Electronic Supplementary Information (ESI) for

Macroscopic Lateral Heterogeneity Observed in a Laterally-Mobile Immiscible Mixed Polyelectrolyte/Neutral Polymer Brush

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S1. Self-Consistent Field (SCF) Weak Polyelectrolyte Brush Theory

The results presented in Figures 1(B) and 4 of the main text were calculated on the basis of a selfconsistent field weak polyelectrolyte brush theory that has been developed in our laboratory; the derivation of the formalism has been discussed in detail in a previous publication.¹ Also, in earlier publications we have presented analyses of the effects of various parameters (such as charge fraction,² salt concentration,² grafting density,² and interfacial curvature³) on the miscibility of mixed polyelectrolyte and neutral polymer brushes. However, it should be noted that these previous studies examined mixed brush systems comprising permanently charged polymers (i.e., strong polyelectrolytes), whereas in the present calculations we take into account the local nature of the charge equilibrium of a weak polyelectrolyte segment; therefore the current approach more realistically models the experimental situation where a weak polyelectrolyte material (i.e., PDMAEMA) is used as the polyelectrolyte brush component.

Below we provide a brief description of the theory and the computational procedures used in this work. Extending our earlier work,¹ the semi-grand canonical partition function for a mixed brush system consisting of charged weak polyelectrolyte and non-charged polymer chains can be written as

$$\mathbb{Z} = \int D\psi \left(\prod_{i} \int D\omega_{i} \int D\rho_{i} \right) \int D\eta \int D\alpha \int Df \int Dg \int D\gamma_{c} \int D\gamma_{U} \int d\lambda \exp(-F)$$
(S1)

where the system free energy, F, can be calculated by

$$F = \int d\mathbf{r} \left[-\sum_{i} \omega_{i}(\mathbf{r}) \rho_{i}(\mathbf{r}) + V_{P_{1}S} \rho_{P_{1}}(\mathbf{r}) \chi_{P_{2}S} \rho_{S}(\mathbf{r}) + V_{P_{2}S} \rho_{P_{2}}(\mathbf{r}) \chi_{P_{2}S} \rho_{S}(\mathbf{r}) \right. \\ \left. + V_{P_{1}P_{2}} \rho_{P_{1}}(\mathbf{r}) \chi_{P_{1}P_{2}} \rho_{P_{2}}(\mathbf{r}) - \eta(\mathbf{r}) + \eta(\mathbf{r}) \sum_{i} v_{i} \rho_{i}(\mathbf{r}) \right. \\ \left. - \left(\gamma_{C}(\mathbf{r}) f(\mathbf{r}) + \gamma_{U}(\mathbf{r}) g(\mathbf{r}) \right) \rho_{P_{1}}(\mathbf{r}) + \alpha(\mathbf{r}) \rho_{P_{1}}(\mathbf{r}) \left(f(\mathbf{r}) + g(\mathbf{r}) - 1 \right) \right] \right.$$

$$\left. + \beta e \psi(\mathbf{r}) \left(f(\mathbf{r}) \rho_{P_{1}}(\mathbf{r}) + \sum_{ion} z_{ion} \rho_{ion}(\mathbf{r}) \right) - \frac{1}{2} \beta \varepsilon \left| \nabla \psi(\mathbf{r}) \right|^{2} \right] \right. \\ \left. - n_{P_{1}} \ln \left(\frac{Q_{P_{1}}}{n_{P_{1}}} \right) - n_{P_{1}} - n_{P_{2}} \ln \left(\frac{Q_{P_{2}}}{n_{P_{2}}} \right) - n_{P_{2}} - \sum_{ion} Q_{ion} - Q_{S} - Q_{C} - Q_{U} \right) \right.$$

In Equation (S1), the subscript *i* represents all species in the system, $\psi(\mathbf{r})$ is the electrostatic potential, $\rho_i(\mathbf{r})$ is the macroscopic density for each *i* species under a conjugate field $\omega_i(\mathbf{r})$, $f(\mathbf{r})$ and $g(\mathbf{r})$ are, respectively, the fractions of charged and non-charged segments on a polyelectrolyte chain for which $\gamma_c(\mathbf{r})$ and $\gamma_U(\mathbf{r})$ are the respective conjugate fields, $\eta(\mathbf{r})$ and $\alpha(\mathbf{r})$ are, respectively, and the functional Lagrange multipliers for the incompressibility and charge fraction normalization constraints. In Equation (S2), the subscripts, *S*, *P*₁, *P*₂, *C*, and *U*, represent the solvent, the polyelectrolyte (i.e., PDMAEMA in our case), the neutral polymer (PEO), the charged segment of the polyelectrolyte, and the uncharged segment of the polyelectrolyte, respectively, χ_{ij} is the Flory-Huggins interaction parameter between species *i* and *j*, *V*_{ij} is a characteristic interaction volume for the two species, *v_i* is the intrinsic volume of each species *i*, *z_i* is the valency of small molecules of type *i*, *n_i* is the number of polymer chains of type *i*, and *Q_i* is the partition function for species *i*.

