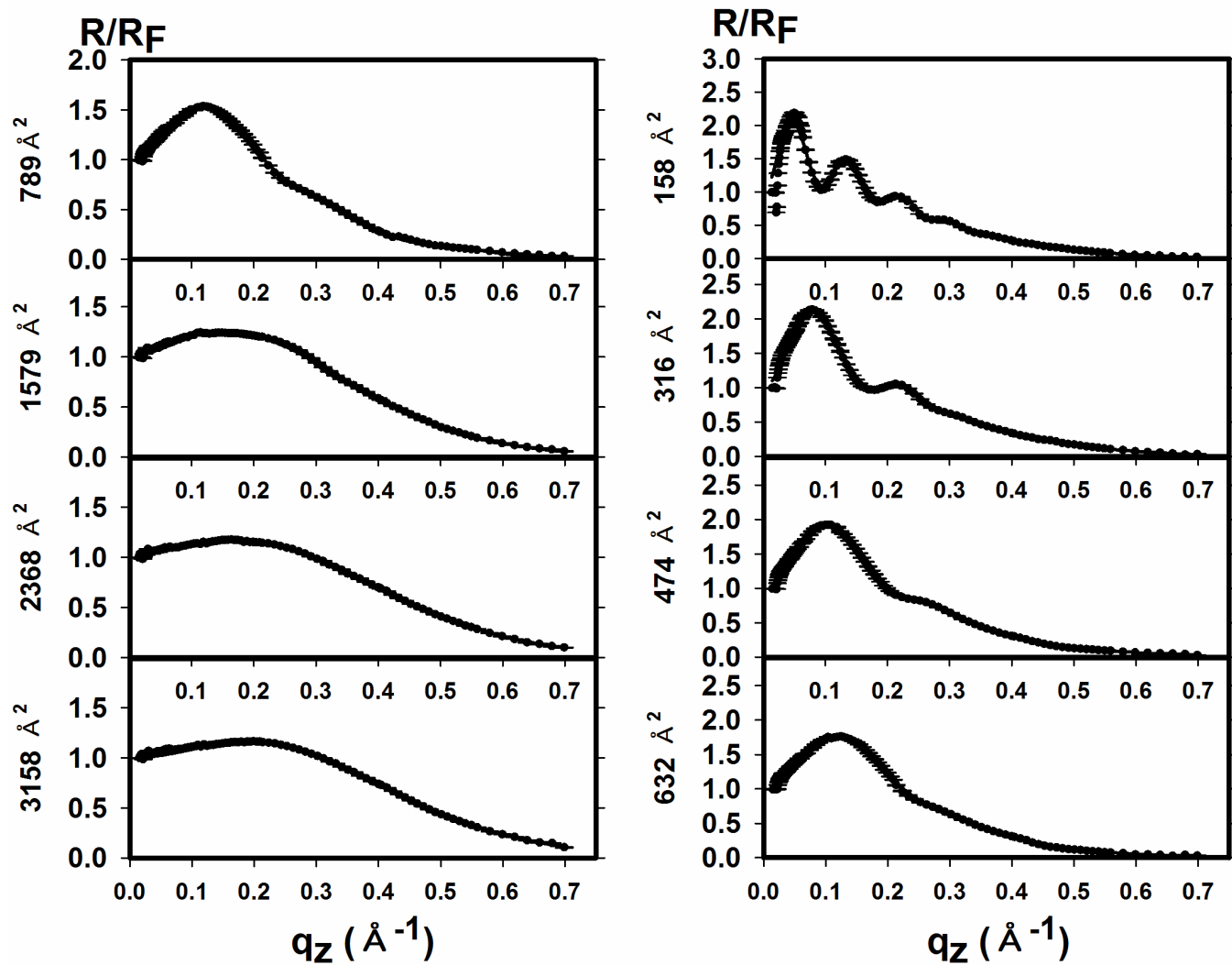
where  $A$  is the area of the grafting surface.

A more detailed discussion of the SCF model has also been presented in Lee et al., *Soft Matter*, 10(21), 3771 (2014).

