Published in final edited form as:

Langmuir. 2013 September 10; 29(36): . doi:10.1021/la401268s.

Structure of biodegradable films at aqueous surfaces: X-ray diffraction and spectroscopy studies of polylactides and tyrosine-derived polycarbonates

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Abstract

Three representative polymers of increasing modulus, poly(D,L-lactic acid), PDLLA, poly(desaminotyrosyl-tyrosine ethyl ester carbonate), PDTEC, and the same polymer with iodinated DTE segments, PI₂DTEC, were characterized by surface-pressure versus area (π -A) isotherms and surface sensitive X-ray diffraction techniques. 10–100 Å thick films were prepared for these studies by spreading dilute polymer solutions at air-water interfaces. The general properties of the isotherms and the Flory exponents, determined from the isotherms, vary in accordance with the increasing modulus of PDLLA, PDTEC, PI₂DTEC, respectively. The analysis of *in-situ* X-ray reflectivity and grazing incidence X-ray diffraction (GIXD) measurements from films at aqueous surfaces provides a morphological picture that is consistent with the modulus of the polymers, and to a large extent, with their packing in their dry-bulk state. Large absorption of X-rays by iodine enabled X-ray spectroscopic studies under near-total-reflection conditions to determine the iodine distribution in the PI₂DTEC film and complement the structural model derived from reflectivity and GIXD. These structural studies lay the foundation for future studies of polymer-protein interactions at aqueous interfaces.

I. Introduction

Performance of a polymer in biomedical devices ultimately depends on its interactions with the surrounding tissue. Cell-polymer interactions are mediated by proteins that are adsorbed onto the polymer surfaces after implantation. Therefore, understanding the interaction of biomedical polymers with proteins is paramount to designing polymers to function in a controlled and predictable manner for specific medical applications. These interactions take place primarily in aqueous environments, either inside or outside cells. Thus, the water-polymer interactions are relevant to the functionality of the polymer. In this context, protein adsorption onto polymer surfaces in aqueous environments is likely the closest model system to the biomedical environment. This model system allows us to answer questions

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Supporting Information Available: Demonstration of surface pressure isotherm measurements and X-ray data analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>

concerning film homogeneity, globular aggregation, multilayering, and conformation compared to the bulk, for each specific polymer prior to advancing to the stage of adding proteins to the mix. The factors that govern the film properties include inter- and intra-monomer-monomer, monomer-water/solute, water-water interactions, steric-hindrance constraints, surface tension, and temperature, the effects of which cannot be trivially untangled. These multiple and competing factors, if known, can be used theoretically to predict polymer film behavior. In this report, we use various complementary experimental techniques to classify distinct polymers and characterize their behavior on fluid surfaces. Pressure-area (π -A) isotherm measurement, X-ray reflectivity (XR), grazing incidence X-ray diffraction (GIXD), and surface fluorescence spectroscopy techniques are employed on films, the densities of which are manipulated in a Langmuir trough, similar to treating lipid monolayers at aqueous/vapor interfaces. In this paper, we illustrate the use of these techniques by studying three polymers that are used in biomedical applications. These studies of polymer films at aqueous interfaces will form the foundation for subsequent studies of their interactions with biologically relevant proteins.

A host of techniques are widely used to characterize a thin polymer film. For instance, a quartz crystal microbalance is used to determine the mass change from which the thickness of the attached film can be determined.¹ Surface plasmon resonance² and ellipsometry³ are used to determine the thickness of the adsorbed layer using the changes in the optical response; the former can be coupled to a microscope to provide a macroscopic image of the surface. The pioneering work on polymer films on aqueous surfaces by Crisp was accomplished by measuring isotherms and surface potentials.^{4,5} X-ray based scattering techniques have also been well established in the investigation of thin films.^{6,7} In particular, instrumentation and methodology have been developed to investigate the Langmuir monolayers on aqueous surfaces.^{8,9} High brilliance synchrotron X-ray radiation enables the *in-situ* characterization of polymer films on aqueous surfaces at different stages of the isotherms, providing direct information about the polymer packing states.¹⁰⁻¹²

In this study, the structure of thin (1–10 nm) polymeric films spread on aqueous surfaces was studied using three hydrolytically degradable polymers (see Figure 1) that encompass a range of moduli. Wet moduli of PDLLA (unpublished, Murthy et al, 2012), PDTEC and PI₂DTEC¹³ are 1.3, 1.47, and 2.19 GPa, respectively. Two of the polymers are tyrosine-derived polycarbonates (Tyr-PCs),^{14,15} made of desaminotyrosyl-tyrosine ethyl ester (DTE) and iodinated DTE segments.¹⁶⁻¹⁸ The behaviors of these polymers are compared with that of a widely used, commercially available polymer, poly(lactic acid) (PLA) or polylactide.¹⁹ PLA is often used as a model polymer for evaluating other biomaterials, however, unlike Tyr-PCs, it produces acidic byproducts as it degrades. The specific PLA we use in this study is poly(D,L-lactic acid) (PDLLA) made of 50:50 D- and L-isomers of lactic acid, which is amorphous so that its behavior can be compared with numerous other polymers used in biomedical devices, including Tyr-PCs.

This paper is organized as follows: Section II describes the materials and experimental methods employed to characterize the polymer films on aqueous surfaces. All the techniques including X-ray fluorescence measurements are provided in more detail elsewhere.²⁰⁻²³ In section III, the experimental results and their analysis are presented, and their implications are discussed. Section IV summarizes our main conclusions.

