

Cite this: DOI: 10.1039/xxxxxxxxxx

Supporting Information: Crossover from Semi-dilute to Densely Packed Thin Polymer Films at the Air-Water Interface and Structure Formation at Thin Film Breakup

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1 Specular Reflectivity on PnBA and PEG-PnBA monolayers

In a quasi 2D system the film thickness is small compared to the actual size of the chain ($d \ll R_G$). As a measure for the confinement of the polymer in a film of thickness d , we compare d to R_G . In general, three different situations can be imagined. In the first situation, the film thickness is much larger than R_G which is comparable to the situation in a bulk solution. Another possibility is that the thickness is comparable to its own size, respectively $2R_G$. Here, the polymer is already in a weak confinement at the interface. In the last situation the film thickness may be much smaller than R_G , leading to a strong confinement of the polymer at the interface (2D confinement). These three situations are illustrated in the sketch in figure 1.

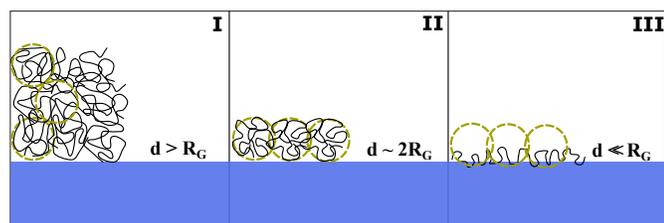


Fig. 1 Different conformations of polymer films on a water subphase. R_G is the radius of gyration. I. $d > R_G$: no confinement. II. $d \sim R_G$: intermediate state. III. $d \ll R_G$: strong confinement.

We aim to characterize the film thickness at the air-water interface which we expect to be a few Ångström. Therefore, we perform in-situ X-ray reflectometry (XRR) on the polymer films at the air-water interface and ex-situ measurements on Langmuir-Blodgett (LB) films. For the ex-situ measurements, the polymer films were transferred on silicon wafers at $\text{mmA}_{\text{trans}}$. The films were transferred while the wafer was pulled out of the monolayer (Z-type deposition) as expected for a monolayer consisting of hy-

drophilic groups in the backbone. The process was monitored and the transfer ratio for all films were close to one, indicating a successfully transferred film from the water surface. The ex-situ measurements were performed because of the lack of scattering contrast between water and the polymer film, as we will briefly comment on in the following. The scattering length density of PnBA is $\rho_{\text{PnBA}} = 10.0 \cdot 10^{-6} \text{ \AA}^{-2}$, which gives a contrast of around 5% to the water subphase ($\rho_{\text{H}_2\text{O}} = 9.427 \cdot 10^{-6} \text{ \AA}^{-2}$)¹. This makes it difficult to differentiate the thin monolayer from the water subphase. Furthermore, for PEG the scattering length densities is $\rho_{\text{PEG}} = (9.6 - 10) \cdot 10^{-6} \text{ \AA}^{-2}$ for thin film measurements², which is in between the already mentioned scattering length densities.

First, we will discuss the results of the LB films shown in Figure 2 (left panel). In this representation of the data we take into account the overall decay of the reflectivity R according to the Fresnel reflectivity $R_F \sim q_z^{-4}$. The raw data already shows the appearance of a first minimum of Kiessig fringes that slightly shifts to larger q_z with increasing molecular weight. As the scattering length density of the PEG and PnBA blocks are very similar, we use a one layer model for both homopolymers and diblock copolymers in order to extract reliable results for the film thickness. The model calculates the reflectivity of an electron scattering density profile along the surface normal using the established matrix formalism³. It consists of a layer with a thickness d , a scattering length density ρ_{SLD} , a roughness of the layer-silicon interface σ_0 and of the layer-air interface σ_1 . The solid lines in Figure 2 are calculated reflectivities according to this model. For better comparison we used the same model for all molecular weights, although we can see that it deviates from the data for the largest molecular weight when q_z is small ($q_z < 0.09 \text{ \AA}^{-1}$). The scattering length density of the films was constrained to $\rho_{\text{SLD}} = 10.0 \cdot 10^{-6} \text{ \AA}^{-2}$ for all films. The roughness $\sigma_0 = 5 \text{ \AA}$ is in agreement with the initial roughness of the silicon wafer determined in a separate XRR experiment. The layer-air surface seems to be very smooth indicated by the relatively low value for $\sigma_1 \approx 3 \text{ \AA}$. The overall film thickness of all films is smaller than 2 nm and decreases with increasing molecular weight of the sample as shown in Figure 3. We understand this as an influence of the PEG block. As mentioned in the main part, at $\text{mmA}_{\text{trans}}$ only a water-free

