Electronic Supplementary Information (ESI) for

Humidity-Dependent Compression-Induced Glass Transition of the Air-Water Interfacial Langmuir Films of Poly(D,L-lactic acid-*ran*-glycolic acid) (PLGA)

Hyun Chang Kim,[a] Hoyoung Lee,[a] Hyunjung Jung,[b] Yun Hwa Choi,[a] Mati Meron,[c] Binhua Lin,[c] Joona Bang,[b] You-Yeon Won[a,*]

[a] School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907

[b] Department of Chemical and Biological Engineering, Korea University, Seoul, Korea 136-713

[c] Advanced Photon Source, University of Chicago, Chicago, Illinois 60439

[*] To whom correspondence should be addressed. E-mail: yywon@ecn.purdue.edu

S1. Box Model Analysis of the XR Data

The so-called box-model method was used to convert the X-ray reflectivity (XR) profiles to the real-space electron density profiles. For this analysis, the original XR data were first shifted horizontally by adding a small offset ($q_{z,offset}$) to the original q_z values, and then also vertically slightly by multiplication of the reflectivity data ($R(q_z)$) by a constant factor (R_{shift}), in order to match the measured values of q_z and $R(q_z)$ at the critical angle to those of the Fresnel reflectivity situation:

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

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

Then this modified reflectivity profile was 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 ($\mathbf{d_1}, \mathbf{d_2}, \mathbf{d_3}, \mathbf{d_4}$) and electron density ($\boldsymbol{\rho_{e,1}}$, $\boldsymbol{\rho_{e,2}}$, $\boldsymbol{\rho_{e,3}}, \boldsymbol{\rho_{e,4}}$), each bounded by error function-type interfaces of variable roughness ($\boldsymbol{\sigma_1}, \boldsymbol{\sigma_2}, \boldsymbol{\sigma_3}, \boldsymbol{\sigma_4}, \boldsymbol{\sigma_5}$):

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

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:

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

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

Figure S1. Surface pressure vs. area isotherms of a PLGA monolayer measured at 25 ℃ during compression at a rate of 3 mm/min at two different Wilhelmy plate orientations relative to the barriers of the Langmuir trough (i.e., "parallel" and "perpendicular"). See Figure 1 of Cicuta & Terentjev, Eur. Phys. J. B, 16, 147 (2005) for graphical illustration of the definitions of the "parallel" vs. "perpendicular" configurations.