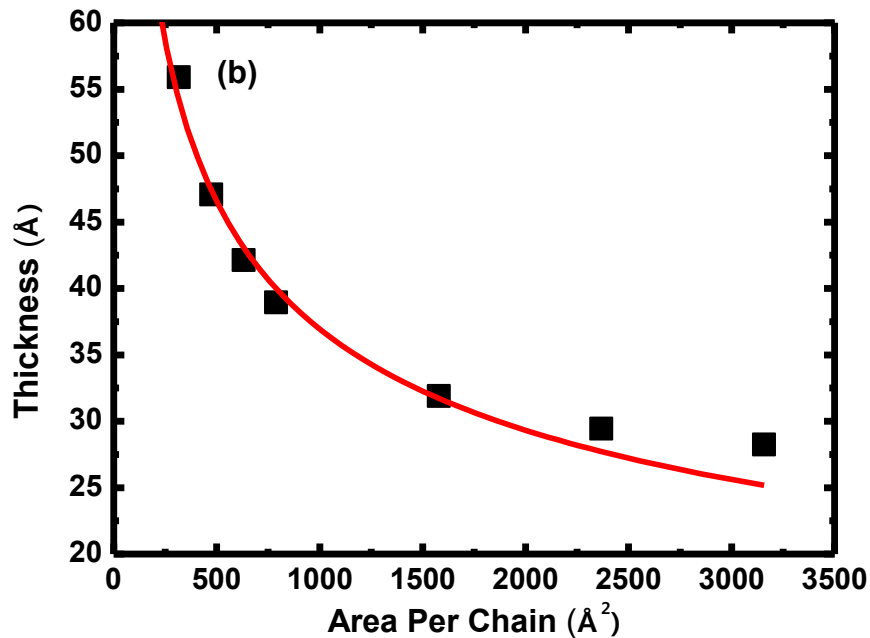
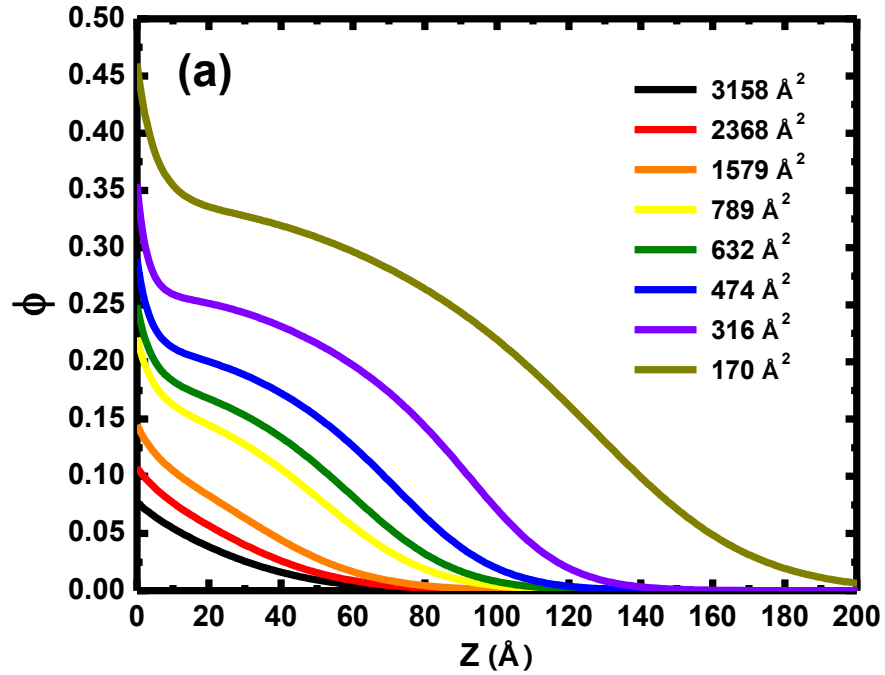
**Table S1.** Box model fit parameters for the normalized electron density profiles shown in Figure 1(b). The actual reflectivity data are presented in Figure S1. The notations,  $d_i$ ,  $\rho_{e,i}$ , and  $\sigma_i$ , denote the thickness, electron density and roughness of the i-th sublayer (or interface) within the monolayer, respectively. The subscript value “1” corresponds to the sublayer (or interface) closest to the bulk air phase, and the highest subscript number designates the sublayer (or interface) closest to the bulk water.

