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

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Abstract

We studied mixed poly(ethylene oxide) (PEO) and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) brushes. The question we attempted to answer was: When the chain grafting points are laterally mobile, how will this lateral mobility influence the structure and phase behavior of the mixed brush? Three different model mixed PEO/PDMAEMA brush systems were prepared: (1) a *laterally-mobile* mixed brush by spreading onto the air-water interface a mixture of poly(ethylene oxide)-poly(*n*-butyl acrylate) (PEO-PnBA) and poly(2-(dimethylamino)ethyl methacrylate)-poly(*n*-butyl acrylate) (PDMAEMA-PnBA) diblock copolymers (the specific diblock copolymers used will be denoted as PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀, where the subscripts refer to the number-average degrees of polymerization of the individual blocks), (2) a *mobility-restricted* (inseparable) version of the above mixed brush prepared using a PEO-PnBA-PDMAEMA triblock copolymer (denoted as PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀) having respective brush molecular weights matched to those of the diblock copolymers, and (3) a different *laterally-mobile* mixed PEO and PDMAEMA brush prepared from a PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer combination, which represents a further more height-mismatched mixed brush situation than described in (1). These three mixed brush systems were investigated by surface pressure-area isotherm and X-ray (XR) reflectivity measurements. These experimental data were analyzed within the theoretical framework of a continuum self-consistent field (SCF) polymer brush model. The combined experimental and theoretical results suggest that the mobile mixed brush derived using the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ combination (i.e., Mixed Brush System #1) undergoes a lateral macroscopic phase separation at high chain grafting densities, whereas the more height-mismatched system (System #3) is only microscopically phase separated under comparable brush density conditions even

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Electronic Supplementary Information (ESI) Available: The numerical SCF theory (Section S1); the procedures for the XR data normalization and analysis (Section S2); box-model analysis results for the XR data (Tables S1 through S6); plots of polymer volume fractions $\phi(z)$ and brush heights (H_{PEO} and $H_{PDMAEMA}$) estimated by the SCF theory for the PEO and PDMAEMA brush chains in the hypothetical laterally mixed state, and representative free energy of mixing (F_{mix}) vs. chain composition (x_{PEO}) plots for the mixed PEO ($DP = 113$) and PDMAEMA ($DP = 118$) brush (Figure S1); sample high- q_z reflectivity ($R(q_z)$) vs. sample height scans from the PDMAEMA₁₁₈-PnBA₁₀₀ monolayer (Figure S2); normalized overall electron density profiles ($\rho_e(z)/\rho_{e,water,\infty}$) obtained from the box-model analysis of the XR data shown in Figures 2 and 4 (Figures S3 – S8); surface pressure (Π) vs. area per PnBA monomer (α) isotherms for PDMAEMA₂₀₀-PnBA₁₀₃, and for the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ mixture (Figure S9).

though the lateral mobility of the grafted chains is unrestricted. The macroscopic phase separation observed in the laterally-mobile mixed brush system is in contrast to the microphase separation behavior commonly observed in two-dimensional laterally-mobile charged small molecule mixtures. Further study is needed to determine the detailed morphologies of the macro and microphase-separated mixed PEO/PDMAEMA brushes.

1. Introduction

When polymer or polyelectrolyte chains are end-grafted to a non-penetrable interface and the grafting density is high enough so that the mean separation between grafting points is less than the coil dimension of the chains in the unbound state, the chains are stretched away from their unperturbed dimension into a “brush” configuration because of the osmotic and/or electrostatic repulsion between monomers. The chain conformational entropy, however, disfavors the stretched state, and the balance between these two opposing forces determines the conformation of the brush.

One-component brushes of neutral polymers^{1–9} and charged polyelectrolytes^{10–23} have been studied extensively. More recently, mixed brushes containing (at least) two chemically distinct polymers have attracted attention; see References^{24–26} for recent reviews. Two commonly studied examples of mixed brushes are those composed of either two neutral chain types^{27–33} or two oppositely charged chain types.^{20, 34–36} By using these mixed brushes, it is possible to create adaptable surfaces that change properties in response to environmental stimuli such as variation of solvent quality^{31, 37, 38} or pH.^{20, 35, 39}

Most previous studies have concerned mixed brushes with fixed grafting points. When the component polymers are mutually immiscible, these immobile mixed brushes exhibit unique molecular-scale (“microscopic”) phase separations along directions both parallel and perpendicular to the grafting surface.^{28–32, 40–44} However, in many common situations, the grafted chains of a polymer brush have lateral mobility. An important example is the corona brushes of micelles (or vesicles) formed by block copolymers.^{3, 45–47} The hydrated portions of the insoluble air-water interfacial monolayers of amphiphilic block copolymers are another important example of laterally-mobile polymer brushes. In laterally-mobile mixed brushes, the phase separation can, in principle, occur on macroscopic length scales.

However, one cannot also ignore the possibility of microphase separation in laterally-mobile mixed brushes. In particular, when a mixed brush is composed of charged polymers, macroscopic segregation is expected to be resisted by the long-range repulsion between like-charged chains, and as a result, phase separation may lead to localized segregation of the brush layer. In fact, the formation of microscopic phase-separated structures has been observed in various small molecule mixtures containing charged and non-charged species in two-dimensional space; examples include cell membranes constituted of mixed lipids with associated proteins and carbohydrates,⁴⁸ mixed assemblies of oppositely charged peptide amphiphilics,^{49–51} and two-dimensional electronic systems composed of coexisting conductive and insulating phases.^{52, 53} It has been predicted that in these systems, phase separation can result in the formation of microscopic phase structures (such as islands, stripes, or two-dimensional bicontinuous microemulsion-like domains) with characteristic

sizes that are determined by the interplay between the incompatibility and the like-charge repulsion.⁵⁰ Therefore, it would not be unreasonable to expect a similar behavior for mixed brushes containing end-mobile polyelectrolyte chains.