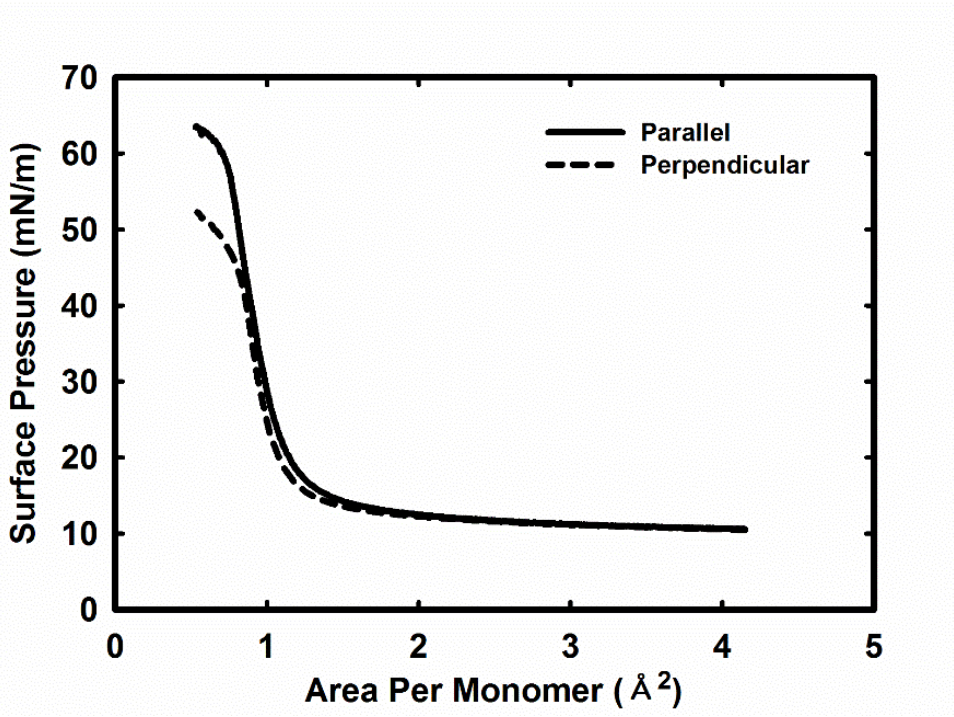
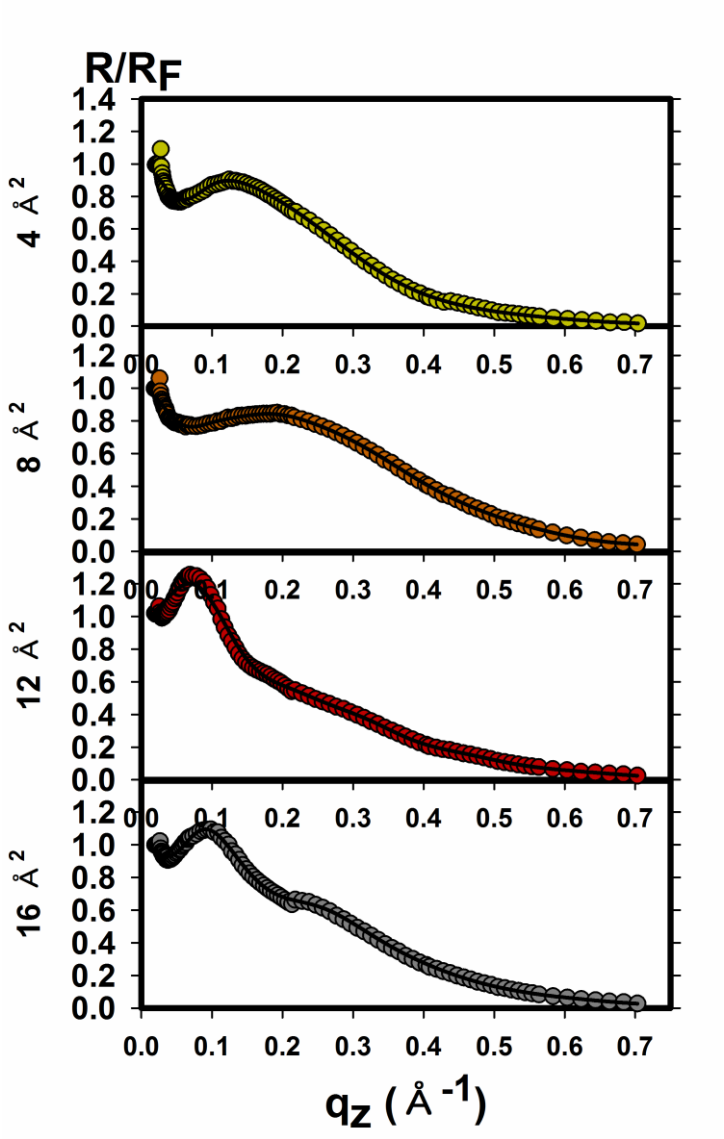


Figure S2. Normalized XR profiles ($R(q_z)/R_F(q_z)$) from PLGA monolayers at eight different area per monomer conditions. Points are experimental data. Solid lines are theoretical fits to the data. The procedures for this box-model fitting analysis are described in Section S1 of the Supporting Information (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 (SI).


R/R_F
4 Å^2
8 Å^2
12 Å^2
16 Å^2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0.1
0.3
0.5
0.7
q_Z (Å^-1)