Monolayer Area (Å <sup>2</sup> per chain)	$d_1$ (Å)	$d_2$ (Å)	$d_3$ (Å)	$d_4$ (Å)	$\rho_{e,1}$ / $\rho_{e,water,\infty}$	$\rho_{e,2}$ / $\rho_{e,water,\infty}$	$\rho_{e,3}$ / $\rho_{e,water,\infty}$	$\rho_{e,4}$ / $\rho_{e,water,\infty}$	$\sigma_1$ (Å)	$\sigma_2$ (Å)	$\sigma_3$ (Å)	$\sigma_4$ (Å)	$\sigma_5$ (Å)
3158	3.67782	N/A	N/A	N/A	1.34756	N/A	N/A	N/A	2.38681	5.81925	N/A	N/A	N/A
2368	3.42174	1.31645	N/A	N/A	1.34751	1.03668	N/A	N/A	2.43873	5.72751	38.6649	N/A	N/A
1579	4.93487	7.93897	N/A	N/A	1.34396	1.06177	N/A	N/A	2.67054	6.36473	26.7177	N/A	N/A
789	10.2035	7.01544	9.72324	N/A	1.21351	1.175	1.07507	N/A	3.10321	3.43788	2.82579	2.91016	N/A
632	14.1574	6.33723	6.73621	11.9139	1.27591	1.23886	1.0991	1.05379	3.17584	1.03874	4.83539	3.34215	31.1427
474	17.0336	9.36355	9.05426	N/A	1.27054	1.20509	1.06325	N/A	3.16806	1.96682	3.50547	2.98587	N/A
316	9.73982	14.5163	8.7605	8.81076	1.24506	1.28551	1.23461	1.14172	2.99123	1.20703	4.86382	4.32063	5.17451
158	7.42356	38.7952	22.9519	N/A	1.13043	1.2513	1.18111	N/A	2.92645	3.31077	13.5795	6.62404	N/A

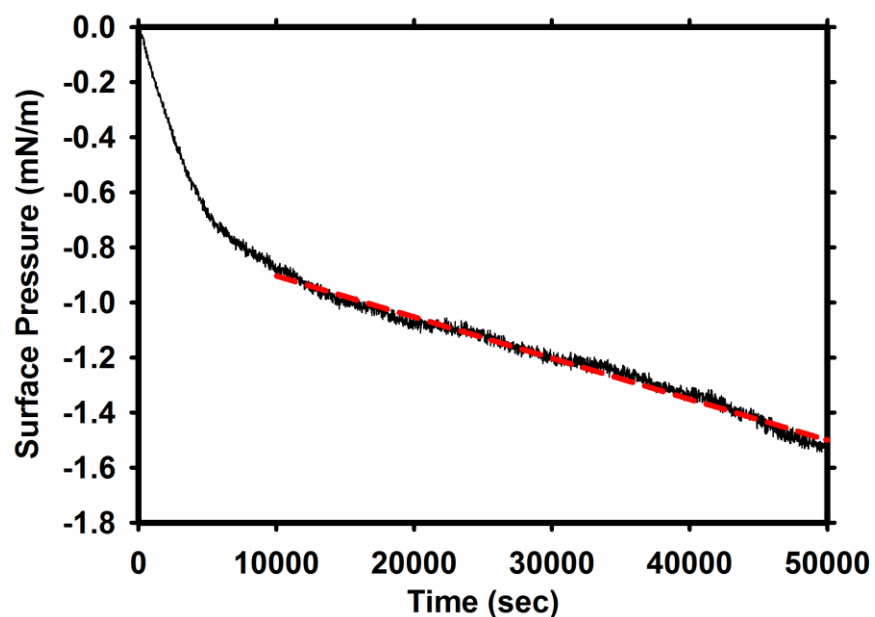
**Figure S1.** Normalized XR profiles ( $R(q_z)/R_F(q_z)$ ) from PLGA-PEG monolayers at eight different area per chain conditions. Points (with error bars) are experimental data. Solid lines are theoretical fits to the data. The procedures for this box-model fitting analysis are described in Section S2 of the Supporting Information (SI). The normalized electron density profiles ( $\rho_e(z)/\rho_{e,water,\infty}$ ) obtained from this analysis are presented in Figure 1(b). The values of the best-fit parameters are presented in Table S1 of the SI.