Interestingly, however, it has also been reported that even in non-charged two-dimensional mixtures, microphase separation is still possible if the constituent molecules have sufficient conformational degrees of freedom;⁵⁴ in binary mixtures of small molecule ligands confined on solid surfaces, microphase separation occurs when the sizes of the two ligands are significantly different, whereas phase separation occurs on macroscopic scales if the two ligands have comparable lengths. In the latter (size-mismatched) situation, the bulk phase separation is driven by the minimization of interfacial energy at the interface between the two phases; however, when the two ligands are unequally sized, this tendency is counterbalanced by the conformational entropy increase associated with the creation of more phase interfaces (because the interfaces allow greater conformational freedom for the ligand molecules), and this competition leads to microphase separation.⁵⁴ This conformational entropy effect is, in fact, expected to be even greater for polymeric mixtures. A recent theoretical study, indeed, predicts rich microphase separation behavior for laterally-mobile mixed non-charged polymer brushes.⁵⁵ To date, however, the problem of under what conditions microphase separation would be favored against macrophase separation (and vice versa) in end-mobile mixed brushes containing charged polyelectrolyte components remains unexplored. The present study attempts to initiate exploration of this question.

For this study, we used a model mixed polymer brush system composed of laterally-mobile, neutral polymer and weak polyelectrolyte chains that are mutually incompatible; the neutral polymer and polyelectrolyte brush components used were poly(ethylene oxide) (PEO) and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA), respectively. Specifically, a laterally-mobile mixed PEO and PDMAEMA brush was prepared by spreading a mixture of two diblock copolymers, poly(ethylene oxide)-poly(*n*-butyl acrylate) (PEO-PnBA) and poly(2-(dimethylamino)ethyl methacrylate)-poly(*n*-butyl acrylate) (PDMAEMA-PnBA), onto the air-water interface. Here, PnBA was used as the common hydrophobic block for these copolymers, because the PnBA polymer forms a flat, single monomer-thick, continuous film (free of bare areas) at the air-water interface,⁵⁶ and also the grafted PEO and PDMAEMA chains do not have any tendency to adsorb to the surface of the anchoring domain formed by PnBA,^{57, 58} which makes the PEO-PnBA and PDMAEMA-PnBA block copolymers uniquely suited for preparation of model non-adsorbing PEO/PDMAEMA brush systems. A laterally-mobile mixed PEO and PDMAEMA brush was prepared from a mixture of PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymers, where the subscripts refer to the number-average degrees of polymerization of the individual blocks; note that, as will be analyzed, in this case the heights of the PEO and PDMAEMA brushes are estimated to be (slightly) mismatched (that is, they differ by a factor less than about two). Another mixed brush sample was prepared using a PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock combination, which represents an even more height-mismatched situation than described above. Also, a mobility-restricted (inseparable) version of the slightly height-mismatched mixed PEO/PDMAEMA brush was prepared using a triblock copolymer (PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀) that shares the identical respective

numbers of EO and DMAEMA repeats with the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymers. These three different mixed PEO/PDMAEMA brush systems were studied using combined experimental techniques of surface pressure-area isotherm and X-ray reflectivity measurements. These experimental investigations were also complemented by self-consistent field (SCF) theoretical studies to establish a consistent and theoretically sound understanding of the experimental results. The results suggest that the laterally-mobile mixed PEO and PDMAEMA brush undergoes a lateral macroscopic phase separation at high chain grafting densities when the heights for the two chain types are not too mismatched, whereas the mobile mixed brush system is only microscopically phase separated under comparable brush density conditions when the two chain types are significantly mismatched in their heights (Scheme 1).

2. Experimental Procedures

Polymer samples

The PnBA₁₀₀ homopolymer, PEO₁₁₃-PnBA₁₀₀, PDMAEMA₁₁₈-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer, and PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ triblock copolymer samples used in this study were synthesized and characterized as described in our previous publications;^{59–62} the subscript numbers represent the number-average degree of polymerization (DP_n) values for the respective component blocks determined by ¹H NMR. The overall molecular weight polydispersity indices were, respectively, 1.12, 1.28, 1.39, 1.36 and 1.32 (determined by gel permeation chromatography (GPC) using a molecular weight calibration based on polystyrene standards).

Surface pressure-area isotherm measurements

Surface pressure-area isotherms were collected using a KSV 5000 Langmuir trough (15.0 cm × 51.0 cm × 1.0 cm) within a plexiglass chamber. The hydrophobic trough and hydrophilic symmetric moving barriers were cleaned by repeated rinsing with ethanol followed by deionized water. The surface pressure was measured by the Wilhelmy method using a platinum plate, located equidistant from each barrier, which was cleaned by rinsing with ethanol and water and then flamed. Deionized Millipore water (18 MΩ·cm resistivity) was used as the substrate, the surface of which was cleaned via aspiration prior to spreading. The cleanliness of the surface and probe were checked by compressing the water surface at 3 mm/min and monitoring the surface pressure. If total change in the pressure was greater than 0.2 mN/m, the surface and probe were recleaned and measurement retaken until the surface pressure change was below this threshold. Polymer solutions in chloroform were prepared in clean, dust-free glass vials. These vials were tightly sealed with Parafilm® and stored at –20 °C prior to use. For a measurement, a designated quantity of the polymer solution was spread dropwise on the water surface using a Hamilton microsyringe. The surface pressure was monitored after spreading until it was stabilized to a constant value, typically 3 – 4 hours. The isotherm was then recorded while compressing the barriers at 3 mm/min. All isotherm data presented in this paper were reproducible for independent repeated trials to within a few percent variation in the surface pressure or mean molecular area values.