II. Experimental details

PDTEC and PI₂DTEC polymers were synthesized by methods reported earlier,¹⁶⁻¹⁸ and their weight averaged molecular weights obtained in dimethylformamide are ~ 107 kDa and 90 kDa, respectively. PDLLA was purchased from Sigma-Aldrich (inherent viscosity 0.55–

0.75 dl/g, molecular weight ~ 96 kDa, determined in tetrahydrofuran solutions). In both cases, a gel permeation chromatograph calibrated with polystyrene standards was used to determine the molecular weight. The values have been corrected for the differences in the swelling behavior of polystyrene and our polymers. In Table 1, the molecular volume and electron density (ED) for a single repeat unit of each polymer based on reported mass density of dry polymers are listed.^{24,25} The polymers were each dissolved in a spreading solvent made of a 3:1 chloroform/methanol mixture to make stock solutions (in the present study, PDTEC at 1.21 g/L, PI₂DTEC at 1.78 g/L and PDLA at 1–4 g/L). Ultrapure water (Millipore, Milli-Q, and NANOpure, Barnstead; resistivity 18.1 M Ω cm) and phosphate buffered saline (sterile-filtered PBS, Dulbecco, without calcium chloride and magnesium chloride, suitable for cell culture was obtained from Sigma-Aldrich Corp.) were used for subphase preparations. Known quantities from the stock solutions were evenly dropwise-deposited on the surface of the solutions in a Teflon Langmuir trough that was kept at a constant temperature ~ 20°C. Surface pressure was recorded with a microbalance using a filter-paper Wilhelmy plate that was calibrated with isotherms of arachidic acid monolayers. Surface pressure against surface area (π -A) isotherm measurements were started 15 minutes after initial spreading of the polymers to allow for spreading solvents to evaporate. Isotherms of all polymers spread on water and on PBS were the same within the uncertainties of the measurements. The Langmuir trough was tightly encapsulated and continuously purged with water-saturated helium (to achieve helium-air exchange in the trough) during X-ray measurements to minimize background scattering from air and to reduce radiation damage due to the formation of ions or radicals.

X-ray reflectivity (XR) and near-total-reflection fluorescence (XNTRF) studies were conducted on the liquid surface spectrometer (LSS) at Ames Laboratory (AL) using UltraX-18 Rigaku X-ray source generator with a copper rotating anode (Cu $K\alpha$, wavelength = 1.54 Å) operated at 50 kV and 250 mA. A Ge(111) crystal was used to select the Cu $K\alpha$ and steer the downstream beam onto the liquid surface at a desired incidence angle. More comprehensive X-ray reflectivity and grazing incidence X-ray diffraction (GIXD) measurements were conducted on the LSS at the 9ID undulator synchrotron beam-line (X-ray energy $E = 13.474$ keV, $\lambda = 0.92017$ Å) at the Advanced Photon Source (APS) at Argonne National Laboratory.

Specular XR, R , as a function of momentum transfer along the surface normal, Q_z ($Q_z = 4\pi \sin \theta_i$; θ_i being the X-ray beam incident angle with respect to the aqueous surface), allows the determination of the ED profile, $\rho(z)$, that in turn is related to the mass density across the interface in z -direction that is normal to the aqueous surface.^{6–8,26,27} To obtain the ED profile $\rho(z)$, a parametrized continuous profile was constructed based on a structural model and further refined by optimizing a best fit of calculated reflectivity to the measured data.^{6–8,26,27} Here, we employed an effective-density model intended for uncorrelated interfaces, for which $\rho(z) = \sum_i f_i \rho_i(z)$, $\rho_i(z)$ being the volume fraction of i -th constituent materials of electron density ρ_i .⁷ The $\rho(z)$ profile was further parsed into thin slices to numerically calculate the reflectivity using a recursive dynamical method.²⁶

To determine possible film in-plane ordering and correlations, GIXD measurements were performed at the APS. For GIXD, the incident beam was kept constant below the critical angle for total reflection, θ_c ($\theta_c = 0.1^\circ$), at $\theta_i = 0.065^\circ$, and the diffracted beam, passing through a Soller slit, was detected with a vertically mounted position sensitive detector (PSD). These measurements were used to obtain two-dimensional (2D) maps of scattering

intensity versus $Q_z = k_0(\sin \theta_i + \sin \theta_f)$ and $Q_{xy} = |\mathbf{Q}_{xy}| = \sqrt{Q_x^2 + Q_y^2} \approx 2k_0 \sin(\varphi_{xy}/2)$ (θ_f is the X-ray exit angle with respect to the aqueous surface, $k_0 = 2\pi/\lambda$, and φ_{xy} is the horizontal angle of the detector with respect to the direction of the incident beam).²³

A Vortex energy dispersive detector (EDD) placed ~ 2 cm above the liquid surface was used to measure the near-total reflection X-ray fluorescence (NTRXF) as a function of ϕ in the vicinity of ϕ_c .^{20,22} This technique is used to corroborate the XR results and is most efficient for polymers that incorporate heavy atoms such as iodine in PI₂DTEC. The scattered primary beam (Thompson and Compton scattering) collected by the EDD, in addition to the emission from the specific ions, was monitored and evaluated to ensure the consistency and proper performance of the silicon-drift diode in the EDD. The details of the experimental setup and analysis are described elsewhere.^{20–23}

The curve-fitting of the X-ray scattering and spectroscopic data represented by symbols (circles, squares and so forth), are based on parametrized models and carried out through non-linear least squares method. The χ^2 represents the sum square of deviations of model-dependent calculations from experimental data weighted by the error bars due to counting statistics (Poisson statistics).²⁸ The refinements of parameters are carried out through minimization of χ^2 to its global minimum value $\chi_{\min}^2$. The upper and lower bounds for each parameters correspond to at least 50% rise in χ^2 with respect to $\chi_{\min}^2$.

III. Results and Discussion

Π -A Isotherms

Cycled (compression-expansion) Π -A isotherms for PDTEC, PI₂DTEC, and PDLLA spread on pure water are shown in Figure 2. The data for PDTEC show that if the polymer is dilutely spread, such that the initial surface-pressure is negligibly small, the isotherm is highly reproducible (see part a of Figure 2), while for a spreading with a small but detectable initial pressure the isotherm starts to be reproducible in the second cycle (within uncertainty $\sim \pm 1$ mN/m) (see part b of Figure 2). We can identify four regions on the isotherms as indicated by arrows in part a of Figure 2. In region I, the surface pressure is nearly zero, corresponding to a gaseous-like phase. In region II, the surface pressure increases upon compression gradually until it plateaus (~ 3 mN/m), a behavior similar to the liquid-expanded (*Le*) phase of lipid monolayers.²⁹ In region III, the surface pressure remains nearly constant at ~ 3 – 5 mN/m, generally associated with the coexistence of liquid-expanded and condensed phases in a lipid monolayer and now considered as a collapse phase for a polymeric monolayer.¹² Upon reaching region IV where $\Pi > 5$ mN/m, increases rapidly, which was reminiscent of a transition from liquid-like state to a glassy state.³⁰ We attribute, the hysteresis manifested upon film expansion to the viscoelastic behavior of polymer film.³⁰ Figure 2(c) shows that the intersection of linear extrapolation of steep Π -A region with the plateau region may yield the limiting surface area at which the aqueous area is just fully covered by polymers and Π starts to rise steeply. The isotherms of PI₂DTEC differ significantly from those of PDTEC in some respects.