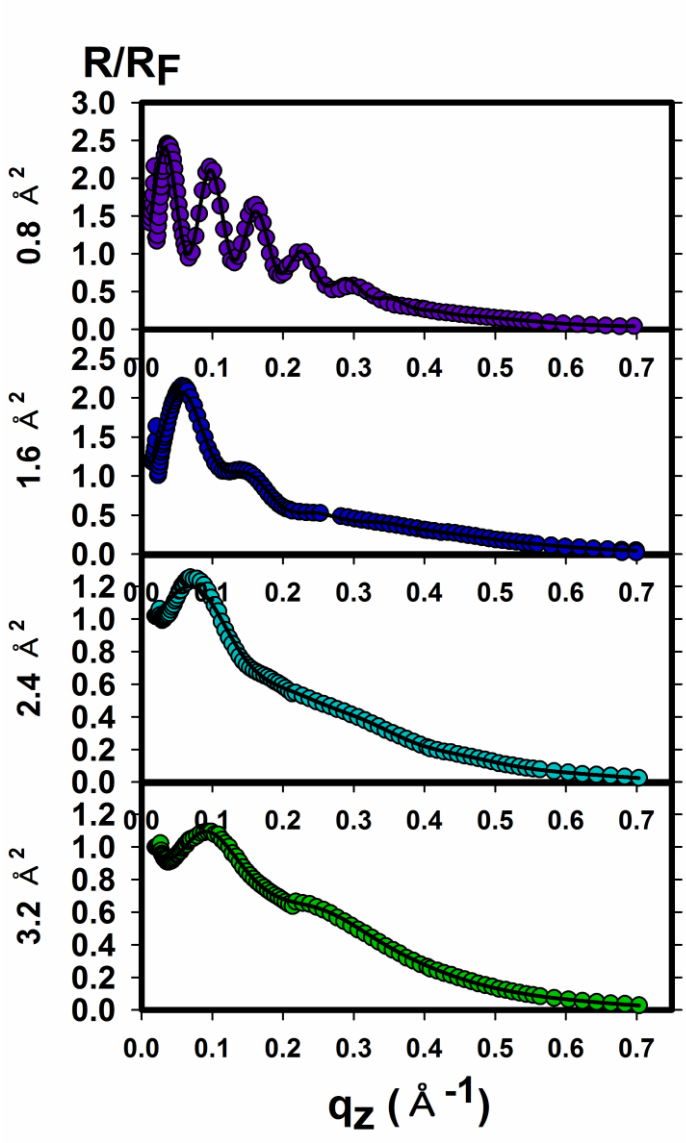

R/RF
0.8 Å2
1.6 Å2
2.4 Å2
3.2 Å2
qz (Å -1)

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 S2. The notations, $\mathbf{d_i}$, $\boldsymbol{\rho_{e,i}}$, and $\boldsymbol{\sigma_i}$, 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^2 per monomer)	$\mathbf{d_1}$ **(Å)**	$\mathbf{d_2}$ **(Å)**	$\mathbf{d_3}$ **(Å)**	$\mathbf{d_4}$ **(Å)**	$\boldsymbol{\rho_{e,1}/\rho_{e,water,\infty}}$	$\boldsymbol{\rho_{e,2}/\rho_{e,water,\infty}}$	$\boldsymbol{\rho_{e,3}/\rho_{e,water,\infty}}$	$\boldsymbol{\rho_{e,4}/\rho_{e,water,\infty}}$	$\boldsymbol{\sigma_1}$ **(Å)**	$\boldsymbol{\sigma_2}$ **(Å)**	$\boldsymbol{\sigma_3}$ **(Å)**	$\boldsymbol{\sigma_4}$ **(Å)**	$\boldsymbol{\sigma_5}$ **(Å)**
16	6.41666	12.9508	8.64105	7.78072	1.03891	0.966563	0.98442	0.990679	2.15735	2.07524	4.06934	3.14518	5.30307
12	8.29242	-4.34333	17.7918	5.33994	1.03461	0.949749	0.91921	0.924015	2.26352	2.18636	0.342399	2.54587	19.9115
8	9.97876	12.858	8.37836	16.1784	0.982394	0.910889	0.92012	0.953104	2.40438	1.91985	1.01643	7.60935	16.1317
4	8.44651	3.82322	9.78025	11.1218	0.965052	1.02311	0.910897	0.85639	2.92373	2.41668	3.97196	10.4873	20.8752
4'	13.9195	-0.07179	17.6792	21.7444	1.00654	0.988154	1.02198	0.938458	2.797	-0.16522	4.63387	6.89831	19.5518
3.2	9.9935	7.26672	14.602	11.6826	0.987367	1.05761	1.08726	1.03757	2.91774	1.69848	1.9078	4.14856	5.4396

2.4	8.6123	19.6905	19.2358	13.7339	0.922695	1.33454	1.21351	1.12368	2.45416	7.00602	8.46657	7.44521	6.68621
1.6	8.01564	22.0499	-29.025392	95.3692	1.08276	1.19639	1.1869	1.28099	2.77802	2.19908	0.076313	4.51489	6.2403
0.8	12.4419	5.42995	12.8531	20.4864	1.0169	0.996301	0.967536	0.95066	2.69695	0.559041	4.77855	4.5459	11.3206

Figure S3. Thicknesses of the PLGA monolayer at various area per chain conditions determined from the XR data shown in Figure 1; the monolayer thickness is defined as the distance between the mid-electron-density point on the air side and the mid-electron-density point on the water side of the monolayer. These experimentally determined thicknesses are compared with the film thickness values calculated using a value of 1.58 g/cc for the bulk density of PLGA.