X-ray reflectivity (XR) experiments

The polymer monolayers at the air-water interface were investigated by using the X-ray reflectivity (XR) technique. Experiments were conducted using the liquid surface spectrometer at the ChemMatCARS synchrotron facility (Sector 15) at the Advanced Photon Source of Argonne National Laboratory.⁶³ The specular reflectivities were measured using an in-plane polarized incident X-ray beam at a wavelength (λ) of 1.24 Å. The reflected intensities were measured in the range of out-of-plane momentum transfer vector (q_z) from 0.016 Å⁻¹ to 0.700 Å⁻¹ (the momentum transfer vector is related to the angle of reflection (θ) by $q_z = (4\pi/\lambda)\sin\theta$), which gives rise to a spatial resolution ($\approx \pi/q_{z,max}$)⁶⁴ of about 4.5 Å. During measurements, the monolayers were kept in a humidified helium atmosphere. All measurements were conducted at room temperature. The exposure of an area of the monolayer sample to the X-ray radiation was, in all experiments, kept below a level of total 1.5×10^{13} photons per mm², which is well within the range that is safe against X-ray damage for an organic monolayer at the air-water interface.⁶⁵

3. Results and Discussion

Surface pressure-area isotherms

Five different insoluble air-water monolayers were prepared from: (1) PnBA₁₀₀; (2) PEO₁₁₃-PnBA₁₀₀; (3) PDMAEMA₁₁₈-PnBA₁₀₀; (4) an equimolar mixture of the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock polymers (premixed before spreading onto the water surface); (5) a triblock copolymer PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ (here the subscripts denote the number-average degrees of polymerization of the respective polymer segments). The surface pressure-area isotherms of these monolayers were measured during monolayer compression using the Langmuir film balance technique. Figure 1(A) displays the results from these measurements in plots of monolayer surface pressure (Π) vs. area per hydrophobic (i.e., PnBA) monomer (α). As discussed in detail in our previous publication,⁵⁶ the sharp plateau transition in the isotherm of the PnBA homopolymer (black curve) at an area per PnBA monomer of $\alpha_o \approx 21.6$ Å² is due to the formation of a flat (i.e., laterally uniform) single-monomer-thick continuous film of PnBA that is free of voids at that polymer surface concentration. Our previous studies have also demonstrated that, thanks to this property of PnBA, at areas per PnBA monomer less than α_o , the monolayer domain formed at the air-water interface by PnBA can be used as end-grafting sites for PEO or PDMAEMA chains for preparation of model *non-adsorbing* PEO^{58, 66} or PDMAEMA^{57, 62} brush systems. As shown in Figure 1(A), the monolayers of the block copolymers also exhibit a similar transition in their isotherm curves, all at an essentially identical value of area per PnBA monomer ($\alpha_o = 21.4 \pm 0.5$ Å²), which indicates that this transition behavior of PnBA is unaffected, regardless of whether the PnBA segment is present as an isolated chain or in the form of a component block of a diblock or a triblock copolymer.

We note that the monolayer isotherms of PEO₁₁₃-PnBA₁₀₀ (blue curve), PDMAEMA₁₁₈-PnBA₁₀₀ (orange curve) and the 1:1 mixture of these two diblock copolymers (green curve) all show an identical value for the surface pressure at the full-coverage transition point ($\Pi_o = 23.5 \pm 0.2$ mN/m), and this transition point pressure of the diblock copolymers is significantly greater than that of the PnBA homopolymer (black curve, $\Pi_o = 21.6$ mN/m).

As has been verified in our previous experiments with PnBA,^{57, 62} the surface pressure at the transition point is equivalent to the surface tension change associated with the removal of the intervening polymer monolayer from the air-water interface (i.e., $\Pi_o = \gamma_{air-water} - \gamma_{polymer-air} - \gamma_{polymer-water}$). On the basis of this concept, the higher transition pressure observed for the diblock monolayers relative to the transition pressure of PnBA (i.e., $\Pi_{o,PEO-PnBA} = \Pi_{o,PDMAEMA-PnBA} > \Pi_{o,PnBA}$) is considered to be due to a decrease in the polymer-water interfacial tension ($\gamma_{polymer-water}$) caused by the presence of the end-grafted hydrophilic PEO/PDMAEMA chains at the PnBA-water interface; hereafter, this effect will be called the “(PnBA-water) interface modification” effect. We believe that at the transition point ($\alpha = \alpha_o$), the lateral osmotic repulsion between the PEO or PDMAEMA brush chains is negligible and does not contribute significantly to the increased surface pressure at the transition point, because at this condition the average interfacial area occupied by a PEO or PDMAEMA brush chain ($A_o \approx 2140 \text{ \AA}^2$) is estimated to be comparable to the πR_G^2 values for the PEO and PDMAEMA segments (that is, the grafted PEO or PDMAEMA chains are non-interacting or at most weakly interacting with one another); here, R_G is the radius of gyration of the PEO or PDMAEMA block in the three-dimensional random-walk configuration, and its values are approximately estimated to be 25.7 Å for the PEO segment and 27.3 Å for the PDMAEMA segment using relevant parameter values reported in References⁶⁷ and⁶², respectively (in the PDMAEMA case the electrostatic interactions are ignored for simplification). This notion that at near the transition point (i.e., at $\alpha \approx \alpha_o$) the brush chains contribute negligibly to the lateral surface pressure of the diblock monolayers is also supported by the fact that at the transition point ($\alpha = \alpha_o$) the PDMAEMA-PnBA monolayer exhibits the same surface pressure as does the PEO-PnBA monolayer even though the PDMAEMA segments are significantly charged at neutral pH conditions;⁶⁸ (as will be discussed in the second next paragraph below) the effect of this electrostatic repulsion between adjacent PDMAEMA chains becomes more clearly manifested in the $\alpha < \alpha_o$ region where the PDMAEMA-PnBA monolayer shows increasingly higher surface pressure than the PEO-PnBA monolayer with decreasing α . The transition point pressure of the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ triblock polymer (red curve, $\Pi_o \approx 26.5 \text{ mN/m}$) is even higher than that of the diblock copolymers ($\Pi_o \approx 23.7 \text{ mN/m}$). This is, we believe, mainly because the (PnBA-water) interface modification effect is much greater in the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ monolayer system; the PEO/PDMAEMA brush chain density per PnBA monomer is higher by a factor of 2.25 ($= 100/(89/2)$) for the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ monolayer than for the PEO₁₁₃-PnBA₁₀₀ or PDMAEMA₁₁₈-PnBA₁₀₀ monolayer. Also, in the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ case the normalized area per brush chain value, $A_o/\pi R_G^2 \approx 0.4$, is less than unity; thus, in this case, one might expect that in addition to the interface modification effect, the lateral (osmotic/electrostatic) repulsion between the brush chains makes an additional contribution to the overall surface pressure of the monolayer even at the full-coverage transition point. However, as will be shown in Figure 1(B), this contribution appears to be insignificant. We also note the observation that in the triblock case the slope change in the isotherm curve across the transition point is significantly smeared relative to what was observed with the diblock copolymers. Currently, it remains a question what contributes to this difference.