Through the saddle point approximation by taking functional derivatives of the free energy expression with respect to the various functional variables, the following set of SCF equations are obtained:

$$\rho_{S}(\mathbf{r}) = \rho_{S}^{b} \exp\left(-V_{P_{1}S} \chi_{P_{1}S} \rho_{P_{1}}(\mathbf{r}) - V_{P_{2}S} \chi_{P_{2}S} \rho_{P_{2}}(\mathbf{r}) - v_{S} \eta(\mathbf{r})\right)$$
(S3)

$$\rho_{ion}(\mathbf{r}) = \rho_{ion}^{b} \exp\left(-\beta z_{ion} e\psi(\mathbf{r}) - v_{ion} \eta(\mathbf{r})\right)$$
(S4)

$$\omega_{P_1}(\mathbf{r}) = V_{P_1S} \chi_{P_1S} \rho_S(\mathbf{r}) + V_{P_1P_2} \chi_{P_1P_2} \rho_{P_2}(\mathbf{r}) + v_{P_1} \eta(\mathbf{r}) - \alpha(\mathbf{r}) - 1$$
(S5)

$$\omega_{P_2}\left(\mathbf{r}\right) = V_{P_2S}\chi_{P_2S}\rho_S\left(\mathbf{r}\right) + V_{P_1P_2}\chi_{P_1P_2}\rho_{P_1}\left(\mathbf{r}\right) + v_{P_2}\eta\left(\mathbf{r}\right)$$
(S6)

$$\alpha(\mathbf{r}) = \ln\left[1 - f^b + f^b \exp\left(-\beta e\psi(\mathbf{r})\right)\right]$$
(S7)

$$f(\mathbf{r}) = \frac{K_b^\circ}{\rho_{OH^-}^b \exp(\beta e\psi(\mathbf{r})) + K_b^\circ}$$
(S8)

$$\sum_{j} v_{j} \rho_{j} \left(\mathbf{r} \right) = 1 \tag{S9}$$

$$\rho_{P_{1}}(\mathbf{r}) = \frac{n_{P_{1}}}{VQ_{P_{1}}} \int_{0}^{N_{P_{1}}} ds q_{P_{1}}(\mathbf{r}, s) q_{P_{1}}^{*}(\mathbf{r}, N_{P_{1}} - s)$$
(S10)

$$\rho_{P_2}\left(\mathbf{r}\right) = \frac{n_{P_2}}{VQ_{P_2}} \int_{0}^{N_{P_2}} ds q_{P_2}\left(\mathbf{r}, s\right) q_{P_2}^*\left(\mathbf{r}, N_{P_2} - s\right)$$
(S11)

$$Q_{P_{\rm I}} = \frac{1}{V} \int d\mathbf{r} q_{P_{\rm I}} \left(\mathbf{r}, N_{P_{\rm I}} \right) \tag{S12}$$

$$Q_{P_2} = \frac{1}{V} \int d\mathbf{r} q_{P_2} \left(\mathbf{r}, N_{P_2} \right)$$
(S13)

$$\nabla^{2}\psi(\mathbf{r}) = -\frac{e}{\varepsilon} \left(f(\mathbf{r})\rho_{P_{1}}(\mathbf{r}) + \sum_{ion} z_{ion}\rho_{ion}(\mathbf{r}) \right)$$
(S14)

$$\int d\mathbf{r} \left(f(\mathbf{r}) \rho_{P_1}(\mathbf{r}) + \sum_{ion} z_{ion} \rho_{ion}(\mathbf{r}) \right) = 0$$
(S15)

where N_i , ρ_i^b , f^b and K_b° denote the number of segments per chain of polymer type *i*, the bulk density of species *i*, the fraction of charged segments (monomers) on a polyelectrolyte chain in the bulk limit, and the standard ionization equilibrium constant of the polyelectrolyte monomer in an imaginary bulk monomeric condition, respectively. Note that $q_i(\mathbf{r}, s)$ represents the probability of finding the *s*-th segment counted from one end of a type-*i* chain at position \mathbf{r} , and $q_i^*(\mathbf{r}, t)$, where $t = N_i - s$, is the same quantity calculated using the other end of the chain as the initial point. These probability distribution functions satisfy the modified diffusion equation

$$\frac{\partial q_i(\mathbf{r},s)}{\partial s} = \frac{b_i^2}{6} \nabla^2 q_i(\mathbf{r},s) - \omega_i(\mathbf{r}) q_i(\mathbf{r},s)$$
(S16)

$$\frac{\partial q_i^*(\mathbf{r},t)}{\partial t} = \frac{b_i^2}{6} \nabla^2 q_i^*(\mathbf{r},t) - \omega_i(\mathbf{r}) q_i^*(\mathbf{r},t)$$
(S17)

where i is either P_1 or P_2 . Simplifying Equation (S2) gives

$$F = -\int d\mathbf{r} \Big[V_{P_{1}S} \rho_{P_{1}}(\mathbf{r}) \chi_{P_{1}S} \rho_{S}(\mathbf{r}) + V_{P_{2}S} \rho_{P_{2}}(\mathbf{r}) \chi_{P_{2}S} \rho_{S}(\mathbf{r}) - \eta(\mathbf{r}) + V_{P_{1}P_{2}} \rho_{P_{1}}(\mathbf{r}) \chi_{P_{1}P_{2}} \rho_{P_{2}}(\mathbf{r}) + \frac{1}{2} \beta \varepsilon |\nabla \psi(\mathbf{r})|^{2} + \sum_{m} \rho_{m}(\mathbf{r}) \Big] - n_{P_{1}} \ln \frac{Q_{P_{1}}}{n_{P_{1}}} - n_{P_{1}} - \ln \frac{Q_{P_{2}}}{n_{P_{2}}} - n_{P_{2}}$$
(S18)

where the subscript *m* refers to all small molecule (non-polymeric) species present in the system.