**Figure S2. (a)** Polymer segment volume fractions,  $\phi(z)$ , estimated by the SCF theory as functions of distance  $z$  from the grafting surface for monodisperse end-grafted PEO chains of length  $DP = 113$  with Kuhn length  $b = 5.93 \text{ \AA}$ , monomer volume  $v_p = 59.3 \text{ \AA}^3$  and Flory-Huggins interaction parameter in water  $\chi_{PEO-water} = 0.70$  at several different area per chain conditions. The water molecular volume is assumed to be  $v_s = 29.9 \text{ \AA}^3$ . **(b)** The brush thickness ( $L$ ) values estimated from the results shown in (a) as a function of area per brush chain ( $A$ ) for the PEG brush chains described in (a) (discrete symbols). The solid line represents a fit to the equation  $L = \alpha/A^{1/3} + \beta$  where  $\alpha$  and  $\beta$  are adjustable parameters.<sup>2</sup>

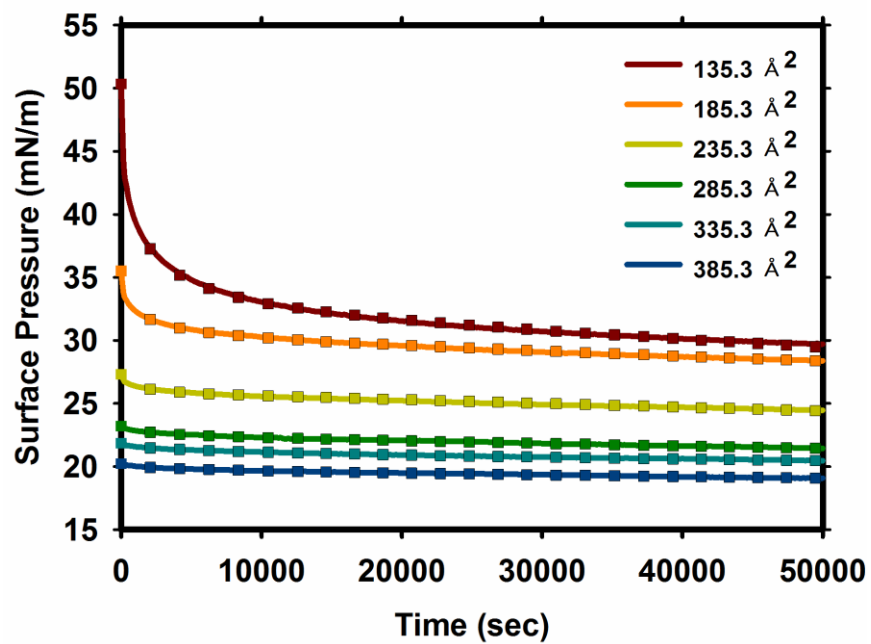


**Figure S3.** The drift in surface pressure reading from a clean air-water interface over a 14-hour period. The surface pressure initially drops relatively rapidly until the Wilhelmy plate (made of platinum) reaches a stable, fully wet state; this process typically takes about 1 – 2 hours. For this reason, in an actual measurement, a polymer sample was spread onto the water surface, after the probe equilibrium is established and then the surface pressure reading was zeroed at the right level. The continuous decrease in surface pressure reading observed at long times ( $> 10,000$  s) is due to the evaporation of water. This measurement was performed at 25 °C and a relative humidity of about 50%.