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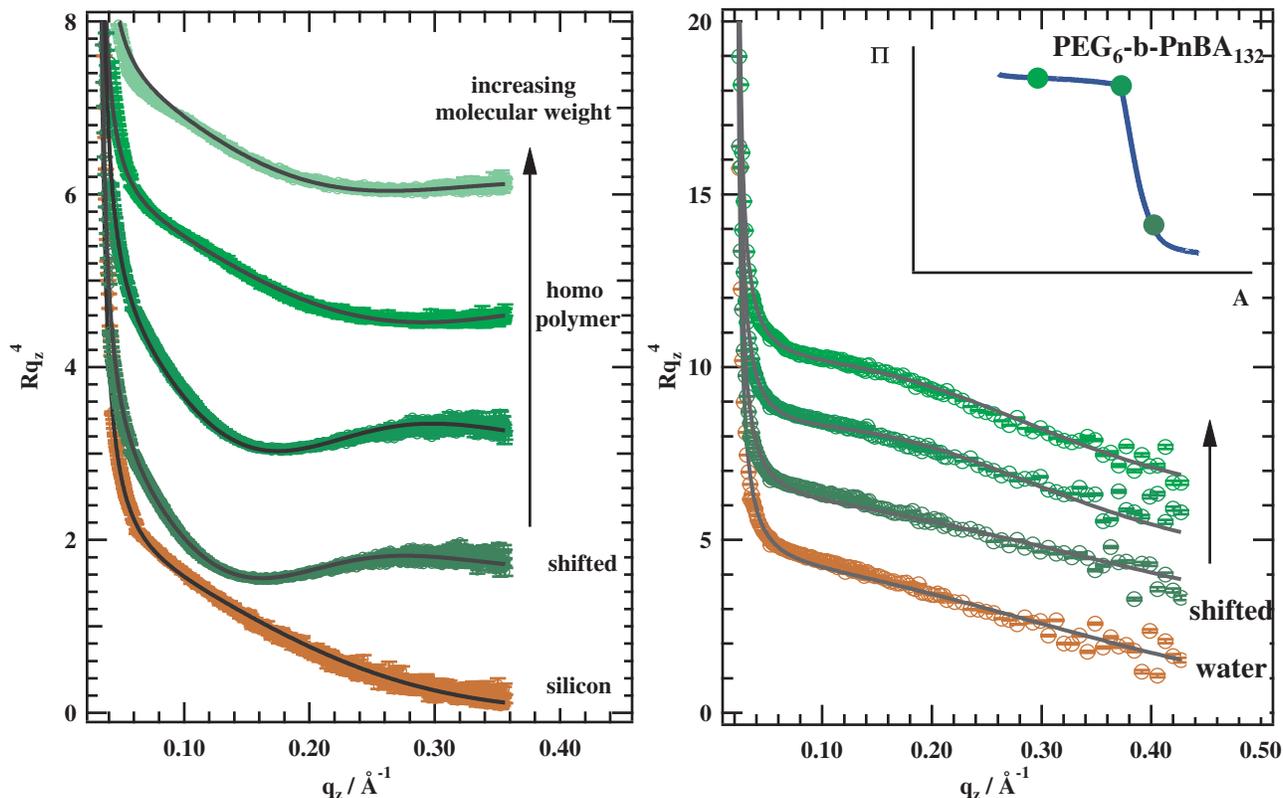


Fig. 2 Left panel: Ex-situ reflectivity curves of $PnBA_{66}$ and $PEG_6-b-PnBA_{37,58,132}$ Langmuir-Blodgett films, produced at the transition point mmA_{trans} , on a silicon wafer. Right panel: Reflectivity curves of $PnBA_{66}$ and $PEG_6-b-PnBA_{132}$ at the air-water interface for different surface pressures of $\Pi \approx (5, 22, 24)$ mN/m. In both panels the reflectivity is multiplied by q_z^4 to emphasize the appearance of Kiessig fringes in the curves.