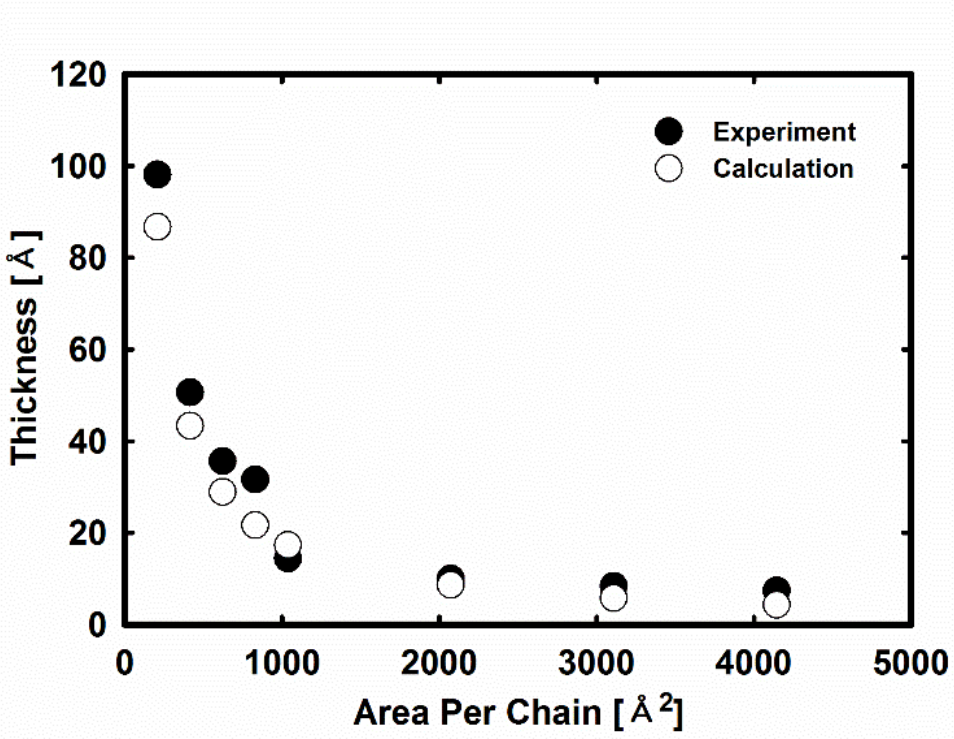
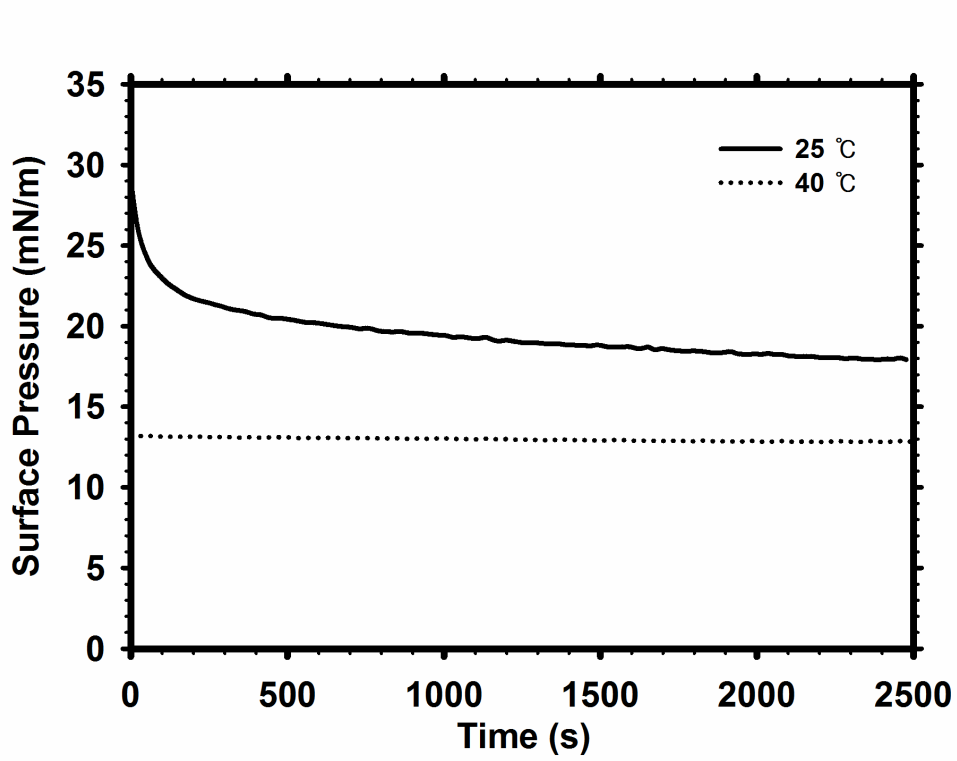