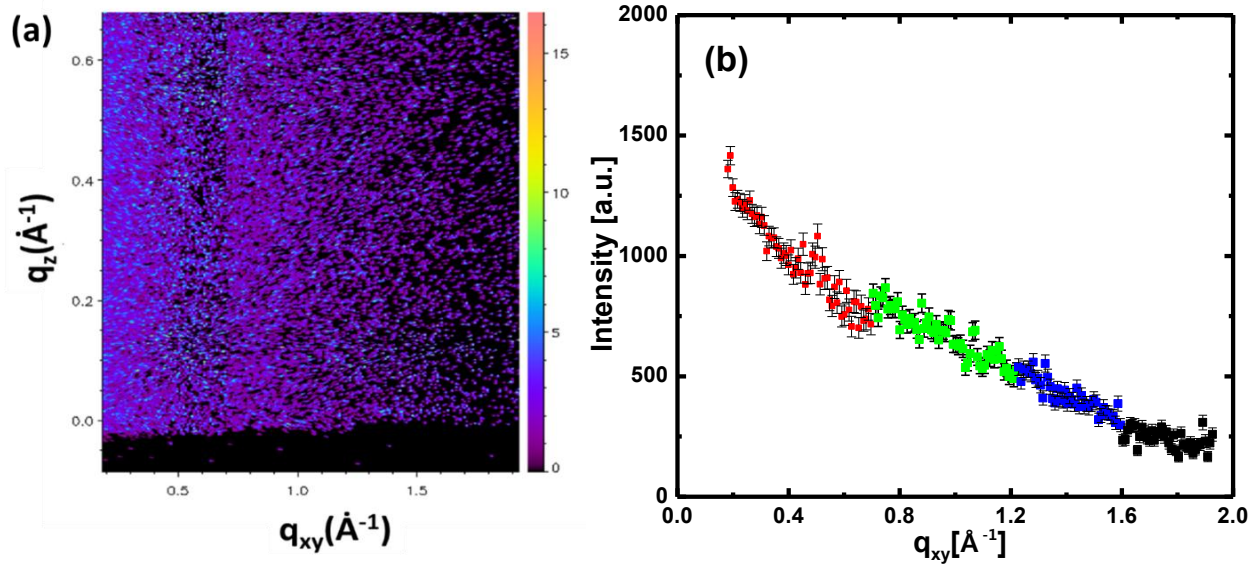




**Figure S4.** A linear-scale replot of Figure 3(a).



**Figure S5. (a)** Two-dimensional GIXD intensity map obtained from a monolayer of a PLGA homopolymer (number-average molecular weight: 49.1 kg/mol) at a monolayer area of 701 Å<sup>2</sup>/chain (which corresponds to an estimated surface pressure of 40 mN/m). **(b)** GIXD intensity as a function of the lateral momentum transfer vector  $q_{xy} = 0.2 - 2.0$  Å<sup>-1</sup> (obtained by integrating the intensities  $I(q_{xy}, q_z)$  (shown in (a)) over the vertical momentum transfer vector ( $q_z$ ) from ~0 to 0.68 Å<sup>-1</sup>. The data shown in (a) and (b) were obtained from four sets of GIXD scans performed in four different  $q_z$  ranges (marked in different colors in (b)). All measurements were performed at 25 °C. The PLGA monolayer was prepared by spreading a PLGA solution in chloroform on a clean water surface in a Langmuir-Pockel trough (9.8 cm x 35 cm) at an initial monolayer area of 2022 Å<sup>2</sup>/chain. After about 3 hours of equilibration at this area condition, the monolayer was compressed at a rate of 4 cm<sup>2</sup>/min to a final area of 701 Å<sup>2</sup>/chain. The sample was again maintained at this condition for 5 hours prior to the GIXD measurements.



## REFERENCES FOR SUPPORTING INFORMATION

1. Garrod, C., *Statistical Mechanics and Thermodynamics*. Oxford University Press: New York, 1995.
2. Wu, T.; Efimenko, K.; Genzer, J., Combinatorial study of the mushroom-to-brush crossover in surface anchored polyacrylamide. *J. Am. Chem. Soc.* **2002**, 124, (32), 9394-9395.