The detailed shapes of the isotherm curves are different from system to system, depending on the chemistry of the hydrophilic (i.e., the brush-forming) polymer component of the block copolymer. Throughout the incomplete surface coverage regime (i.e., when $\alpha > \alpha_o$), the PEO-PnBA monolayer (isotherm shown with a blue curve in Figure 1(A)) exhibits significantly higher surface pressures than the homopolymer monolayer (black curve) because of the strong adsorption of the PEO segments to the areas of the water surface that have not been coated with the PnBA segments.^{58, 66} However, in this same surface coverage regime, the surface pressure profile of the PDMAEMA-PnBA copolymer (orange curve) traces very closely that of the PnBA homopolymer (black curve), because, unlike PEO, PDMAEMA does not have a tendency to adsorb to the air-water interface.^{57, 62} The 1:1 mixture of PEO-PnBA and PDMAEMA-PnBA shows surface pressure behavior (green curve) that is exactly intermediate between the two parent systems.

In the area per PnBA monomer range $\alpha < \alpha_o$ where the water surface is fully covered with PnBA, the PEO-PnBA monolayer becomes increasingly resistant to area compression with decreasing area because of increasing lateral steric repulsion between the PEO brush chains (blue curve). As has been mentioned above, this trend is much steeper for PDMAEMA-PnBA because of the additional electrostatic repulsive forces between adjacent PDMAEMA chains (orange curve). Again in this regime, the mixed monolayer behaves intermediately to the two parent systems (green curve).

In order to quantitatively compare the lateral brush pressure behavior between the two different types of mixed PEO and PDMAEMA brush systems (i.e., the laterally-mobile (macroscopically phase-separable) mixed brush prepared using the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ mixture, and the mobility-restricted (inseparable) mixed brush prepared from the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ triblock copolymer), the original isotherm data shown in Figure 1(A) were further analyzed as follows. For this analysis, we hypothesized that in the full surface coverage regime ($\alpha < \alpha_o$) the measured overall surface pressure of the block copolymer monolayer at a given value of α ($\Pi_{block\ copolymer}(\alpha)$) is the sum of two contributions: (1) the surface pressure due to the reduction of the interfacial tension due to the presence of the polymer monolayer ($\Pi_{interfacial\ tension}(\alpha)$), which, as discussed earlier, is equal to $\gamma_{air-water}(\alpha) - \gamma_{polymer-air}(\alpha) - \gamma_{polymer-water}(\alpha)$, and (2) the surface pressure due to the lateral interaction of the brush chains ($\Pi_{brush}(\alpha)$) (therefore $\Pi_{brush}(\alpha)$ can be computed by subtracting $\Pi_{interfacial\ tension}(\alpha)$ from $\Pi_{block\ copolymer}(\alpha)$). So the first step of this analysis was to calculate the $\Pi_{interfacial\ tension}(\alpha)$ profile. For the cases involving the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ polymers, this function was calculated by multiplying the surface pressure values of the PnBA homopolymer isotherm with a constant factor ($= 23.5/21.6$) to match its transition point pressure (originally $\Pi_o \approx 21.6$ mN/m) to that of the *diblock* monolayers ($\Pi_o \approx 23.5$ mN/m); this rescaling is necessary because of the presence of the “interface modification” effect in the diblock (and triblock) monolayer systems (see the discussion presented earlier). In the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ case, the PnBA homopolymer curve was shifted upward by a greater amount, i.e., by a factor of 2.44 ($= (23.5/21.6) \times (100/(89/2))$), in order to take into account the higher density of brush grafting points per PnBA monomer. Once these respective rescaled Π vs. α profiles of the PnBA homopolymer $\Pi_{PnBA(rescaled)}(\alpha)$ ($= \Pi_{interfacial\ tension}(\alpha)$) are

obtained, the brush pressure profiles for the diblock mixture and triblock copolymer systems ($\Pi_{brush}(\alpha)$) can be computed by subtracting $\Pi_{PnBA(rescaled)}(\alpha)$ from the original Π - α isotherm of the PEO-PnBA/PDMAEMA-PnBA mixture or that of the PEO-PnBA-PDMAEMA triblock copolymer ($\Pi_{block\ copolymer}(\alpha)$), that is, by the relation, $\Pi_{brush}(\alpha) = \Pi_{block\ copolymer}(\alpha) - \Pi_{interfacial\ tension}(\alpha)$ (or if one writes in more specific subscript notations, $\Pi_{PEO/PDMAEMA(diblock)}(\alpha) = \Pi_{PEO-PnBA/PDMAEMA-PnBA}(\alpha) - \Pi_{PnBA(rescaled)}(\alpha)$, and $\Pi_{PEO/PDMAEMA(triblock)}(\alpha) = \Pi_{PEO-PnBA-PDMAEMA}(\alpha) - \Pi_{PnBA(rescaled)}(\alpha)$ for the diblock mixture and triblock cases, respectively). Lastly, after this subtraction process, the x -axis variable was transformed to area per brush chain (A) from area per PnBA monomer (α) for direct comparison between the diblock vs. triblock results; the area per brush chain variable was calculated by $A = \alpha DP_{PnBA}/\beta$, where $\beta = 1$ for the diblock system, but $\beta = 2$ in the triblock case because each triblock chain contains two separate (PEO and PDMAEMA) brush strands. The resulting Π vs. A profiles of the laterally-mobile mixed PEO/PDMAEMA brush and of the mobility-restricted mixed brush (which will be denoted, respectively, as $\Pi_{PEO/PDMAEMA(diblock)}(A)$ and $\Pi_{PEO/PDMAEMA(triblock)}(A)$) are presented in Figure 1(B). Also displayed in the same figure for comparison are the brush pressure vs. area profiles of the corresponding one-component brushes (i.e., $\Pi_{PEO}(A)$ and $\Pi_{PDMAEMA}(A)$). As can be seen in the figure, both the mixed brush pressure profiles, $\Pi_{PEO/PDMAEMA(diblock)}(A)$ (solid green curve) and $\Pi_{PEO/PDMAEMA(triblock)}(A)$ (red curve), lie between the two pure-component curves, $\Pi_{PEO}(A)$ (blue curve) and $\Pi_{PDMAEMA}(A)$ (orange curve). We first note that the non-macroscopically-phase-separable mixed PEO/PDMAEMA brush system (where the PEO and PDMAEMA chains are chemically constrained to be located in close contact with each other) shows comparable lateral pressures to the macrophase-separable analogue in the highly compressed region, i.e., at areas per brush chain less than about $700\ \text{\AA}^2$. Therefore, the Π - A data were insufficient to determine whether in the macroscopically phase-separable situation the PEO and PDMAEMA chains indeed exist in a macrophase-separated state. It should also be noted that regardless of whether the mixed brush system is macroscopically phase-separable or inseparable, its lateral pressure always lies below that of the single-component PDMAEMA brush, which, we believe, is due to the dilution of the repulsive electrostatic interactions between the charged PDMAEMA chains by the coexisting PEO chains in the mixed situation.⁶⁹ As will be discussed in the next subsection, these observations are in agreement with theoretical predictions.