$PnBA$ layer exists at the interface. This means that when we produce our LB films at mmA_{trans} , the number of $PnBA$ chains that are transferred is the same. However, for the block copolymers the PEG block is also transferred on the wafer. This can lead to a slightly larger thickness of the layer because the transferred volume increases with increasing volume fraction of PEG. Another possibility is that microphase separation occurs for the block copolymers. The underlying structure can depend on the volume fraction of PEG in the blocks as similar observed for PS-PEG diblock copolymers⁴.

In Figure 2 (right panel), we show the in-situ reflectivity of the films at air-water interface for $PEG_6-b-PnBA_{132}$. As expected we can barely differentiate the reflectivity from different positions in the isotherm and a bare water surface. However, small changes can be distinguished. For the first measurement point in the semi-dilute regime at a surface pressure $\Pi \approx 5$ mN/m, the reflectivity reduces a little less compared to water. With increasing surface pressure small changes become visible that can be fitted with the already described 1-layer model. We constrain the scattering length density of the layer to $\rho_{SLD} = 10.0 \cdot 10^{-6} \text{ \AA}^{-2}$. The roughness $\sigma_0 = 2.6 \text{ \AA}$ is in agreement with the roughness of water and the layer-air roughness $\sigma_1 = 3 - 5 \text{ \AA}$ is slightly larger compared to the ex-situ results.

The film thickness of in-situ and ex-situ measurements are summarized in Figure 3. The film thicknesses d , shown in figure 3, can be compared to calculated values of $R_{G,3D PnBA}$. The

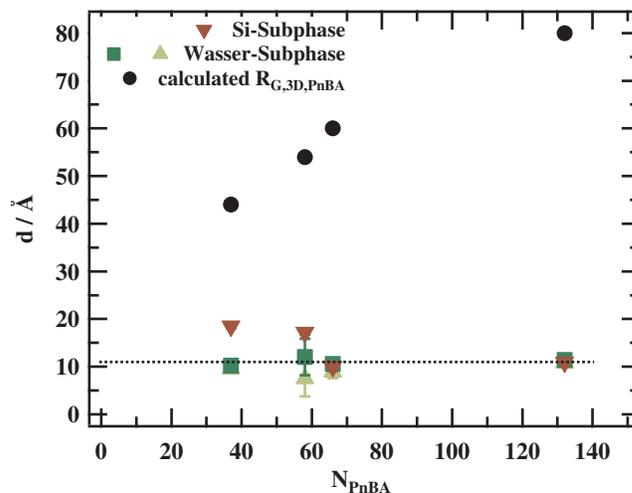


Fig. 3 Film thickness d vs. number of $PnBA$ monomers N_{PnBA} in the samples. The films form thin layers at the water and silicon interface of less than 20 \AA .

values were calculated with a power law fitted to light scattering data on $PnBA$ solved in Tetrahydrofuran.⁵ The results show that for all our samples d is smaller than the respective radius of gyration R_G for both in-situ measurements on the water surface and ex-situ measurement on silicon wafers. Obviously in our films, polymers are strongly confined to a thin layer. Consequently their

chain conformation will have to adapt to this 2D situation.

2 Polymer Synthesis

Materials. All solvents and reagents were purchased from Alfa Aesar, Sigma Aldrich, Fisher Scientific, ABCR and used as received unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Cu^IBr was washed five times with glacial acetic acid and ethanol. Butyl acrylate (BA) was destabilized by passing through an Al₂O₃ column. BA, *N,N,N',N',N''*-pentamethylethylenetriamine (PMDETA), anisole, and 2-bromoisobutyric *tert*-butyl ester (tBbiB) were degassed and stored under an argon atmosphere or in a glovebox. All syntheses were carried out under an atmosphere of argon using Schlenk techniques.

Characterization. Standard SEC was performed with THF as the mobile phase (flow rate 1 ml/min, sample concentration of 1...4 g/l) on a high resolution column set from Polymer Standard Service (PSS, Mainz) (SDV 5 μm 10⁶ Å, SDV 5 μm 10⁵ Å, SDV 5 μm 10³ Å) at 30°C. Calibration was carried out using PS standards (from PSS). A system composed of a 1260 IsoPump - G1310B (Agilent Technologie), a 1260 VW-detector - G1314F - at 254 μm (Agilent Technologie), a 1260 RI-detector - G1362A - at 30°C (Agilent Technologie), and a manual injector (100 μl) Rheodyne Ventil 7725 was used for SEC-experiments using PSS WinGPC UniChrom 8.2 for data acquisition. NMR spectra were recorded on a Bruker DRX 300 spectrometer working at 300 MHz (¹H NMR) using MestReNova 11.0 for data acquisition. NMR chemical shifts are referenced relative to tetramethylsilane.