First, Π rises abruptly only near limiting area, lacking an apparent plateau region. Secondly, the whole isotherm shifts to lower limiting area and lowering $\Pi_{\max}$ (that is, at $A_{\min}$, minimum film area accessible), after each compression. The fact that Π -A slope near limiting area is sharp indicates the film enters the condensed phase abruptly by coalescing aggregates that are likely formed upon spreading at $\Pi = 0$. We envision the coalescence of the aggregates as a percolation-like transition where connectivity between infinitely distant points on the surface are established but the coverage is incomplete. Thus, with each compression the surface coverage increases and that would explain the shift of the isotherms upon compression-expansion cycles. This behavior implies that inter-chain interactions are likely stronger in PI₂DTEC than in PDTEC. Thus upon expansion, PDTEC partially uncoils to its stable form while PI₂DTEC aggregates grow laterally in size, thus decrease in total circumference upon re-compression cycles.

A more detailed view of interpreting Π - A isotherms for an insoluble polymers is to consider the air-water interface as a two-dimensional (2D) solvent. In the semi-dilute regime of surface concentration, polymer coils begin to interact with one another³¹ for which a scaling law for Π - A has been developed^{12,32-34}

$$\Pi \sim A^{-\frac{2\nu}{2\nu-1}} \quad (1)$$

where ν is so-called “Flory exponent” for the radius of gyration of the polymer, R_G , ($R_G = N^{1/2}$, N being the number of polymer repeat units). A good 2D solvent would then yield a $\nu \approx 0.75$ while at the theta-condition $\nu \approx 0.50$ or close to the 3D case.^{12,30,32-35} Part d, e and f in Figure 3 show log-log plots of compression isotherms with a linear best curve-fit to determine ν of the power law Eq. (1). The two extreme cases of a theta solvent ($\nu = 0.51$) and a good solvent ($\nu = 0.78$) are shown as dotted lines in Figure 3. Part a and c in Figure 3 show that both PDTEC and PDLLA are characterized with a plateau on the Π - A isotherms. Part d and f in Figure 3 show that the Π - A isotherms are subjected to the power law described in Eq. (1) for PDTEC and PDLLA at low- Π region below the plateau. It appears that the air-water interface acts as an almost theta-solvent for PDTEC, which is consistent with other studies^{34,36} of similar polymers such as, poly(methyl-methacrylate) (PMMA) ($\nu \approx 0.56$)³² and poly(n-butyl acrylate) (PnBA; $\nu \approx 0.57$) on water surfaces.¹² By contrast, the larger ν value for PDLLA indicates stronger interaction of the polymer with the aqueous surface compared to monomer-monomer (M-M) interactions. Thus the PDLLA is likely to unfold to form a more open structure in order to maximize its contact with the aqueous surface, thus wetting the surface, and even partially protruding into the subphase. This suggests that the fraction of hydrophilic components in the PDLLA is sufficient to unfold the polymer but insufficient to make the polymer soluble in water. Thus, upon compression beyond the formation of a single layer one expects multilayer formation. Therefore, $A_{\min}$ per repeat unit of PDLLA can be much smaller than any cross-section of a repeat unit. These conclusions are consistent with the XR results discussed below. Though the ν values differ significantly, the origin of the plateau exhibited on both Π - A isotherms of PDTEC and PDLLA can be both related to the formation and collapse of monolayers.^{12,30} For instance, Witte et al showed that the plateau on the Π - A isotherms for PnBA ($\nu = 0.57$) arises from the formation of many far-apart, localized, globule-like and amorphous domains on a continuous monolayer that are observed in Brewster angle microscopy (BAM) images.¹² Similarly, Park et al. reported that for poly(D,L-lactic acid-co-glycolic acid) (PLGA) ($\nu = 0.76$) with the atomic force microscopy (AFM) imaging.³⁰ The isotherms shown in part b and e in Figure 3 for PI₂DTEC exhibit significant fluctuations rather than an apparent plateau at low- Π region. We speculate that PI₂DTEC molecules forms aggregate islands upon spreading, giving rise to fluctuations before surface pressure stabilizes and uniformly increasing as aggregate islands coalesce. If this is the case, the scaling law slope analysis to PI₂DTE in Figure 3(e) for PI₂DTEC is questionable as the scaling law is more suitable under the condition of semi-dilute concentrations. Also, it indicates that PI₂DTEC have stronger M-M interactions that lead to the formation of aggregates, while for PDTEC the aggregates are not as rigid and dissociate upon expansion. This is also consistent with the glass transition temperature (T_g) measurements (wet $T_g = 64^\circ\text{C}$ for PDTEC and 113°C for PI₂DTEC) which indicate the PI₂DTEC is more rigid than PDTEC.¹³

We set out to employ surface-sensitive X-ray diffraction and spectroscopy techniques to examine and complement the models of polymer structures derived from the analysis of the isotherm data in this section.

X-ray Reflectivity (XR)