Theoretical analysis

In order to validate the above interpretations, the brush pressure vs. area isotherm data were quantitatively compared to the predictions of a self-consistent field (SCF) polymer brush theory. The continuum SCF formalism used in this analysis has been described in detail in our previous publications;^{58, 70} a brief summary of the SCF equations used is presented in Section S1 of the Electronic Supplementary Information (ESI). Specifically, the following procedure was used for this analysis. First, the Flory-Huggins interaction parameter characterizing the interaction of PEO with water ($\chi_{PEO-water}$) was determined by fitting the SCF model to the $\Pi_{PEO}(A)$ data; the best-fit $\chi_{PEO-water}$ value was found to be 0.70, and the corresponding best-fit prediction of the SCF model is included in Figure 1(B) (closed blue squares); note for the values of the solvent and monomer volumes used in our calculation (i.e., $v_{water} = 29.9\ \text{\AA}^3$ and $v_{PEO} = 59.3\ \text{\AA}^3$), the theta-solvent condition corresponds to a

$\chi_{PEO-water}$ value of 0.686. A similar fitting analysis of the $\Pi_{PDMAEMA}(A)$ data led to an estimated value of 1.50 for $\chi_{PDMAEMA-water}$ (for the values of the solvent and monomer volumes used (i.e., $v_{water} = 29.9 \text{ \AA}^3$ and $v_{PDMAEMA} = 225.0 \text{ \AA}^3$), the chi parameter $\chi_{PDMAEMA-water}$ is equal to 1.439 at the theta condition); the fit result is also shown in Figure 1(B) (closed orange squares). As can be seen from the figure, in both the PEO and PDMAEMA brush cases, the excellent fit quality supports the reasonableness of the estimates of the chi parameters. These $\chi_{PEO-water}$ and $\chi_{PDMAEMA-water}$ values were then used in the analysis of the mixed brush results. We attempted to estimate the Flory-Huggins interaction parameter for the PEO-PDMAEMA pair ($\chi_{PEO-PDMAEMA}$) by fitting the inseparable mixed brush data (i.e., $\Pi_{PEO/PDMAEMA(triblock)}(A)$) with the SCF theory, under the assumption that the PEO and PDMAEMA segments are homogeneously distributed along the lateral direction. This lateral “mean-field” approximation, however, was found to be incapable of quantitatively describing the experimental $\Pi_{PEO/PDMAEMA(triblock)}(A)$ profile within the reasonable range of $\chi_{PEO-PDMAEMA}$ values (i.e., > 0); this discrepancy is likely due to the fact that the inseparably mixed PEO/PDMAEMA brush exists in a laterally microphase-separated structure (rather than in a laterally homogeneous state). We would also like to note that in our previous publications^{56, 57, 62} we have shown that in the full-coverage regime (i.e., once the PnBA chains completely cover the water surface in a uniform phase), the surface pressure becomes independent of PnBA molecular weight, because the surface pressure at that condition is simply equivalent to the surface tension change associated with the removal of the intervening polymer monolayer from the air-water interface (i.e., $\Pi_o = \gamma_{air-water} - \gamma_{polymer-air} - \gamma_{polymer-water}$); for this reason, we believe that the difference in the PnBA block size between the diblock and triblock copolymer materials used (i.e., $DP_{n,PnBA} \approx 100$ for the diblock copolymers used vs. $DP_{n,PnBA} \approx 90$ for the triblock copolymer used) cannot be the cause of this discrepancy between the experiment and calculation for the triblock copolymer brush pressure prediction.

Therefore, for the purpose of demonstrating the effect of macroscopic phase separation on the brush pressure-area profile of the mixed PEO/PDMAEMA brush system, we simply chose a reasonable estimate of 0.75 for $\chi_{PEO-PDMAEMA}$ that guarantees sufficient incompatibility between the PEO and PDMAEMA segments; as shown in Figure S1(A) of ESI, at this $\chi_{PEO-PDMAEMA}$ condition the two chain types undergo vertical microphase-segregation when they are forced to stay homogeneously mixed in the lateral direction. Using these values of the $\chi_{PEO-water}$, $\chi_{PDMAEMA-water}$ and $\chi_{PEO-PDMAEMA}$ parameters, we quantitatively modeled the Π vs. A profile of the laterally-mobile macroscopically phase-separable mixed PEO/PDMAEMA brush ($\Pi_{PEO/PDMAEMA(diblock)}(A)$) by the SCF equations without any further adjustable parameters. The goal was to theoretically examine whether or not a lateral macroscopic phase separation would produce any significant change in the surface pressure profile. For this purpose, the composition-dependent thermodynamic stability of the single-phase (mixed) states in this mixed brush system was analyzed for various area per brush chain conditions; the free energy change of mixing equation used in this calculation is given as Equation S22 in the ESI. As illustrated in Figure S1(C) of the ESI, in the range of area per brush chain investigated, the typical free energy of mixing vs. composition curve exhibits a local maximum at compositions not far from the 50:50 split, which suggests that at around 50:50 overall molar composition the mixed PEO/PDMAEMA