Figure S4. (a) Surface pressure relaxation profiles of Langmuir PLGA films at a constant film area of 0.8 $Å^2$ per monomer at 25 and 40 ℃. **(b)** A surface area vs. time profile of a Langmuir PLGA film at a constant pressure of 30 mN/m at 25℃. The monolayer samples were initially prepared at 2.78 $Å^2$ per monomer and then compressed at a rate of 3 mm/min to the 0.8 $Å^2$ per monomer condition (i.e., to the 30 mN/m surface pressure condition) before these measurements began.



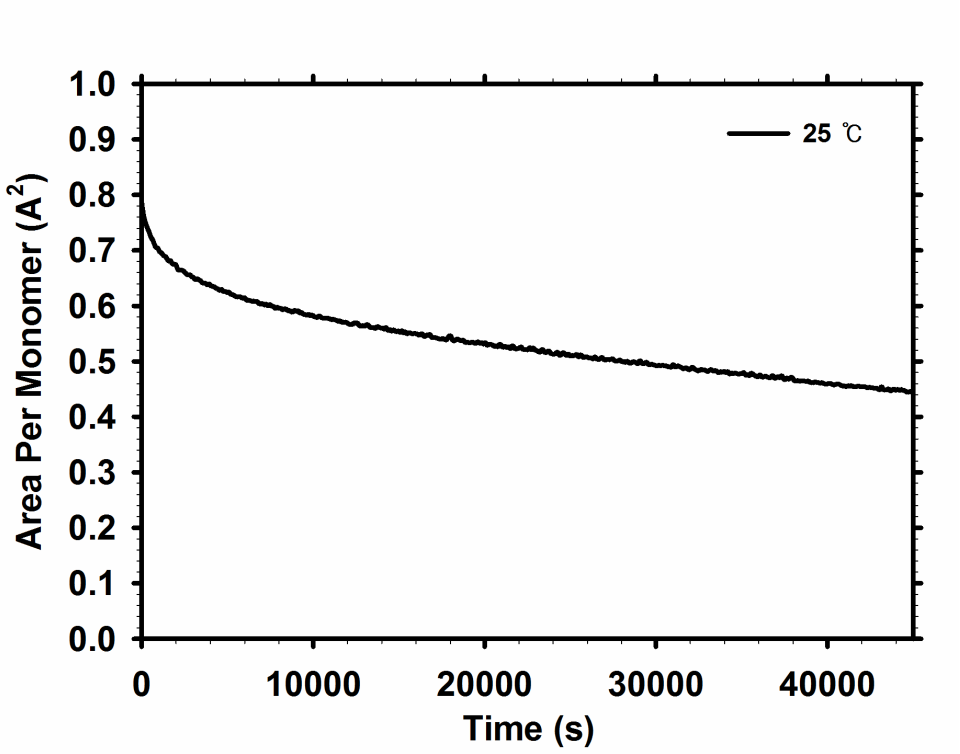
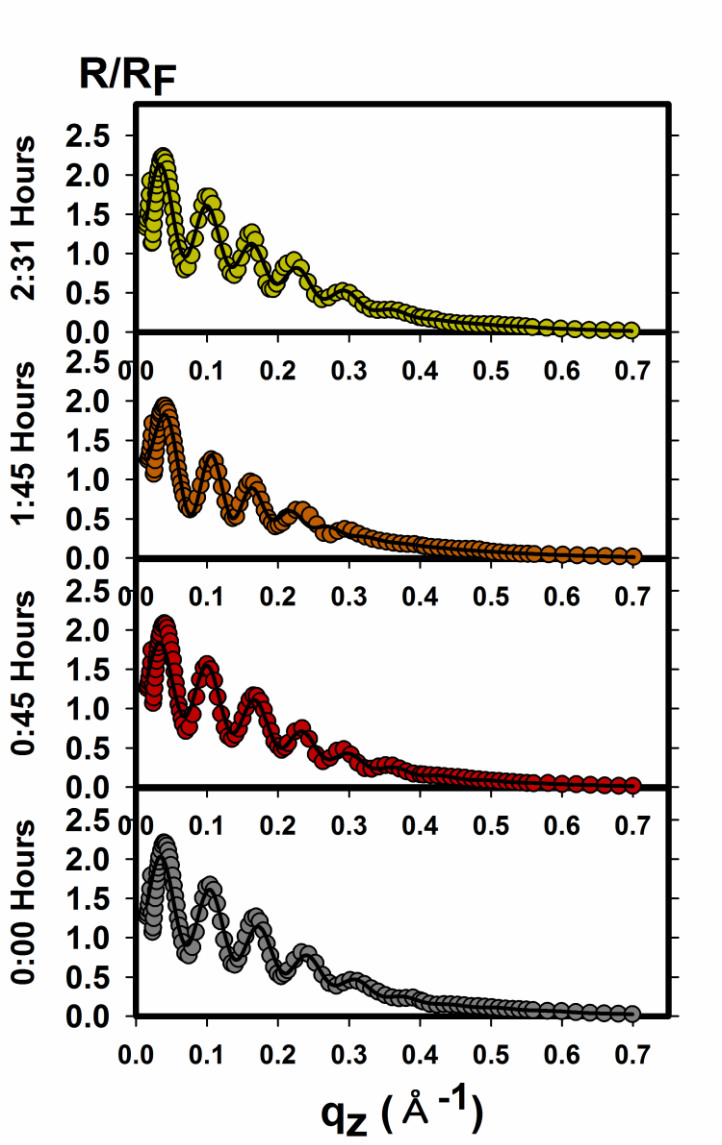