Polymer Synthesis. *Exemplary synthesis of poly(butyl acrylate)₂₅₅ featuring a molar mass of 32700 g/mol (M_n).* In an argon atmosphere butyl acrylate (2200 mg, 17.16 mmol) and 2-bromoisobutyric *tert*-butyl ester (12.5 μl, 0.067 mmol) were dissolved in degassed anisole (2.0 ml) and heated to 88°C. The polymerization was initiated by quick addition of a [Cu^I(PMDETA)Br] stock solution (0.2 M, 0.4 ml, 0.08 mmol in anisole) via syringe. After 36 h the solution was cooled with an ice bath and passed through an Al₂O₃ column to remove the copper catalyst. Remaining monomer and solvent was removed under reduced pressure and dried in vacuum (2095 mg, 95.2%).

M_n: 32700 g/mol, M_w: 37200 g/mol (SEC vs. PS standards), PDI: 1.14

¹H NMR (300.0 MHz, CDCl₃) 4.02 (b, 2 H; CH₂O_{PnBA}), 2.28 (b, 1 H; CH_{PnBA}), 1.91/1.58/1.47 (b, 2 H; CH_{2PnBA-Backbone}), 1.58 (b, 2 H; CH_{2PnBA}), 1.36 (b, 2 H; CH_{2PnBA}), 0.93 (b, 3 H; CH_{3PnBA})

Exemplary synthesis of poly(ethylene glycol)₆-Br macroinitiator by esterification. The macroinitiator was synthesized in modification as reported elsewhere². In an argon atmosphere 2-bromo-2-methylpropionic acid (5.35 g, 32.04 mmol) was dissolved in dry THF (20 ml) and oxalyl chloride (4.05 mg, 31.09 mmol) and 2 drops of DMF were added. The solution was added by syringe in a second flask filled with poly(ethylene glycol monomethylether) (11.2 g, 32.0 mmol, M_n: 350 g/mol). The mixture was cooled with an ice bath and imidazole (6.01 g, 88.3 mmol) dissolved in THF (40 ml) was added dropwise within 15 min. The solution was allowed to warm up, stirred overnight and the residue was fil-

tered. The filtered organic fraction was evaporated under reduced pressure and the residue was purified by column chromatography (ethyl acetate as solvent) (14.89 g; 93%).

¹H NMR (300.0 MHz, CDCl₃) 4.30 (t, 2 H; CH₂OCO); 3.74-3.51 (b, 26 H; PEG); 3.36 (s, 3 H; OCH₃); 1.92 (s, 6 H; (CCH₃)₂).

Exemplary synthesis of poly(ethylene glycol monomethylether)₆-b-poly(butyl acrylate)₂₂₄ featuring a molar mass of 29000 g/mol (M_n). In an argon atmosphere butyl acrylate (4000 mg, 31.21 mmol) and poly(ethylene glycol monomethylether)₆-Br (33.5 mg, 0.067 mmol) were dissolved in degassed anisole (3.0 ml) and heated to 88°C. The polymerization was initiated by quick addition of a [Cu^I(PMDETA)Br] stock solution (0.2 M, 0.4 ml, 0.08 mmol in anisole) via syringe. After 40 h the solution was cooled with an ice bath and passed through an Al₂O₃ column to remove the copper catalyst. Remaining monomer and solvent was removed under reduced pressure and dried in vacuum (2240 mg, 56%).

M_n: 29000 g/mol, M_w: 31700 g/mol (SEC vs. PS standards), PDI: 1.09

¹H NMR (300.0 MHz, CDCl₃) 4.03 (b, 2 H; CH₂O_{PnBA}), 3.65 (b, 26 H; PEG); 3.38 (s, 3 H; OCH_{3PEG}); 2.29 (b, 1 H; CH_{PnBA}), 1.92/1.59/1.49 (b, 2 H; CH_{2PnBA-Backbone}), 1.59 (b, 2 H; CH_{2PnBA}), 1.40 (b, 2 H; CH_{2PnBA}), 0.93 (b, 3 H; CH_{3PnBA}).

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