brush is thermodynamically unstable, and thus undergoes phase separation on a macroscopic scale because of the lateral mobility of the chains. For each different value of A , the overall free energy of the phase-separated system ($F_{\text{phase-separated}}(A)$) was computed by the common tangent construction on the free energy of mixing vs. composition curve. From these free energy values, the lateral pressure of the phase-separated PEO/PDMAEMA brush was estimated as a function of area per brush chain ($\Pi_{\text{phase-separated}}(A) = -F_{\text{phase-separated}}(A)/A$). The results of this calculation are presented in Figure 1(B). As can be seen from this figure, the theoretical values of the lateral pressure of the macrophase-separated brush mixture ($\Pi_{\text{phase-separated}}(A)$; shown in the figure as green points with dotted connection) are quite comparable to those representing a laterally homogeneous state ($\Pi_{\text{mixed}}(A) = -F(A)/A$ where $F(A)$ is calculated using Equation S18; red points with dotted line), which lends a possible explanation for the comparable brush chain lateral pressures exhibited between the mixed PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymer monolayer versus the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ triblock monolayer ($\Pi_{\text{PEO/PDMAEMA(diblock)}}(A) \approx \Pi_{\text{PEO/PDMAEMA(triblock)}}(A)$) if $\Pi_{\text{phase-separated}}(A)$ and $\Pi_{\text{mixed}}(A)$ are taken, respectively, as representations of $\Pi_{\text{PEO/PDMAEMA(diblock)}}(A)$ and $\Pi_{\text{PEO/PDMAEMA(triblock)}}(A)$; that is, even if in the laterally-mobile system the PEO and PDMAEMA brush chains are indeed macroscopically phase separated, that would not significantly influence the brush pressure-area profile of the system. **Macroscopic heterogeneities.** To experimentally examine the possibility of macroscopic phase separation of the laterally-mobile macrophase-separable mixed PEO and PDMAEMA brush, the lateral structural heterogeneity of this mixed brush sample was examined by X-ray reflectivity (XR) experiments. The XR profiles of the sample were measured in the (out-of-plane) momentum transfer vector (q_z) range from 0.016 to 0.700 Å⁻¹. In each XR run, a fresh area of the sample was exposed to the X-ray beam at the beginning, and at one point in the middle of the run, the sample was horizontally shifted by 2.0 mm in the direction (i.e., the x -direction) perpendicular to the X-ray beam axis (y -axis) to keep the exposure of the area of the sample to the X-ray radiation below a level of total 1.5×10^{13} photons per mm²; this radiation level is well within the range that is safe against X-ray damage for an organic monolayer at the air-water interface.⁶⁵ The measurements were performed at several different area per brush chain values. For each area per brush chain condition, the XR profiles were recorded from at least three different locations of the sample that are separated from one another by at least 6.0 mm along the x -direction; note that the x -dimension of the X-ray beam footprint on the liquid surface was 2.0 mm, and thus each run consumes a total area spanning a length of about 6.0 (= 2.0 + 2.0 + 2.0) mm in the x -direction because of the horizontal shift of the sample position during the run. Therefore, there was no overlap between the different areas probed by the X-ray beam. At each location probed, the absence of any impurities (e.g., dust particles) or surface non-uniformities (due to, for example, defects) was tested by performing a height scan at a fixed q_z value of 0.2 Å⁻¹ incidence, prior to the actual reflectivity scan over various scattering angles; as demonstrated in Figure S2, the height scan profile from a clean (dust-free), laterally-uniform monolayer region exhibits a square wave shape with a (nearly) flat top and steep rise and fall, whereas the surface height fluctuations due to contamination or defects give rise to a non-flat (modulating) pattern on the roof of the square wave-like height scan profile. We selected only these uniform monolayer areas for the actual reflectivity measurements so that any

variation in the reflectivity profile from one area to another within the same sample can be safely attributed to macroscopic heterogeneities in mixed brush composition. Using these same procedures, the lateral uniformity of the other types of brush systems (i.e., the respective one-component PEO and PDMAEMA brushes, and the inseparable mixed PEO/PDMAEMA brush) was also examined by X-ray reflectivity. As shown in Figures 2(A), 2(B) and 2(D), in these single-component and non-macrophase-separable binary brush systems, the XR profiles taken from different areas of the sample were reproducible within the bounds of small deviations, which suggests that these systems are indeed laterally molecularly homogeneous over macroscopic length scales. To the contrary, the macrophase-separable mixed PEO and PDMAEMA brush exhibited significant area-to-area variations in XR characteristics (Figure 2(C)), which suggests that this system exists in a macrophase-separated state.

Discussion

In this subsection, we will comment on an issue associated with the observed macrophase separation behavior of the laterally-mobile mixed brush system: Why is this macrophase separation process preferred over microscopic phase separation which has been more commonly observed in two-dimensional mixtures of small molecular compounds?

To begin to discuss this question, we first note the notion that a binary mixture of charged and non-charged species confined in two-dimensional space can exhibit unique phase separation behavior which differs qualitatively from those of non-charged mixtures. The explanation is as follows. The chemical dissimilarity between the two species drives macroscopic phase separation. However, the macroscopic segregation is hindered by the long-range electrostatic repulsion between the like-charged components. A competition between these two opposing effects can lead to formation of microscopic phase-separated structures. This long-range-hindered phase separation has been suggested as a mechanism responsible for the formation of microscopic patterns observed in various two-dimensional mixed systems, such as biological membranes (i.e., “lipid rafts”),⁴⁸ assemblies of mixed peptide amphiphiles,⁵⁰ and bilayer electronic systems (i.e., “electronic microemulsion phases”).⁵³ Therefore, the macrophase separation behavior observed with the laterally-mobile mixed PEO and PDMAEMA brush system appears to challenge our current understanding of this widely-observed phenomenon, generally termed as “frustrated phase separation”.