Normalized reflectivities, R/R_F , (R_F being the Fresnel intensity reflectivity at a flat and sharp air-water interface) for the three polymers at two representative values are shown in Figure 4 as indicated. Qualitatively, we observe that the patterns become more oscillatory with a higher maximum that shifts to lower Q_z as increases, implying that the films at higher become more well-defined and thicker with higher excess surface ED compared to that at lower. These features are better illustrated by the ED profiles that best fit the R/R_F data as shown in Figure 4. We adopt the effective-density model proposed by Tolan⁷ to construct an arbitrary electron density profile assuming uncorrelated interfacial roughness and allowing for large interfacial roughness. The interpretation of R/R_F is model-dependent and more parameters would result in better fitting. Here, we used least number of structural parameters to carry out the R/R_F refinements and focused on the integral properties such as integral thickness ($\int$) and surface adsorption (σ), which are insensitive to individual structural parameters. The ED profiles are constructed as $\rho(z) = \rho_{\text{sub}} \rho_{\text{sub}}(z) + \rho_{\text{polymer}} \rho_{\text{polymer}}(z) + \rho_{\text{vapor}} \rho_{\text{vapor}}(z)$, where the volume fraction profiles $\rho_{\text{sub}}(z)$ of subphase, $\rho_{\text{polymer}}(z)$ of polymers and $\rho_{\text{vapor}}(z)$ of vapor satisfy $\rho_{\text{sub}}(z) + \rho_{\text{polymer}}(z) + \rho_{\text{vapor}}(z) = 1$.⁷ Here, the subphase ED is $\rho_{\text{sub}} = 0.334 \text{ e}/\text{\AA}^3$ and the vapor phase ED is $\rho_{\text{vapor}} = 0$. A set of four independent structural parameters (ρ_{polymer} , $\rho_{\text{polymer/subphase}}$ and $\rho_{\text{polymer/vapor}}$) are used to construct the ED profile $\rho(z)$ for PDTEC and PI₂DTEC and are further refined. The subphase-free polymer ED, ρ_{polymer} , and the effective thickness of the film, $\int$, (the integral width based on the volume fraction profile of polymer) are listed Table 2.²² In practice, the transition of ED from one medium to another can be approximated with an error function (erf), i.e. $\text{erf}(z/\sqrt{2}\sigma)$, where σ is a measure of the thickness of the boundary centered at $z = 0$ between two media. Here, the subscript “polymer/vapor” represents a polymer and vapor interface and “polymer/subphase” a polymer and subphase interface. More details of the model can be found in supporting information and Tolan’s book.^{7,23} If both $\rho_{\text{polymer/subphase}}$ and $\rho_{\text{polymer/vapor}}$ are smaller than the integral film thickness, $\int$, the construction of $\rho(z)$ reduces to the *one box* model.^{7,8,27} The normalized R/R_F comparing PDTEC and PI₂DTEC films obtained using the laboratory X-ray source at Ames Laboratory and the corresponding ED profiles are shown in Figure 5. The structural information based on R/R_F data are listed in Table 2.

For PDTEC, we find that the film ED, ρ_{polymer} , is slightly smaller than its bulk value and approaches it by compression. At high- σ , the average film thickness is nearly twice that at low- σ (roughly at half molecular area) such that the integral of the ED across the interface roughly scales with the molecular area. The mass adsorption of PDTEC derived from the ED (Table 1) indicates that there is no material loss upon film compression. Based on the ED and the area occupied by a repeat unit ($A_0 \approx 28 \text{ \AA}^2$), the film thickness is estimated at $\sim 17 \text{ \AA}$, which is about the same as that determined directly from the refinement of the XR ($\approx 15 \text{ \AA}$; Table 2). This suggests that at the incipient of region III of σ - A isotherms, PDTEC polymers are at most one repeat unit thick, i.e. a monolayer. In region IV, the polymers are packed in a bulk-like state, and deform like a glassy material;³⁰ the differential scanning calorimetry (DSC) and X-ray diffraction (XRD) data have shown that these polymers are amorphous in bulk state.^{13,24} This is consistent with our conclusions from the analysis of the isotherms that the polymer, although weakly interacting with water, is susceptible to folding-unfolding by compression-expansion.

For PI₂DTEC polymer films, the reflectivities and the ED profiles, within uncertainties, are the same at low- σ and high- σ . This is consistent with the isotherm showing an abrupt rise in σ at around A_{min} . Estimate, based on the ED and A_0 , yields a $\sim 19 \text{ \AA}$ film thickness, close to the spatial separation ($\sim 17 \text{ \AA}$) of iodine along the chain. The ED profiles also show that PDTEC and PI₂DTEC films are not oriented at high- σ and imply that PDTEC is softer and

more deformable than the more rigid PI₂DTEC, which is consistent with recent bulk studies.¹³

The XR from PDLA is significantly different than PDTEC or PI₂DTEC. To best-fit the data, the construction of ED profiles required at least one additional interface (equivalent to a *two box* model) compared to that of PDTEC and PI₂DTEC. At relatively high ~ 15 mN/m, the R/R_F has a single feature at low Q_z that falls off monotonically, generally indicating a less organized film. Analysis of the XR shows that the ED profile gradually decreases from the air-water interface toward the subphase, suggestive of partial protrusion of the polymer into the aqueous subphase. Compression of the film to the first (~ 21 mN/m) brings about regularly separated multiple peaks, indicating the formation of a more stable, uniform polymer film. The density gradient ED transforms into a 70 Å thick polymer film with symmetrically 20 Å gradients at the vapor and subphase interfaces.

GIXD

Figure 6 shows the GIXD patterns (integrated over 0–0.2 Å⁻¹ Q_z range) as a function of the in-plane momentum transfer, Q_{xy} , for a bare water and polymer-coated surfaces. The expression used to curve-fit the experimental data is

$$I(Q_{xy}) = \underbrace{I_{\text{diffuse}} \cdot Q_{xy}^{-\eta}}_{\text{Capillary wave}} + p \cdot \underbrace{\sum_{m=1}^2 I_m \cdot f_L(Q_{xy}, Q_m, \Delta Q_m)}_{\text{Water}} + (1-p) \cdot \underbrace{\sum_{n=1}^2 I_n \cdot f_L(Q_{xy}, Q_n, \Delta Q_n)}_{\text{polymer film}} \quad (2)$$

where I_{diffuse} , I_m and I_n are intensity scale factors. f_L is a Lorentzian-like function defined as follows:

$$f_L(Q_{xy}, Q_m, \Delta Q) = \left[1 + \left(\frac{Q_{xy} - Q_m}{\Delta Q} \right)^2 \right]^{-1} \quad (3)$$