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Area Per Monomer (A^2)
0
10000
20000
30000
40000
Time (s)
25 ℃

Figure S5. A time series of normalized XR profiles ($R(q_z)/R_F(q_z)$) from a Langmuir PLGA film at a constant surface pressure of 30 mN/m; the monolayer was initially prepared at an area of 4 $Å^2$ per monomer and then compressed at a rate of 2 cm^2/min (trough width 98 mm, length 350 mm) to the 30 mN/m surface pressure condition before these measurements began. Points are experimental data. Solid lines are theoretical fits to the data. The procedures for this box-model fitting analysis are described in Section S1 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 5(b). The values of the best-fit parameters are presented in Table S2 (SI).


R/RF
2:31 Hours
1:45 Hours
0:45 Hours
0:00 Hours
0.0
0.5
1.0
1.5
2.0
2.5
0.1
0.2
0.3
0.4
0.5
0.6
0.7
qz (Å -1)

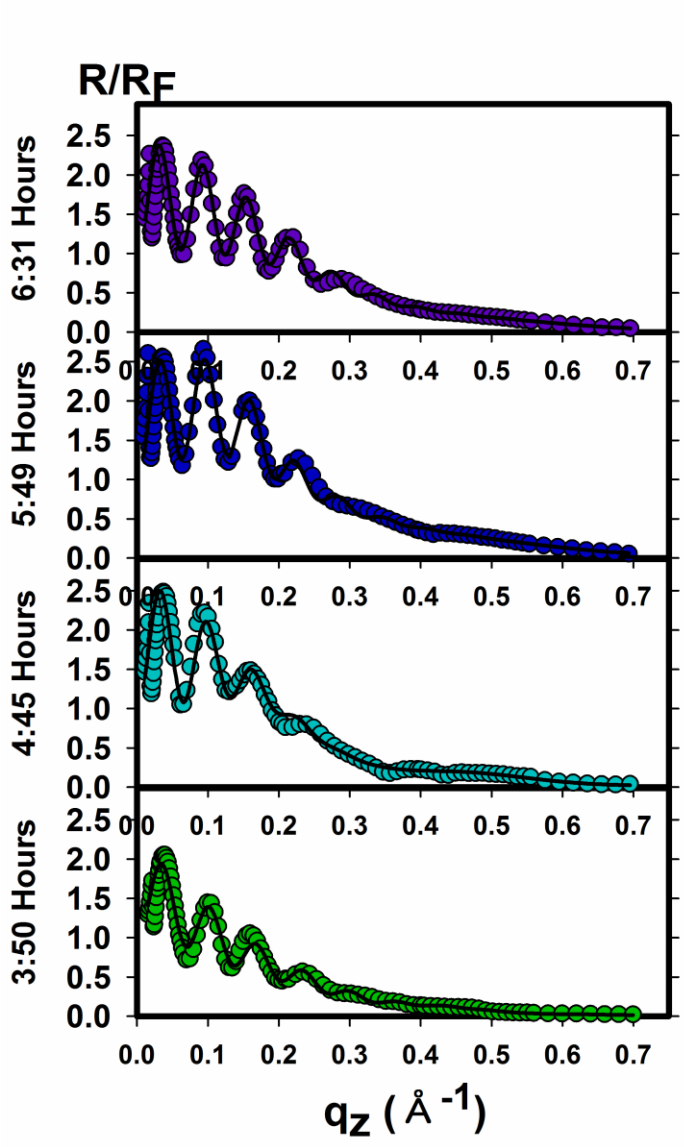

R/RF
6:31 Hours
5:49 Hours
4:45 Hours
3:50 Hours
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
qz (Å -1)

Table S2. Box model fit parameters for the normalized electron density profiles shown in Figure 5(b). The actual reflectivity data are presented in Figure S5. The notations, $\mathbf{d_i}$, $\boldsymbol{\rho_{e,i}}$, and $\boldsymbol{\sigma_i}$, 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.