We find that the results of our present study in fact align better with a different line of thought proposed by Glotzer, Stellacci, and coworkers.⁵⁴ These authors showed that a laterally-mobile mixture of two immiscible ligands on a surface undergoes macroscopic phase separation in the two-dimensional space if the two ligands are of comparable length. However, the mixed system favors a microphase-separated state when the sizes of the two ligands are significantly different. In the size-mismatched situation, microphase separation is preferred because of the gain in chain conformational entropy at phase interfaces; however, when the two ligands have comparable sizes, the entropy gain becomes insufficient to compensate for the increased interfacial energy, and thus phase separation occurs on a macroscopic scale (Scheme 1). More recently, the same behavior has also been predicted for

polymeric brush mixtures.⁵⁵ In order to gauge the possible role that the size similarity (or difference) between the end-grafted PEO ($DP_n = 113$) and PDMAEMA ($DP_n = 118$) chains plays in their observed macrophase separation behavior, we first estimated the heights of the individual one-component PEO and PDMAEMA brushes under identical grafting density conditions using the SCF theoretical model and the best-fit interaction parameters obtained from the analysis of the pressure-area isotherm data (discussed in the “Theoretical analysis” subsection); we would like to note that the determination of the PEO and PDMAEMA brush heights from the experimental XR data presented in Figures 2(A) and 2(B) is not straightforward, if not impossible, because of the possible rarefaction of water inside the brush layer.⁶⁶ Figures 3(A) and 3(B), respectively, display the theoretically estimated values of the in-plane-averaged segment volume fractions of the PEO and PDMAEMA chains as functions of distance z from the grafting surface at various grafting density conditions, and the PEO and PDMAEMA brush heights (the root mean square averages of the individual segment positions) as functions of polymer grafting density; in the calculations, each respective brush system was assumed to be a one-component system composed solely of either of the two polymer types, and the PEO and PDMAEMA polymers were both assumed to be monodisperse in molecular weight. As shown in the figure, at $A = 1500$ (or 1100) $\text{\AA}^2$ per brush chain, for instance, the height ratio between the PEO ($DP = 113$) and PDMAEMA ($DP = 118$) brushes, $H_{PDMAEMA}/H_{PEO}$, was estimated to be about 1.5 (or 1.7), which is not equal to, but not much different either, from unity. These results seem to support that in this laterally-mobile mixed PEO/PDMAEMA brush system, the similarity in the heights of the PEO and PDMAEMA brush chains makes provision for macroscopic phase separation.

Therefore, to further experimentally test the above argument for validity, we prepared a more significantly height-mismatched version of the PEO and PDMAEMA mixed brush system using a 1:1 (by mole) mixture of PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymers, and examined the lateral heterogeneity (or uniformity) of this system by X-ray reflectivity (XR). The XR experiments were performed using the same protocol as described in the “Macroscopic heterogeneities” subsection. The sample was probed at several different area per brush chain conditions. For each area per chain condition, the XR profiles were measured from at least three different locations of the sample. As displayed in Figure 4(A), in this sample we did not observe any detectable area-to-area variations in the XR characteristics, which suggests that contrary to the slightly height-mismatched situation, this more significantly mismatched system is indeed laterally homogeneous over macroscopic length scales. This result supports the idea that the relative sizes of the component chains play an important role in determining the detailed mechanisms of the lateral phase separation (i.e., macroscopic vs. microscopic phase separation) in a laterally-mobile mixed brush system. Further study is required to determine the detailed phase-separated domain structures of the macro and microphase-separated mixed PEO/PDMAEMA brushes and also the detailed mechanisms (e.g., whether the macrophase separation involves a nucleation and growth or spinodal decomposition process) and kinetics (i.e., time scales) associated with these phase separation processes.

Given that we do not currently have sufficient information about the time scales of the macrophase separation processes, a reader might question whether the experimental

procedures used (in particular the 3 mm/min monolayer compression speed used) were appropriate for probing the macrophase separation transition. However, we would like to note that in a previous study of the phase behavior of bidisperse colloidal mixtures at the air-water interface, we have confirmed that under comparable compression speed conditions two-dimensional phase-separated domains of macroscopic size are easily achieved even though in these cases the monolayer systems were constituted of micrometer-sized silica colloids.⁷¹ Based on this previous data, we are certain that in the mixed brushes prepared using PEO-PnBA/PDMAEMA-PnBA block copolymers (these polymers are believed to have orders of magnitude higher lateral mobilities at the air-water interface than the silica microspheres), the lateral monolayer compression rate used (i.e., 3 mm/min) should provide sufficient time for the mixed brush system to undergo macroscopic phase separation. We plan to conduct an imaging study to investigate this issue in the future.

4. Conclusion

The *laterally-mobile* mixed PEO and PDMAEMA brush (prepared from a mixture of PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymers) shows comparable lateral brush pressures to the *mobility-restricted* (inseparable) version of the mixed brush (prepared using a triblock copolymer PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀) (Figure 1(B)); while the former system is macrophase-separable, in the latter case the chemical connectivity between the PEO and PDMAEMA blocks does not allow the two polymers to become macroscopically phase separated, but instead they are forced to stay close to each other either in a seemingly mixed state or in a state where the PEO and PDMAEMA segments are only locally (microscopically) segregated. The detailed analysis of this result based on the SCF polymer brush theory suggests that a lateral macroscopic phase separation would not produce any significant difference in the lateral pressure of the mixed brush layer. XR measurements on randomly selected regions of these mixed brush samples indicate that this *slightly height-mismatched laterally-mobile* mixed PEO ($DP_n = 113$) and PDMAEMA ($DP_n = 118$) brush is significantly laterally heterogeneous in structure (Figure 2(C)), indicating that this system is macrophase separated. In similar XR experiments conducted with the *more significantly height-mismatched laterally-mobile* mixed PEO and PDMAEMA brush sample (prepared using a PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer mixture), we did not detect any significant lateral structural heterogeneity even at high grafting density conditions (Figure 4(A)). Taken together, we conclude that the laterally-mobile immiscible mixed PEO/PDMAEMA brush undergoes a macroscopic phase separation at high chain grafting densities when the grafted PEO and PDMAEMA chains have comparable heights (i.e., when the height ratio, $H_{PDMAEMA}/H_{PEO}$, is of the order of unity), whereas the more significantly height-mismatched mixed PEO/PDMAEMA brush is only microscopically phase separated under comparable brush density conditions even though the PEO and PDMAEMA chains are laterally mobile. These results support the prediction that the conformational entropy associated with the arrangement of the chains near the phase interfaces indeed plays an important role in determining the phase-separated domain structures in immiscible mixed brushes composed of laterally-mobile chains.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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(A)

(B)

Figure 1.