By initial guesses for $\omega_{P_1}(\mathbf{r})$ and $\omega_{P_2}(\mathbf{r})$, the diffusion equations are solved using a Crank-Nicholson scheme with the following initial conditions

$$q_{i}(\mathbf{r},0) = \begin{cases} 1 & if \ \mathbf{r} = \mathbf{r}_{surface} \\ 0 & if \ \mathbf{r} \neq \mathbf{r}_{surface} \end{cases}$$
(S19)
$$q_{i}^{*}(\mathbf{r},0) = \begin{cases} 0 & if \ \mathbf{r} = \mathbf{r}_{surface} \\ 1 & if \ \mathbf{r} \neq \mathbf{r}_{surface} \end{cases}$$

The first condition defines a chain that is end-grafted to a surface at s = 0, while the second defines a chain that has a free end at t = 0. Both these functions are subject to the boundary conditions

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

$$q_i(\mathbf{r}, s > 0) = 0, \ q_i^*(\mathbf{r}, t > 0) = 0 \quad if \ \min\left(\left| \mathbf{r} - \mathbf{r}_{surface} \right|\right) \ge Nb$$
(S20)

where the first condition assumes an indifferent surface, while the second equation accounts for the finite extensibility of the chains. The Poisson-Boltzmann equation (Equation S14) was solved using the following boundary conditions; the grafting surface is uncharged $(\nabla \psi |_{surface} = 0)$, and the bulk solution is electrically neutral $(\psi |_{bulk} \rightarrow 0)$. The grand potential was calculated from the free energy by $\varphi = -F - \int d\mathbf{r} \rho_{solvent} (\mathbf{r})$.⁴ The surface pressure produced by the lateral interchain interactions between the end-grafted polymer chains can be calculated from the grand potential by

$$\Pi = \left(\frac{\partial \varphi}{\partial A}\right)_{n_p, n_s, T}$$
(S21)

where A denotes the area of the grafting surface.

Also, the mixing free energy can be calculated as a function of the molar composition of the mixed brush in the standard way

$$\Delta F_{mix} = F(x_{p_1}) - x_{p_1} F(x_{p_1} = 1) - (1 - x_{p_1}) F(x_{p_1} = 0)$$
(S22)

The spinodal points can be determined by locating the inflection points of the ΔF_{mix} vs. x_{P_1} curve.

S2. Procedures for the Normalization and Box-Model Analysis of the XR Data

For the analysis of specular reflectivity data using the first Born approximation (Equation S23), the reflectivity data first need to be normalized by the theoretical reflectivity values calculated for an infinitely-sharp interface between air and water (this theoretical reflectivity profile can be calculated using the Fresnel equation (Equation S24)):

$$R(q_z) / R_F(q_z) \approx (1/\rho_{e,\infty}) \left| \int (d\rho_e(z)/dz) \exp(iq_z z) dz \right|^2$$
(S23)

$$R_{F} \approx \left| \left(q_{z} - \sqrt{q_{z}^{2} - q_{c}^{2}} \right) / \left(q_{z} + \sqrt{q_{z}^{2} - q_{c}^{2}} \right) \right|^{2}$$
(S24)

where the critical momentum transfer vector, q_c , is estimated to be 0.02176 Å⁻¹ for the air-water interface; $q_{c,water} = (4\pi/\lambda)\sin(\theta_{c,water})$ where $\theta_{c,water} = (r_e\rho_e\lambda^2/\pi)^{V_2}$. In the figure below, the original reflectivity profile obtained from the PDMAEMA₁₁₈-PnBA₁₀₀ monolayer at A = 700 Å² per chain is compared to the theoretical Fresnel reflectivity profile for a step-function interface between air and water. However, as shown in the figure, the q_c value of the XR profile is found to be lower than the $q_{c,water}$ value (likely because of an offset in the determination of q_z and/or the absorbance of the x-ray by the sample). This q_c mismatch artificially produces a spike in the normalized reflectivity profile near the q_c point, and, as a result, causes a poor quality of fitting.



In order to avoid this problem, the following procedure was used. The original reflectivity profile was shifted, first horizontally by addition of an offset (q_{z_off}) (Equation S25), and then vertically shifted by multiplying the original reflectivity values by a constant factor (R_{norm}) (Equation S26). This adjusted experimental reflectivity profile was fitted with the theoretical Fresnel reflectivity profile for a rough interface (calculated using Equations S27 and S28).

$$q_z = q_{z,ori} + q_{z,off} \tag{S25}$$

$$R = R_{ori} \times R_{norm} \tag{S26}$$

$$R_{F}(q_{z}) = \left| \frac{q_{z} - \sqrt{q_{z}^{2} - q_{c}^{2} - 4ik\mu}}{q_{z} + \sqrt{q_{z}^{2} - q_{c}^{2} - 4ik\mu}} \right|^{2}$$
(S27)

$$R_{F,rough} = R_F \times \exp\left(-q_z^2 \sigma^2\right) \tag{S28}$$

Five parameters (q_{z_off} , R_{norm} , q_c , $k\mu$ and σ) were adjusted to minimize the fitting metric defined as

$$\chi^{2} = \sum_{i=1}^{N} \frac{\left(R_{i} - R_{F, rough, i}\right)^{2}}{\gamma_{i}^{2}}$$
(S29)

where γ^2 is the variance of the experimental reflectivity value. In the figure below, the best-fit shifted experimental reflectivity curve (black) is compared to both the theoretical Fresnel reflectivity profiles of an infinitely-sharp interface (red) and of an interface with a Gaussian roughness (blue). After this adjustment, the resulting normalized reflectivity profile (R/R_F) shows a more reasonable (i.e., smoother) variation near the q_c value.