XR Measurement Start Time (hours:minutes)	$\mathbf{d_1}$ **(Å)**	$\mathbf{d_2}$ **(Å)**	$\mathbf{d_3}$ **(Å)**	$\mathbf{d_4}$ **(Å)**	$\boldsymbol{\rho_{e,1}/\rho_{e,water,\infty}}$	$\boldsymbol{\rho_{e,2}/\rho_{e,water,\infty}}$	$\boldsymbol{\rho_{e,3}/\rho_{e,water,\infty}}$	$\boldsymbol{\rho_{e,4}/\rho_{e,water,\infty}}$	$\boldsymbol{\sigma_1}$ **(Å)**	$\boldsymbol{\sigma_2}$ **(Å)**	$\boldsymbol{\sigma_3}$ **(Å)**	$\boldsymbol{\sigma_4}$ **(Å)**	$\boldsymbol{\sigma_5}$ **(Å)**
0:00	6.81956	15.1051	46.6486	22.4012	0.962798	1.19847	1.22417	1.21899	2.74565	-3.52975	-3.08839	-0.16186	5.42636
0:45	6.95511	11.8359	55.5987	19.5438	0.945524	1.16703	1.18555	1.19567	2.91141	-3.69149	-4.05022	-4.51263	5.16644
1:45	8.82472	9.26637	78.1733	18.0869	0.926803	1.01601	1.19394	0.753539	3.01792	2.44715	-16.4992	16.6875	7.91894
2:31	6.51163	14.6399	53.2566	21.1705	0.978127	1.22029	1.24558	1.20635	2.91861	-4.1058	-2.87444	-4.25562	5.78533
3:50	4.24449	23.6119	50.655	15.3985	0.735033	1.19613	1.21529	1.17425	2.86493	6.74756	-0.34623	12.2267	5.42157
4:45	8.18154	9.71121	2.59892	75.6624	1.12115	1.35999	1.32104	1.29872	2.83579	2.96559	-1.15006	-1.17637	9.52863
5:49	7.982	5.284	46.72	38.85	1.23853	1.55243	1.28876	1.27178	2.607	-	-	-	6.605

	47	81	8	66					48	3.80171	12.9802	5.1055	93
6:31	7.916 76	4.926 26	43.58 78	45.75 07	1.108	1.37735	1.28171	1.26792	2.612 07	- 3.77783	- 4.61015	- 12.9379	6.195 25

Figure S6. Normalized electron density profiles ($\rho_e(z)/\rho_{e,water,\infty}$) obtained from the box-model analysis of the XR data for the compressed and as-spread PLGA films at an area of 0.8 $Å^2$ per monomer.