where Q_m and ΔQ are peak position and half-width at half-maximum (HWHM) of the Lorentzian-like function, respectively. The first term in the right-hand-side of Eq. (2) accounts for diffuse scattering arising primarily from capillary waves of the liquid surface (and to a lesser degree from the intrinsic roughness) with an exponent $\eta > 0$ associated with the surface tension. η is called “capillary exponent”.⁹ $\eta = k_B T \langle Q_z^2 \rangle / 2\pi\gamma$, where γ is the surface tension, k_B and T are Boltzmann’s constant and absolute temperature, respectively. $\langle Q_z^2 \rangle$ represents an effective Q_z^2 accounting for the integration of GIXD intensity over a Q_z range.^{7–9,39} For $p = 1$, the calculated pattern exclusively applies to a bare water surface (phenomenologically), and is used to estimate the subphase contribution to the GIXD of the polymer films as shown in Figure 6(a). For pure water, a weak and broad Lorentzian-like peak centered at $Q_{xy} \approx 2.0$ Å⁻¹ and a shoulder near $Q_{xy} = 2.9$ Å⁻¹ are observed, in agreement with previous reports.⁴⁰ The X-ray diffuse scattering, at low Q_{xy} values, is adequately described with the exponent $\eta \approx 1.1$ in Eq. (2). For fitting the patterns of the deposited films, the water-surface terms are kept constant and their contribution is scaled by the factor p in Eq. (2). Implied in this procedure is the assumption that the scattering from the water surface and the film are incoherent, and therefore the GIXD from a deposited film can be considered as a simple sum of scattering from the bare subphase surface and a hypothetically vacuum-suspended polymer film. This is consistent with Langmuir monolayer (ML) observations⁸ where the bare surface and the ML were kept under the same conditions (in particular, complete exchange of air by water-saturated helium in the trough).

For this approach to be applicable, the scattering patterns from the bare and covered surfaces should overlap at very small and very large Q_{xy} in regions where the scattering from the film is negligible. This indeed is the case for the different polymers in Figure 6. The good overlap at low Q_{xy} suggests that there are no correlations on a large length scale at low-. At high-, the additional Lorentzian-like peaks, similar to those of water, due to nearest neighbor correlation in the polymer but with no long-range order, are frequently attributed to amorphous phase (short-range order) in the polymer community. Superimposed in the figures are wide-angle X-ray diffraction (WAXD) peaks obtained from bulk materials. We note that while for all polymers the main diffraction pattern (one or two peaks) are in good agreement with those of the bulk materials, the peak linewidths of films are visibly narrower compared to those observed in the bulk. This suggests that relaxation of steric-hindrance at the interface promotes a more ordered polymer in general. More extreme cases where interfacial boundary conditions induce an ordered surface, crystallization for instance, were manifested as the coexistence of surface alkane chains in crystalline state and bulk alkane chains in liquid state.^{41–43}

For PDTEC at high-, we find a peak at $Q_{xy} = 1.35 \pm 0.25 \text{ \AA}^{-1}$ and a shoulder at $Q_{xy} = 0.73 \pm 0.25 \text{ \AA}^{-1}$ associated with d -spacings $4.7 \pm 1 \text{ \AA}$ and $8.6 \pm 1.3 \text{ \AA}$, respectively. The $0.73 \text{ \AA}^{-1}$ shoulder, that is also observed in bulk samples,²⁴ reflects a tendency of the polymers to form clusters with a loosely packed cell with edges $a \sim 4.7 \text{ \AA}$ and $b \sim 8.6 \text{ \AA}$. The broad linewidths of the diffraction peaks are obviously due to both small cluster size and a distribution of lattice constants. Correlations along the chain direction (c -edge), approximately spanning over a repeat unit and expected to peak at $2/c \sim 0.3 \text{ \AA}^{-1}$, is hard to disentangle from our GIXD data because of the strong diffuse scattering at low angles, (unfortunately the published WAXD does not cover this region either).

The GIXD pattern for the PI₂DTEC film although similar to that of PDTEC is shifted to larger Q_{xy} values indicating similar packing to that of PDTEC with smaller d -spacing compared to PDTEC. The main peak is centered near $Q_{xy} \approx 1.45 \text{ \AA}^{-1}$ implying $a \sim 4.3 \text{ \AA}$. We note that at the high end of the Q_{xy} range, the observed diffraction intensity from the film is greater than the sum of contributions from polymer and water. This extra scattering peak could arise, at least partially, from the polymer itself.²⁴ In addition, it may arise from water moats at the interface. Higher chain rigidity in PI₂DTEC that arises from intermolecular affinity and chain conformational entropy, along with air/water, air/polymer and polymer/water interfacial tensions, could contribute to the final wetting behavior. The GIXD results are in agreement with conclusions drawn from the isotherms and XR analysis discussed above. The isotherms show that the change in corresponds to a $\sim 10\%$ change in molecular area, which results in only a few percent change in ED profiles and thus has insignificant effect on the reflectivity shown in Figure 4(c) and (d). Similar but less dramatic effects are also observed for the more ordered lipid monolayers when small change in molecular area induces significant in-plane structural transitions probed with GIXD as opposed to negligible effect to XR.⁴⁴

For PDLA we observe a major peak at $Q_{xy} \sim 1.1 \text{ \AA}^{-1}$ and a shoulder at $Q_{xy} \sim 1.44 \text{ \AA}^{-1}$ corresponding to d -spacing ~ 5.7 and $\sim 4.2 \text{ \AA}$. Such a pair of peaks typically arise when the chains are packed with two separate interchain correlations lengths.²⁵ This bi-directionality is consistent with recent molecular dynamics simulations, which show that while C-C correlations contribute to both peaks, C-O correlations contribute primarily to the $1.44 \text{ \AA}^{-1}$ peak.²⁵ In addition to the two reflections the bulk WAXD shows a third reflection at $Q_{xy} \sim 2.2 \text{ \AA}^{-1}$ possibly the second order reflection of the first reflection at $Q_{xy} \sim 1.1 \text{ \AA}^{-1}$.