For the analysis of the XR data, we used the so-called multiple-box model in which the scattering volume is divided into a finite number of horizontal sublayers of distinct electron densities with smeared interfaces between adjacent sublayers. The electron density profiles calculated based on this multiple-box model were converted through the first Born approximation to the expected reflectivity profiles, and the resulting predicted reflectivities were compared with the experimental results. It was observed that at least four sublayers of variable electron density ($\rho_{e,l}$, $\rho_{e,2}$, $\rho_{e,3}$, $\rho_{e,4}$) and thickness (d_1 , d_2 , d_3 , d_4), each bounded by error function-shaped interfacial regions of variable width (σ_1 , σ_2 , σ_3 , σ_4 , σ_5), should be included in the box model in order to satisfactorily reproduce the complicated shapes of the normalized reflectivity curves. The actual box model equation used was

$$\rho_{e}(z) = \frac{\left(\rho_{e,1} - \rho_{e,air}\right)}{2} \left(1 + erf\left(\frac{z}{\sqrt{2\sigma_{1}^{2}}}\right)\right) + \frac{\left(\rho_{e,2} - \rho_{e,1}\right)}{2} \left(1 + erf\left(\frac{z - d_{1}}{\sqrt{2\sigma_{2}^{2}}}\right)\right) + \frac{\left(\rho_{e,3} - \rho_{e,2}\right)}{2} \left(1 + erf\left(\frac{z - (d_{1} + d_{2})}{\sqrt{2\sigma_{3}^{2}}}\right)\right) + \frac{\left(\rho_{e,4} - \rho_{e,3}\right)}{2} \left(1 + erf\left(\frac{z - (d_{1} + d_{2} + d_{3})}{\sqrt{2\sigma_{4}^{2}}}\right)\right)\right)$$
(S30)
$$+ \frac{\left(\rho_{e,sub} - \rho_{e,4}\right)}{2} \left(1 + erf\left(\frac{z - (d_{1} + d_{2} + d_{3} + d_{4})}{\sqrt{2\sigma_{5}^{2}}}\right)\right)$$

All the thirteen ρ_e , *d* and σ variables listed above were used as fitting parameters. The values of the fit parameters that gave the least errors in simulating the experimental data are presented in Tables S1 – S6; the objective function of the fitting procedure, defined as the sum of absolute error values (Equation S31),

was minimized using a Matlab constrained nonlinear regression routine ("fmincon").

$$\varepsilon = \sum_{i=1}^{N} \left\{ abs \left(R_{\exp,i} \left(q_z \right) - R_{cal,i} \left(q_z \right) \right) / R_{F,i} \left(q_z \right) \right\}$$
(S31)

As shown in Figures 2 and 4, the model's fit quality under the best-fitting parameter estimates was almost impeccable at all *A* conditions examined, which fully supports the reasonableness of the estimated parameters.

Table S1. Results of the three-box model analysis of the XR data obtained from the PEO₁₁₃-PnBA₁₀₀ diblock copolymer monolayer (Figure 2(A)): the best-fit values for the thicknesses (d_i), electron densities ($\rho_{e,i}$) and roughnesses (σ_i) of the constituent sublayers of the monolayer determined at four different area per brush chain (A) conditions (A = 2000, 1500, 1100, and 700 Å²). As can be deduced from Equation S30, 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.

| A (Å ²) | $d_1(\text{\AA})$ | $d_2(\text{\AA})$ | $d_{\mathfrak{z}}(\mathbf{\mathring{A}})$ | $ ho_{e,1'}$ $ ho_{e,water,\infty}$ | $ ho_{e,2'}$ $ ho_{e,water,\infty}$ | ρ _{e,3} / ρ _{e,water,∞} | $\sigma_1(\text{\AA})$ | $\sigma_2(\text{\AA})$ | $\sigma_3(\text{\AA})$ | $\sigma_4({ m \AA})$ |
|---------------------|-------------------|-------------------|---|-------------------------------------|--|--|------------------------|------------------------|------------------------|----------------------|
| 2000 | 5.004 | 10.919 | 24.650 | 1.1575 | 0.9783 | 0.9913 | 2.911 | 2.961 | 4.115 | 7.498 |
| 2000 | 6.443 | 7.986 | 21.292 | 1.0867 | 0.9495 | 0.9866 | 2.638 | 5.413 | 1.878 | 8.220 |
| 2000 | 4.879 | 8.831 | 20.433 | 1.1316 | 0.9402 | 0.9879 | 2.700 | 5.593 | 2.645 | 8.199 |
| 1500 | 4.989 | 8.544 | 24.627 | 1.1725 | 0.9435 | 0.9882 | 2.853 | 4.858 | 2.178 | 8.012 |
| 1500 | 5.168 | 9.052 | 22.800 | 1.1472 | 0.9387 | 0.9815 | 2.788 | 5.018 | 2.033 | 8.544 |
| 1500 | 4.691 | 7.973 | 23.802 | 1.2485 | 0.9279 | 0.9831 | 2.979 | 4.099 | 2.832 | 8.470 |
| 1100 | 4.786 | 10.177 | 24.867 | 1.2133 | 0.9459 | 0.9815 | 3.223 | 4.888 | 2.229 | 14.449 |
| 1100 | 5.455 | 9.714 | 21.361 | 1.1869 | 0.9353 | 0.9818 | 3.186 | 5.153 | 2.555 | 8.524 |
| 1100 | 5.410 | 8.881 | 24.545 | 1.2458 | 0.9325 | 0.9853 | 3.332 | 4.497 | 2.957 | 8.336 |
| 700 | 5.181 | 9.721 | 12.695 | 1.2385 | 0.9407 | 1.0082 | 3.337 | 4.035 | 3.926 | 4.903 |
| 700 | 6.134 | 10.673 | 13.031 | 1.1751 | 0.9487 | 1.0087 | 3.404 | 2.965 | 3.567 | 6.100 |