(A) Surface pressure (Π) versus area per PnBA monomer (α) isotherms for air–water interfacial monolayers of PnBA₁₀₀ (black), PEO₁₁₃-PnBA₁₀₀ (blue), PDMAEMA₁₁₈-PnBA₁₀₀ (orange), an equimolar mixture of the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymers (green), and a triblock polymer PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ (red). (B) Lateral brush pressure (Π) versus area per brush chain (A) isotherms of the respective one-component PEO (blue) and PDMAEMA (orange) brushes, the laterally-mobile mixed PEO/PDMAEMA brush prepared using the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock mixture (green), and the mobility-restricted mixed brush prepared from the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ triblock copolymer (red). Solid lines represent estimates obtained from the experimental data shown in (A) using the procedure described in the “Surface pressure-area isotherms” subsection. Symbols with dotted lines represent the best fits of the SCF theoretical predictions to the experimental data (discussed in the “Theoretical analysis” subsection).

(A)

(B)

(C)

(D)

Figure 2.

(A) Normalized XR profiles ($R(q_z)/R_F(q_z)$) from the PEO₁₁₃-PnBA₁₀₀ diblock copolymer monolayer at four different area per brush chain (A) conditions: $A = 2000, 1500, 1100$ and 700 Å^2 from bottom to top. For clarity, the top three data sets were shifted upward by 3, 2 and 1 units from top to bottom, respectively. (B) Normalized XR profiles from the PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymer monolayer at $A = 2000, 1500, 1100$ and 700 Å^2 . (C) Normalized XR profiles from the mixed PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₁₁₈-PnBA₁₀₀ diblock copolymer monolayer at $A = 2000, 1500, 1100$ and 700 Å^2 . (D) Normalized XR profiles from the PEO₁₁₃-PnBA₈₉-PDMAEMA₁₂₀ triblock copolymer monolayer at $A = 1500, 1100, 700$ and 350 Å^2 . For each area per brush chain (A) condition, the XR profiles were obtained from at least two different, randomly-selected areas of the sample. Also shown for each set of XR data are the overall electron density profiles ($\rho_e(z)$) obtained from the box-model analysis of the XR data (plotted in a normalized form where the $\rho_e(z)$ quantities are referenced to the electron density of bulk water $\rho_{e,water,\infty}$). The corresponding best-fit XR profiles are shown as solid lines. The procedures for the

normalization and the box-model analysis of the XR data are described in Section S2 of the Electronic Supplementary Information (ESI). Also see Figures S3 – S6 for separate presentations of the electron density profiles obtained at different areas per brush chain.

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(A)

(B)

Figure 3.

(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 (solid curves) of length $DP = 113$ with Kuhn length $b = 5.93 \text{ \AA}$, monomer volume $v = 59.3 \text{ \AA}^3$ and Flory-Huggins interaction parameter in water $\chi_{PEO-water} = 0.70$, and for monodisperse end-grafted PDMAEMA chains (dotted curves) of length $DP = 118$ with Kuhn length $b = 6.03 \text{ \AA}$, monomer volume $v = 225.0 \text{ \AA}^3$, Flory-Huggins interaction parameter $\chi_{PDMAEMA-water} = 1.50$ and intrinsic $pK_b^\circ = 8.4$ (in its monomeric form) in an aqueous solvent with an ionic strength of 0.0182 mM NaCl equivalent and $\text{pH } 7.25$. The water molecular volume is assumed to be $v = 29.9 \text{ \AA}^3$. (B) Brush heights (H_{PEO} and $H_{PDMAEMA}$) estimated from the results shown in (A) as a function of area per brush chain (A), respectively, for the one-component PEO (black line) and PDMAEMA (red line) brush chains described in (A).

(A)

(B)

Figure 4.

(A) Normalized XR profiles ($R(q_z)/R_F(q_z)$) from the mixed PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer monolayer at four different area per brush chain (A) conditions: $A = 2000, 1500, 1100$ and $700 \text{ \AA}^2$ from bottom to top. For clarity, the top three data sets were shifted upward by 3, 2 and 1 units from top to bottom, respectively. Also shown for comparison in (B) are normalized XR profiles from the PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer monolayer at $A = 2000, 1500, 1100$ and $700 \text{ \AA}^2$. For each area per brush chain (A) condition, the XR profiles were obtained from at least two different, randomly-selected areas of the sample. Also shown for each set of XR data are the overall electron density profiles ($\rho_e(z)$) obtained from the box-model analysis of the XR data (plotted in a normalized form where the $\rho_e(z)$ quantities are referenced to the electron density of bulk water $\rho_{e,water,\infty}$). The corresponding best-fit XR profiles are shown as solid lines. The procedures for the normalization and the box-model analysis of the XR data are described in Section S2 of the Electronic Supplementary Information (ESI). Also see Figures S7 and S8 for separate presentations of the electron density profiles obtained at

different areas per brush chain. Surface pressure (Π) versus area per PnBA monomer (α) isotherms for the PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer and for the PEO₁₁₃-PnBA₁₀₀ and PDMAEMA₂₀₀-PnBA₁₀₃ diblock copolymer mixture are also presented in Figure S9 of the ESI.

(A) **(B)** **Scheme 1.**

Schematic illustrations of **(A)** the macrophase-separated structure of a laterally-mobile mixed PEO (blue) and PDMAEMA (red) brush (macrophase separation can occur even when the heights of the grafted PEO and PDMAEMA chains are mismatched, that is, if the height mismatch is not too large), and **(B)** the microphase-separated structure of a more significantly height-mismatched laterally-mobile mixed PEO (blue) and PDMAEMA (red) brush. The polymer compositions in the PEO- and PDMAEMA-rich phases are exaggerated for clarity.