X-ray Fluorescence (XF)

Taking advantage of the presence of a relatively heavy element, i.e., iodine, in PI₂DTEC allows us to employ near-total-reflection fluorescence measurements for this film. To calibrate intensity of the emission lines to the number of iodine ions, fluorescence from pure NaI solutions of known concentrations has been used. The combined effect of element specificity and surface sensitivity of XNTRF can be visualized by organizing the fluorescence intensity data in a 2D color map as shown in Figure 7. Part a and b show 2D fluorescence data for NaI and PI₂DTEC solutions spread on PBS solution, respectively. For NaI solution, the L and L emission lines for iodine are readily identified only above $Q_c = 0.0217 \text{ \AA}^{-1}$, Q_c being the Q_z corresponding to the critical incident angle for total reflection. The fluorescence signal in the $Q_z < Q_c$ range is below the detection limit of our experimental setup, because of the finite penetration depth of the X-ray beam (less than $\sim 80 \text{ \AA}$) and the low iodine ion concentration near the bare surface. On the other hand, in the presence of PI₂DTEC on the surface, there is a strong enhancement of fluorescence intensity at $Q_z < Q_c$, only from iodine indicating accumulation of iodine at the surface. The maximum intensity at Q_c is due to multiple scattering indicating the emitting ions reside within the penetration-length of evanescent waves. By contrast, the strong chlorine K emission lines and relative weak potassium K emission lines originating from Cl^- and K^+ ions in the PBS solutions are only observed for $Q_z > Q_c$, indicating there is no monovalent ionic enrichment of chlorine and potassium near the surface, for both the bare and covered surfaces.

Figure 8 shows two sets of the spectra, part a is the set obtained below the critical angle at $Q_z = 0.018 \text{ \AA}^{-1}$, and part b is the set obtained above the critical angle at $Q_z = 0.035 \text{ \AA}^{-1}$. Each of these figures contains an overlay of the spectra from a NaI solution, a PBS solution and a PBS solutions spread with PI₂DTEC. Qualitatively, the spectra shown below Q_c is primarily from surface ions whereas above Q_c it is a sum of the same surface ions and bulk ions. For $Q_z > Q_c$, the X-ray penetration depth normal to the surface tends to infinity with respect to the shallow surface thickness and the fluorescence intensity is simply proportional to the amount of elements illuminated by the X-ray.^{20–22}

As mentioned above, the spectra of known NaI concentration (C_{bulk}) is used to calibrate a scale factor that relates intensity to the concentration of iodine ions (C_{surface}) within the film that floats on the surface.^{20–22} At a given Q_z that is larger than Q_c , the film thickness (on the length scale of nanometer) is much less than the X-ray penetration depth normal to the surface (on the length scale of micrometer). Assuming the fluorescence from the bulk iodine is negligible for a water coated with I₂DTEC, the surface adsorption of iodine ($= C_{\text{surface}} \cdot A$) can be obtained by normalization of fluorescence intensity to that from a bulk solution of NaI at concentration C_{bulk} .^{20–22}

With an appropriate model, a global-fit to the Q_z -dependent fluorescence intensity can be achieved yielding not only the surface adsorption of iodine with better precision, but also their spatial distribution. For more details, see supporting information.²³ The Q_z dependence of the fluorescence, by integrating over an energy range that includes the major emission lines of iodine (i.e., from 3.7 to 5 keV) is shown in Figure 9. We assume that the iodine-enriched layer has a characteristic thickness δ , and consider two cases: Case 1: the surface layer is fully occupied by I₂DTEC groups. The concentration of iodine within the film is thus determined as $C_{\text{surface}} = 2/\nu_m$, ν_m being the I₂DTEC group volume from Table 1. Case 2: the surface layer is a mixture of I₂DTEC groups and subphase (water in this study), the average value can be determined based on their relative ratio as follows. Assuming the volume fraction of I₂DTEC groups in surface layer is ϕ on average (0 $\leq \phi \leq 1$). The average electron density $\langle \rho \rangle$ and absorption coefficient $\langle \mu \rangle$ of the surface layer is expressed as $\langle \rho \rangle = \rho_{\text{I2DTEC}} \cdot \phi + \rho_{\text{sub}} \cdot (1 - \phi)$ and $\langle \mu \rangle = \mu_{\text{I2DTEC}} \cdot \phi + \mu_{\text{sub}} \cdot (1 - \phi)$, where ρ_{I2DTEC} and μ_{I2DTEC} are electron density and absorption coefficient for a pure I₂DTEC group, while ρ_{sub} and μ_{sub}

are for water that are intermixed with I₂DTEC groups in the surface layer. So that, the average index of refraction with respect to the X-ray is given by $\langle n \rangle = 1 - \langle \rho \rangle + i \langle \kappa \rangle$ where $\langle \rho \rangle = \langle \rho_0 \rangle^2/2$ and $\langle \kappa \rangle = \langle \mu \rangle/4$ (see notes to the Table 3 for definitions of parameter notations in the refractive index formula). Consequently, there are totally four adjustable parameters in global-fitting of $I_F(\theta)$, namely, ρ , κ , ρ_{sub} and μ_{sub} . Eventually, the C_{surface} can be obtained as $C_{\text{surface}} = 2/\nu_m$. Figure 9 shows the best fit to the fluorescence data in terms of Eq.S3 in supporting information.²³ The data for pure NaI solutions and its fitting in terms of Eq.S2 in supporting information²³ are also shown for comparison. The calculated bulk contribution (represented by dashed line) for a PI₂DTEC-coated surface are negligible, suggesting the fluorescence signals originate primarily from the surface for a PBS solution covered with PI₂DTEC. The quantitative results are summarized in Table 4 and described as follows. (1) Change in ρ is inversely proportional to κ in curve-fitting, which results in the small variance in (ρ/κ) with relative small uncertainty, even though both of ρ and κ have much larger relative error individually. The mass adsorption of I₂DTEC in terms of XF can be estimated as the (ρ/κ) multiplied by its mass density (1.952 g/cm³) (from Table 1 for consistency). Comparing the mass adsorption of I₂DTEC evaluated by XF and XR results, XF yields $\sim 3.9 \times 10^{-4}$ mg/cm³, which falls within the range based on XR. (2) Iodinated polymers form an iodine-enriched layer of $\sim 15\text{--}30$ Å thick, coincident with the dimension of most-electron-populated segment shown in XR measurements. The best-fitting suggests $\rho/\kappa = 1$, i.e. no water is intermixed with I₂DTEC at high- ρ . (3) The larger relative errors on ρ reflect our ignorance on ρ . If $\rho/\kappa = 1$, PI₂DTEC polymer film thickness d is narrowed down to 20 ± 1 Å, which is very close to the d based on XR methodology.