Table S2. Results of the three-box model analysis of the XR data obtained from the PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymer monolayer (Figure 2(B)): the best-fit values for the thicknesses (d_i), electron densities ($\rho_{e,i}$) and roughnesses (σ_i) of the constituent sublayers of the monolayer determined at four different area per brush chain (A) conditions (A = 2000, 1500, 1100, and 700 Å²). As can be deduced from Equation S30, 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.

| A (Å ²) | <i>d</i> ₁ (Å) | $d_2(\text{\AA})$ | $d_3(\text{\AA})$ | $d_4(\text{\AA})$ | $ ho_{e,1'} ho_{e,water,}$ | $ ho_{e,2'} ho_{e,water,}$ | $ ho_{e,3'} ho_{e,water,}$ | $ ho_{e,4'} ho_{e,water,}$ | $\sigma_{I}(\text{\AA})$ | $\sigma_2(\text{\AA})$ | $\sigma_{_{\mathcal{J}}}(\mathrm{\AA})$ | $\sigma_4(\text{\AA})$ | $\sigma_{_{5}}(\text{\AA})$ |
|---------------------|---------------------------|-------------------|-------------------|-------------------|----------------------------|----------------------------|----------------------------|----------------------------|--------------------------|------------------------|---|------------------------|-----------------------------|
| 2000 | 6.514 | 7.432 | 16.340 | 30.627 | 1.2232 | 1.3408 | 0.9576 | 0.9918 | 7.845 | 2.746 | 3.155 | 5.998 | 5.340 |
| 2000 | 4.744 | 9.928 | 17.797 | 27.255 | 1.1314 | 1.2462 | 0.9683 | 0.9918 | 7.410 | 2.487 | 2.214 | 4.611 | 4.219 |
| 1500 | 2.883 | 8.478 | 26.934 | 12.068 | 1.0924 | 1.4485 | 1.0181 | 0.9880 | 8.568 | 3.714 | 2.963 | 6.444 | 5.774 |
| 1500 | 3.251 | 9.077 | 28.909 | 12.555 | 1.1144 | 1.4429 | 1.0095 | 0.9916 | 9.003 | 3.804 | 2.868 | 4.761 | 5.856 |
| 1100 | 2.611 | 9.316 | 28.524 | 13.492 | 0.9328 | 1.4989 | 1.0353 | 0.9942 | 10.141 | 4.044 | 2.793 | 4.917 | 6.320 |
| 1100 | 0.542 | 8.940 | 29.636 | 16.447 | 1.1122 | 1.4805 | 1.0374 | 0.9957 | 8.262 | 3.695 | 2.918 | 5.130 | 3.431 |
| 700 | 11.951 | 9.841 | 12.313 | 16.457 | 1.0866 | 1.3352 | 0.8199 | 1.0750 | 9.211 | 2.700 | 2.559 | 4.255 | 4.165 |
| 700 | 11.148 | 9.596 | 13.015 | 16.540 | 1.0214 | 1.3381 | 0.8396 | 1.0648 | 8.945 | 2.823 | 2.831 | 4.262 | 4.255 |

Table S3. Results of the four-box model analysis of the XR data obtained from the mixed PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymer monolayer (Figure 2(C)): the best-fit values for the thicknesses (d_i), electron densities ($\rho_{e,i}$) and roughnesses (σ_i) of the constituent sublayers of the monolayer determined at four different area per brush chain (A) conditions (A = 2000, 1500, 1100, and 700 Å²). As can be deduced from Equation S30, 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.

| A (Å ²) | $d_{I}(\text{\AA})$ | $d_2(\text{\AA})$ | d ₃ (Å) | $d_4(\text{\AA})$ | $ ho_{e,1'} ho_{e,water,}$ | $ ho_{e,2'} ho_{e,water,}$ | $ ho_{e,3'} ho_{e,water,}$ | $ ho_{e,4'} ho_{e,water,}$ | $\sigma_{I}(\text{\AA})$ | $\sigma_2(\text{\AA})$ | $\sigma_{_{\mathcal{J}}}(\text{\AA})$ | $\sigma_4^{}(\text{\AA})$ | $\sigma_{_{5}}(\text{\AA})$ |
|---------------------|---------------------|-------------------|--------------------|-------------------|----------------------------|----------------------------|----------------------------|----------------------------|--------------------------|------------------------|---------------------------------------|---------------------------|-----------------------------|
| 2000 | 5.360 | 7.299 | 12.790 | 3.555 | 1.1170 | 1.3717 | 0.8183 | 1.3069 | 6.729 | 2.619 | 2.207 | 7.170 | 4.801 |
| 2000 | 6.240 | 8.072 | 13.960 | 3.847 | 1.0723 | 1.3848 | 0.8115 | 1.3472 | 7.394 | 2.927 | 2.112 | 7.699 | 5.303 |
| 1500 | 5.333 | 8.439 | 13.022 | 4.717 | 1.1357 | 1.3811 | 0.8250 | 1.2474 | 7.494 | 2.547 | 2.017 | 7.842 | 4.952 |
| 1500 | 5.564 | 7.873 | 13.035 | 3.984 | 1.1186 | 1.4337 | 0.8199 | 1.3158 | 7.594 | 3.055 | 2.243 | 8.151 | 5.594 |
| 1100 | 8.498 | 8.086 | 18.144 | 3.307 | 1.1170 | 1.4748 | 0.8473 | 1.4221 | 8.599 | 3.343 | 2.510 | 9.741 | 7.101 |
| 1100 | 4.504 | 8.502 | 12.540 | 3.964 | 1.1394 | 1.4134 | 0.8606 | 1.1759 | 7.716 | 2.701 | 2.186 | 8.009 | 4.927 |
| 1100 | 6.607 | 7.989 | 17.571 | 3.502 | 1.0481 | 1.4765 | 0.8430 | 1.4134 | 8.715 | 3.370 | 2.427 | 9.809 | 7.898 |
| 1100 | 5.346 | 7.140 | 12.016 | 3.963 | 1.1206 | 1.4918 | 0.7978 | 1.2965 | 7.848 | 3.197 | 2.658 | 8.288 | 6.322 |
| 700 | 5.687 | 8.556 | 17.620 | 3.150 | 1.2330 | 1.4262 | 0.8812 | 1.2515 | 8.286 | 2.651 | 2.472 | 8.836 | 5.771 |
| 700 | 4.882 | 7.379 | 12.330 | 3.915 | 1.1364 | 1.4534 | 0.8669 | 1.1673 | 7.514 | 2.973 | 2.749 | 7.421 | 4.551 |
| 700 | 3.400 | 9.168 | 11.699 | 5.202 | 1.1823 | 1.3476 | 0.8794 | 1.0994 | 7.248 | 1.481 | 1.919 | 7.813 | 3.492 |

Table S4. Results of the four-box model analysis of the XR data obtained from the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ triblock copolymer monolayer (Figure 2(D)): the best-fit values for the thicknesses (d_i), electron densities ($\rho_{e,i}$) and roughnesses (σ_i) of the constituent sublayers of the monolayer determined at four different area per brush chain (A) conditions (A = 1500, 1100, 700, and 350 Å²). As can be deduced from Equation S30, 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.

| A (Å ²) | $d_1(\text{\AA})$ | $d_2(\text{\AA})$ | $d_3(\text{\AA})$ | $d_4(\text{\AA})$ | $ ho_{e,1'} ho_{e,water,}$ | $ ho_{e,2'} ho_{e,water,}$ | $ ho_{e,3'} ho_{e,water,}$ | $ ho_{e,4'} ho_{e,water,}$ | $\sigma_{I}(\text{\AA})$ | $\sigma_2(\text{\AA})$ | $\sigma_{_{3}}(\mathrm{\AA})$ | $\sigma_4(\text{\AA})$ | $\sigma_{_{5}}(\text{\AA})$ |
|---------------------|-------------------|-------------------|-------------------|-------------------|----------------------------|----------------------------|----------------------------|----------------------------|--------------------------|------------------------|-------------------------------|------------------------|-----------------------------|
| 1500 | 7.586 | 8.725 | 17.005 | 4.011 | 1.0738 | 1.3758 | 0.8107 | 1.3957 | 8.074 | 3.072 | 2.451 | 8.920 | 6.358 |
| 1500 | 6.971 | 8.207 | 16.917 | 3.799 | 1.1910 | 1.4540 | 0.8149 | 1.4063 | 8.846 | 2.985 | 2.712 | 9.139 | 6.757 |
| 1100 | 5.613 | 8.169 | 13.668 | 4.215 | 1.1456 | 1.3676 | 0.8534 | 1.1835 | 7.453 | 2.801 | 2.691 | 7.556 | 4.612 |
| 1100 | 6.647 | 8.618 | 14.380 | 4.444 | 1.1023 | 1.3453 | 0.8286 | 1.2572 | 7.573 | 3.032 | 2.581 | 8.338 | 5.346 |
| 700 | 4.384 | 9.793 | 12.392 | 4.851 | 1.0769 | 1.2363 | 0.9187 | 1.1306 | 6.689 | 1.452 | 1.847 | 7.546 | 3.051 |
| 700 | 4.353 | 9.599 | 11.753 | 5.313 | 1.0703 | 1.2241 | 0.9038 | 1.0980 | 6.459 | 1.270 | 1.918 | 8.171 | 2.232 |
| 350 | 4.139 | 7.772 | 9.655 | 5.697 | 1.1856 | 1.3533 | 0.9194 | 1.1493 | 6.582 | 4.217 | 2.581 | 4.959 | 2.900 |
| 350 | 2.791 | 9.425 | 9.338 | 5.442 | 1.1556 | 1.3498 | 0.9309 | 1.1225 | 6.961 | 4.136 | 2.544 | 3.983 | 3.037 |

Table S5. Results of the four-box model analysis of the XR data obtained from the mixed PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer monolayer (Figure 4(A)): the best-fit values for the thicknesses (d_i), electron densities ($\rho_{e,i}$) and roughnesses (σ_i) of the constituent sublayers of the monolayer determined at four different area per brush chain (A) conditions (A = 2000, 1500, 1100, and 700 Å²). As can be deduced from Equation S30, 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.