IV. Conclusions

A combination of ρ -A isotherm, X-ray reflectivity, and GIXD measurements provides a comprehensive understanding of the structure of thin films on aqueous surfaces as illustrated using three biomedically relevant representative polymers, PDTEC, PI₂DTEC and PDLLA that were selected for their differing Young's modulus. (1) The morphology of films and the Flory exponents (determined from the isotherms) of these polymers were found to correlate with their rigidity and are consistent with their bulk behavior. (2) While the more rigid PI₂DTEC forms a monolayer presumably, due to steric-hindrance effects, the softer PDLLA forms multi-layers that result from a pile-up upon compression. (3) XR analysis shows that the thickness of these films varies from 10 to 100 Å, and the obtained electron densities at high- ρ are, within error, very close to or even higher than the reported values for materials in amorphous state, suggesting more compact packing of repeat units compared to bulk. (4) The GIXD patterns with broad peaks are very similar to those observed in the bulk materials. The slightly sharper peaks in the GIXD compared to the WAXD, indicate slightly increased ordering of the polymer chains at the aqueous surface, consistent with the higher ED extracted from the XR. (5) Taking advantage of the presence of iodine in PI₂DTEC, we used X-ray spectroscopic data obtained at near-total-reflection to determine specifically the iodine distribution in the film to complement the structural models derived from XR and GIXD. The iodination leads to a thinner DTE film thickness, approximately one repeat unit thick, suggesting a steric-hindrance that prevent from polymer pile-up.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank A. Hekes, R. Y. Park and W. R. Lindemann for technical support. We thank Joachim Kohn for administrative support of this study and for editing the manuscript. Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. Ames Laboratory is

operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. The work of N. S. Murthy was supported by the New Jersey Center for Biomaterials at Rutgers University and by Award Number P41EB001046 from the National Institute of Biomedical Imaging and Bioengineering. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institute of Biomedical Imaging and Bioengineering or the National Institutes of Health.

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Figure 1. Chemical structure of (a) PDTEC and PI₂DTEC polymers and (b) PDLLA polymer investigated in this study. The corresponding molecular volume and electron density of each repeat unit are listed in Table 1.

Figure 2.

-A isotherms for PDTEC polymer films over pure water subphases. The surface area, A , is normalized to a minimum surface area $A_{\min}$ ($\approx 120 \text{ cm}^2$). Isotherms for (a) 30 μL PDTEC solution and (b) 60 μL PDTEC. In (a) and (b), dashed line corresponds to the first compression and solid line to the ensuing compression and expansion. (c) Linear extrapolation of region IV to obtain limiting film area.

Figure 3.

Plot of surface pressure against molecular area of polymeric repeat units A_0 (shown in Figure 1) for (a) PDTEC (b) PI₂DTEC, and (c) PDLA. The values of A_0 , the surface area per repeat unit, at the maximum surface pressure on the isotherm plot, Π_{max} , are indicated. Due to the finite compression ratio of the trough, the isotherm plot for PDLA is a combination of two isotherms of different spreading volumes of PDLA solution. A log-log plot of compression isotherm (solid line) with a linear best curve-fit to determine the power law $\Pi \sim A^{-\frac{2\nu}{2\nu-1}}$ (dashed line) for (d) PDTEC (e) PI₂DTEC, and (f) PDLA. The dotted lines represent two extreme cases for a theta ($\nu = 0.51$) and good solvent ($\nu = 0.78$) as indicated.

Figure 4.

X-ray measurements using synchrotron radiation obtained at APS. (a,c,e) Measured R/R_F of polymer films on the aqueous surface at different surface pressures and with different spreading amount as indicated. The R/R_F for PI_2DTEC is displayed on semi-logarithm scale to accentuate the ripple at high Q_z . (b,d,f) Corresponding electron density profiles generated by best-fit parameters.

Figure 5.

(a) Measured R/R_F of PDTEC, and PI_2DTEC on aqueous surfaces at high- (maximum surface compression) using laboratory X-ray source. The solid lines are calculated reflectivity based on best-fit parameters. (b) Corresponding electron density profiles generated by best-fit parameters.

Figure 6.

Integrated GIXD over Q_z as a function of in-plane scattering vector component, Q_{xy} , at $\theta_i = 0.065^\circ$. Left panel and right panel correspond to low- and high- conditions, respectively. The GIXD data points are represented by symbols and each symbol is the intensity binning over the nominal Q_{xy} over the range $Q_{xy} \pm 0.023 \text{ \AA}^{-1}$ and $0 < Q_z < 0.2 \text{ \AA}^{-1}$. Error bars are smaller than symbols and thus invisible. Solid lines are best-fit profiles using Eq. (2). The best-fit profile (dotted lines) for GIXD of water surface is also used for clarity of display. Dashed lines are component Lorentzian-like functions used for fitting. The arrows point to the maximum difference for GIXD of polymer-coated surface with respect to that of the bare water surface. WAXD data from dry bulk polymers are rescaled and overlaid over the extracted GIXD from surface polymers in (b), (d) and (f). (a) PDTEC film at $\approx 3.0 \text{ mN/m}$. (b) PDTEC film at $\approx 11.0 \text{ mN/m}$. (c) PI₂DTEC film at $\approx 2.5 \text{ mN/m}$. (d) PI₂DTEC film at $\approx 15 \text{ mN/m}$. (e) PDLLA film at $\approx 15 \text{ mN/m}$. (f) PDLLA film at $\approx 22 \text{ mN/m}$. The curve-fitting for GIXD of PI₂DTEC-coated surface is over the range of $Q_{xy} < 3.0 \text{ \AA}^{-1}$.

Figure 7.

Color map of fluorescence intensity as a function of photon energy and Q_z . (a) Fluorescence from 3 mM NaI bulk solution. (b) Fluorescence from PBS solution with PI_2DTEC film at ≈ 9 mN/m.

Figure 8.

Fluorescence spectra obtained from a bare NaI solution of known concentration, a bare PBS solution and a PBS solution covered with PI₂DTE ($\approx 9 \text{ mN/m}$). (a) Fluorescence spectrum obtained at $Q_z = 0.018 \text{ \AA}^{-1}$ corresponding to the X-ray penetration depth approximately $80 \text{ \AA}$. (b) Fluorescence spectrum obtained at $Q_z = 0.035 \text{ \AA}^{-1}$ corresponding to the X-ray penetration depth approximately $3.4 \text{ \mu m}$.

Figure 9.