| A (Å ²) | $d_1(\text{\AA})$ | $d_2(\text{\AA})$ | $d_{3}(\text{\AA})$ | $d_4(\text{\AA})$ | $ ho_{e,1'} ho_{e,water,}$ | $ ho_{e,2'} ho_{e,water,}$ | $ ho_{e,3'} ho_{e,water,}$ | $ ho_{e,4'} ho_{e,water,}$ | $\sigma_{I}(\text{\AA})$ | $\sigma_2(\text{\AA})$ | $\sigma_{_{3}}(\text{\AA})$ | $\sigma_4^{}(\text{\AA})$ | $\sigma_{_{5}}(\text{\AA})$ |
|---------------------|-------------------|-------------------|---------------------|-------------------|----------------------------|----------------------------|----------------------------|----------------------------|--------------------------|------------------------|-----------------------------|---------------------------|-----------------------------|
| 2000 | 8.723 | 15.991 | 7.708 | 15.648 | 1.2683 | 0.9986 | 0.9797 | 0.9843 | 5.801 | 2.239 | 1.914 | 5.840 | 6.366 |
| 2000 | 8.344 | 9.966 | 13.073 | 17.334 | 1.2660 | 1.0097 | 0.9909 | 0.9852 | 5.750 | 2.303 | 5.235 | 4.957 | 5.939 |
| 1500 | 6.621 | 19.135 | 8.984 | 16.997 | 1.3946 | 1.0174 | 1.0038 | 0.9895 | 5.637 | 2.768 | 2.012 | 2.966 | 3.720 |
| 1500 | 7.031 | 18.550 | 9.934 | 16.780 | 1.4091 | 1.0119 | 0.9990 | 0.9884 | 5.952 | 2.754 | 1.781 | 2.624 | 3.877 |
| 1100 | 8.439 | 7.599 | 22.401 | 16.517 | 1.1522 | 0.9993 | 1.0310 | 0.9921 | 4.687 | 1.365 | 4.484 | 5.375 | 3.254 |
| 1100 | 8.291 | 6.878 | 9.481 | 11.953 | 1.1715 | 0.9760 | 1.0323 | 1.0325 | 4.771 | 1.776 | 4.604 | 5.510 | 4.512 |
| 700 | 7.238 | 9.908 | 12.715 | 13.089 | 1.2529 | 0.9388 | 1.0006 | 1.0295 | 4.934 | 2.454 | 4.922 | 2.676 | 4.755 |
| 700 | 8.412 | 9.588 | 11.180 | 12.869 | 1.1563 | 0.9530 | 1.0128 | 1.0328 | 4.650 | 1.610 | 4.422 | 2.168 | 5.400 |

Table S6. Results of the four-box model analysis of the XR data obtained from the PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer monolayer (Figure 4(B)): the best-fit values for the thicknesses (d_i), electron densities ($\rho_{e,i}$) and roughnesses (σ_i) of the constituent sublayers of the monolayer determined at four different area per brush chain (A) conditions (A = 2000, 1500, 1100, and 700 Å²). As can be deduced from Equation S30, 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.

| A (Å ²) | $d_1(\text{\AA})$ | $d_2(\text{\AA})$ | $d_{3}(\text{\AA})$ | $d_4(\text{\AA})$ | $ ho_{e,1'} ho_{e,water,}$ | $ ho_{e,2'} ho_{e,water,}$ | $ ho_{e,3}/ ho_{e,water,}$ | $ ho_{e,4'} ho_{e,water,}$ | $\sigma_{I}(\text{\AA})$ | $\sigma_2(\text{\AA})$ | $\sigma_3(\text{\AA})$ | $\sigma_4(\text{\AA})$ | $\sigma_5(\text{\AA})$ |
|---------------------|-------------------|-------------------|---------------------|-------------------|----------------------------|----------------------------|----------------------------|----------------------------|--------------------------|------------------------|------------------------|------------------------|------------------------|
| 2000 | 4.692 | 6.345 | 9.174 | 8.061 | 1.1883 | 1.3324 | 0.9292 | 1.0627 | 6.554 | 3.007 | 2.901 | 4.508 | 2.929 |
| 2000 | 4.305 | 7.716 | 11.185 | 5.917 | 1.1741 | 1.3359 | 0.9179 | 1.1434 | 6.914 | 3.856 | 2.669 | 6.796 | 3.699 |
| 1500 | 4.288 | 9.012 | 9.244 | 11.652 | 1.1216 | 1.3667 | 0.9178 | 1.0693 | 7.466 | 1.722 | 3.351 | 3.953 | 5.066 |
| 1500 | 5.392 | 8.093 | 11.019 | 11.338 | 1.1589 | 1.3913 | 0.9600 | 1.0632 | 7.551 | 2.070 | 2.896 | 1.939 | 3.841 |
| 1500 | 6.704 | 6.649 | 9.832 | 11.441 | 1.1879 | 1.4110 | 0.8914 | 1.0671 | 7.010 | 1.660 | 4.020 | 2.312 | 2.484 |
| 1100 | 4.941 | 9.989 | 14.920 | 15.560 | 1.0808 | 1.4602 | 0.9332 | 1.0312 | 10.663 | 2.195 | 3.575 | 4.634 | 4.028 |
| 1100 | 3.916 | 10.285 | 16.005 | 14.824 | 1.0362 | 1.4727 | 0.9692 | 1.0319 | 11.009 | 2.361 | 3.604 | 3.953 | 4.241 |
| 700 | 8.801 | 9.928 | 15.202 | 19.789 | 1.0881 | 1.4328 | 0.8766 | 1.0339 | 10.662 | 2.275 | 3.875 | 5.664 | 5.051 |
| 700 | 8.679 | 9.874 | 16.575 | 17.550 | 1.0563 | 1.4643 | 0.9000 | 1.0430 | 10.845 | 2.584 | 4.067 | 5.465 | 5.489 |