Fluorescence intensity as a function of Q_z for a bare NaI solution and a PBS solution covered with PI₂DTE (≈ 9 mN/m) as indicated. Each point in the figure is an integration over 3.7–5.0 keV, which contains iodine L , L and L characteristic emission lines exclusively. The Poisson statistics were used to estimate the counting uncertainty. The error bar represents one standard deviation. The data are curve-fit in terms of the electric field calculations.²³ The solid lines are calculated based on the the best-fit parameters. The dashed lines correspond to the components attributed to the bulk signal in Eq.S3 in supporting information.²³ The best-fitting gives $\chi^2_v \approx 1.0$.

Table 1

Relevant parameters of polymers used in data analysis.

Polymer repeat unit (group)	Mass density ^a ρ_m (g/cm ³)	Repeat unit volume ^b v_m (Å ³)	Electron density ^c ρ_e (e/Å ³)
PDTEC	1.31	486	0.416
PI ₂ DTEC	1.95	540	0.567
PDLLA	1.25	96	0.397

^aThe superscript “m” in ρ_m denotes mass density to distinguish the symbol ρ_e that represents electron density in this article. These parameter values are from literature (Murthy et al. ^{24,25}).

^bThis value is calculated based on measured mass density and molar mass of the repeat unit shown in Figure 1.

^cThis value is calculated based on measured mass density, molar mass and total number of electrons possessed by one repeat unit.

Table 2

Thickness and surface adsorption of the polymer on the aqueous surface characterized by XR using a one-box model for PDTEC and PI₂DTEC and a two-box model for PDLA.^a The superscripts “AL” and “APS” represent XR measurements performed at Ames Laboratory using laboratory X-ray source (over a time scale of 15 hours) and at APS using synchrotron radiation (over a time scale of 30 minutes), respectively.

	PDTEC			PI ₂ DTEC _e			PDLA		
	Low- APS ≈ 3 mN/m	High- APS ≈ 11 mN/m		High- APS ≈ 10 mN/m	High- AL ≈ 9 mN/m	Low- APS ≈ 15 mN/m	High- APS ≈ 21 mN/m		
(Å) ^b	14.7 ± 1.0	24.0 ± 1.0		19.0 ± 0.6	18.9 ± 0.2	56 ± 25	70 ± 1		
max (e/Å ³)	0.392 ± 0.003	= polymer		0.587 ± 0.010	0.590 ± 0.025	0.346 ± 0.005	0.386 ± 0.006		
polymer (e/Å ³)	0.416 ^d	0.408 ± 0.007		0.609 ± 0.013	0.597 ± 0.020				
polymer/vapor (Å)	3.5 ± 0.1	3.3 ± 0.1		5.8 ± 0.1	3.4 ± 0.1				
polymer/subphase (Å)	5.8 ± 0.1	5.3 ± 0.5		2.7 ± 0.1	4.2 ± 0.3				
(× 10 ⁻⁴ mg/cm ²) ^c	1.6 ± 0.3	3.3 ± 0.1		3.5 ± 0.1	3.6 ± 0.1	5.9 ± 2.7	~ 8.7		

^aThe upper bound and lower bound of each parameter correspond to a 50% increase in χ^2 from a global $\chi^2_{\min}$. The data fitting for R/R_F based on laboratory X-ray source at Ames Laboratory have $\chi^2_{\min}$ corresponding to $\chi^2_v \sim 0.8 - 1.2$, χ^2_v being the reduced χ^2 , 28 for Q_Z ranging over 0.01–0.55 Å⁻¹.

^bThe effective thickness of the film, t , is defined as $\zeta \equiv \frac{1}{\Phi_{\max}} \int \Phi(z) dz$. The volume fraction of polymer $\Phi(z) = \frac{\rho(z) - \rho_{\text{ref}}(z)}{\rho_{\text{polymer}} - \rho_{\text{sub}}}$, where $\rho_{\text{ref}}(z)$ is the electron density profile obtained by replacing the adsorbed polymers with the subphase solution and $\Phi_{\max}$ is the maximum value of $\Phi(z)$, 22, 37, 38.

^cThe mass adsorption of polymer repeat units, Γ , is calculated in terms of the volume fraction profiles, $\Phi(z)$, of polymer in terms of R/R_F data and polymer mass density, i.e. $\Gamma = \int \Phi(z) dz$. The mass density values are constants from Table 1.

^dThe value of Γ_{polymer} is set to constant ($= 0.416 \text{ e/Å}^3$) for PDTEC at low- Q_Z due to the insensitivity of $\chi^2_{\min}$ near this constant value in data fitting.

^eThe XR results from AL and APS are both given at high- Q_Z . The parameters in terms of APS data at low- Q_Z are within the uncertainties the same as those at high- Q_Z , thus are not given.

Table 3

The parameters (electron density ρ , a and b) used for calculating the index of refraction, n , for the selected materials at X-ray $\lambda = 1.54 \text{ \AA}$ for Cu K characteristic radiation.

	($\text{e}/\text{\AA}^3$)	($\times 10^{-6}$) a	($\times 10^{-8}$) b
H ₂ O	0.334	3.555	1.216
I ₂ DTEC ^c	0.567	6.035	28.15

^a $a = r_0^2/2$, where r_0 ($= 2.82 \times 10^{-5} \text{ \AA}$) is known as the Thomson scattering length.

^b The value of b is given by $b = \mu/4$, where the absorption coefficient μ derived from attenuation length can be found from web source.⁴⁵

^c These values are based on the electron density and mass density of PI₂DTEC given in Table 1.

Table 4

The PI₂DTEC film at ≈ 9 mN/m characterized by the X-ray fluorescence measurements.^a

surface composition	volume fraction	thickness (Å)	$\cdot$ Å	mass adsorption ^b ($\times 10^{-4}$ mg/cm ³)
I ₂ DTEC	1.0	20^{+1}_{-1}	$20.0^{+0.1}_{-0.1}$	~ 3.9
I ₂ DTEC/water	$1.0^{+0.0}_{-0.3}$	20^{+8}_{-1}	$20.0^{+1.0}_{-0.1}$	~ 3.9

^aThe electron density of a I₂DTEC group is from Table 1.

^bThe mass adsorption is referred to I₂DTEC groups and is evaluated with the mass density of I₂DTEC in Table 1, i.e. 1.952 g/cm³.