Figure S1. (A) Polymer volume fractions, $\phi(z)$, estimated by the SCF theory as functions of distance z from the grafting surface for the PEO (solid curves) and PDMAEMA (dotted curves) chains in a 1:1 mixed PEO and PDMAEMA brush system (i.e., $x_{PEO} = 0.5$) that is assumed to exist in a laterally homogeneous state. All polymers are assumed to be monodisperse. The molecular weight values used are DP = 113 for PEO and DP = 118 for PDMAEMA. The PEO has a Kuhn monomer length of b = 5.93 Å, a monomer volume of v = 59.3 Å³, and a Flory-Huggins interaction parameter in water of $\chi_{PEO-water} = 0.7$. The PDMAEMA has a Kuhn monomer length of b = 6.03 Å, a monomer volume of v = 225.0 Å³, a Flory-Huggins interaction parameter in water of $\chi_{PDMAEMA-water} = 1.5$, and an intrinsic pK_b° value of 8.4 in its monomeric form in water. Water has a molecular volume of v = 29.9 Å³. We assume that the water solvent has an ionic strength of 0.0182 mM NaCl equivalent and a pH of 7.25. The value of $\chi_{PEO-PDMAEMA}$ is assumed to be 0.75. (B) Brush heights (H_{PEO} and $H_{PDMAEMA}$) estimated from the results shown in (A) as a function of area per brush chain (A) for the PEO (black line) and PDMAEMA (red line) chains in the mixed brush system described in (A). These results demonstrate that when the grafted PEO and PDMAEMA chains are forced to be in close proximity, the two chain types will be vertically microphaseseparated even when the polymer grafting density is relatively low (e.g., at $A = 2000 \text{ Å}^2$ per brush chain), and the height ratio between the PEO and PDMAEMA chains in this hypothetical laterally mixed situation (hypothetical in the sense that such state is thermodynamically unstable as will be demonstrated in (C)), $H_{PDMAEMA}/H_{PEO}$, is estimated to be significantly greater than the height ratio estimated for the onecomponent brushes; see Figure 3(B). For instance, for the mixed brush system, $H_{PDMAEMA}/H_{PEO} = 2.8$ at A = 1500 Å² per brush chain, and $H_{PDMAEMA}/H_{PEO}$ = 3.3 at A = 1100 Å² per brush chain, whereas the values of the height ratio ($H_{PDMAEMA}/H_{PEO}$) between the corresponding one-component PEO (DP = 113) and PDMAEMA (DP = 118) brushes are estimated to be about 1.5 at A = 1500 Å² per brush chain and 1.7 at $A = 1100 \text{ Å}^2$ per brush chain (Figure 3(B)). (C) Representative plots of free energy of mixing (ΔF_{mix}) calculated using the SCF theory for the mixed PEO and PDMAEMA brush system as a function of PEO chain composition (x_{PEO}) for four different values of the area per brush chain (A = 2000, 1500, 1100 and 700 $Å^2$ from top to bottom), showing the change in miscibility of the two brush types with changing polymer grafting density. All parameters are the same as in (A).



(A)





Figure S2. Examples of high- q_z reflectivity ($R(q_z)$) scans with varying sample height from (**A**) a clean (dust-free) uniform region versus (**B**) a contaminated non-flat region in a PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymer monolayer sample at $A = 700 \text{ Å}^2$ per brush chain. For these tests, the q_z value was fixed at 0.2 Å⁻¹.

(A)





Figure S3. Normalized overall electron density profiles $(\rho_e(z)/\rho_{e,water,\infty})$ obtained from the box-model analysis of the XR data for the PEO₁₁₃-PnBA₁₀₀ diblock copolymer monolayer at four different area per brush chain (*A*) conditions: *A* = 2000 (black), 1500 (red), 1100 (orange), and 700 (blue) Å².



Figure S4. Normalized overall electron density profiles $(\rho_e(z)/\rho_{e,water,\infty})$ obtained from the box-model analysis of the XR data for the PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymer monolayer at four different area per brush chain (*A*) conditions: *A* = 2000 (black), 1500 (red), 1100 (orange), and 700 (blue) Å².



Figure S5. Normalized overall electron density profiles $(\rho_e(z)/\rho_{e,water,\infty})$ obtained from the box-model analysis of the XR data for the mixed PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymer monolayer at four different area per brush chain (*A*) conditions: A = 2000 (black), 1500 (red), 1100 (orange), and 700 (blue) Å².



Figure S6. Normalized overall electron density profiles $(\rho_e(z)/\rho_{e,water,\infty})$ obtained from the box-model analysis of the XR data for the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ triblock copolymer monolayer at four different area per brush chain (*A*) conditions: *A* = 1500 (black), 1100 (red), 700 (orange), and 350 (blue) Å².



Figure S7. Normalized overall electron density profiles $(\rho_e(z)/\rho_{e,water,\infty})$ obtained from the box-model analysis of the XR data for the mixed PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer monolayer at four different area per brush chain (*A*) conditions: *A* = 1500 (black), 1100 (red), 700 (orange), and 350 (blue) Å².



Figure S8. Normalized overall electron density profiles $(\rho_e(z)/\rho_{e,water,\infty})$ obtained from the box-model analysis of the XR data for the PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer monolayer at four different area per brush chain (*A*) conditions: *A* = 1500 (black), 1100 (red), 700 (orange), and 350 (blue) Å².



Figure S9. Surface pressure (II) versus area per PnBA monomer (α) isotherms for air–water interfacial monolayers of PnBA₁₀₀ (black), PEO₁₁₃-PnBA₁₀₀ (blue), PDMAEMA₂₀₀-PnBA₁₀₃ (orange), and an equimolar mixture of the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymers (green).



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