Reversible control of the 3D structure of polyelectrolyte/surfactant films at the air/water interface is showcased. A recently discovered mechanism is exploited to form highly efficient, stable and biocompatible films by spreading aggregates composed of poly-L-lysine and sodium dodecyl sulfate on the surface of water. Reversible control of: (1) the surface monolayer coverage, (2) the switching on or off discrete extended structures, and (3) the extended structure coverage is demonstrated for the first time. The intricacy by which the film structures can be controlled is unprecedented and opens exciting potential to optimize film properties by chemical design for novel biomedical transfer applications.

The design of polymer-based nanofilms with controllable architecture attracts strong attention due to applications in areas such as biosensing, tissue engineering and drug delivery. Preparation approaches include Langmuir Blodgett (LB) and Langmuir Schaeffer (LS) deposition onto solids from monolayers at the air/water interface, the formation of layer-by-layer (LbL) films on solids, and the formation of multilayer structures at both fluid and solid interfaces. LB and LS deposition methods benefit from use of a Langmuir trough as the density, morphology and in-plane structural analysis: fitting, (4) ellipsometry data on PLL/SDS spread film dynamics, (5) BAM images, (6) full-Q, structural analysis: fitting and parameters, and (7) mid-Q, structural dynamics analysis: fitting. See DOI: https://doi.org/10.1039/d2cc03766a

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Polyelectrolyte/surfactant films: from 2D to 3D structural control†

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† Electronic supplementary information (ESI) available: (1) Zeta potential measurements of PLL/SDS aggregates, (2) materials and methods, (3) low-Q, compositional analysis: fitting, (4) ellipsometry data on PLL/SDS spread film dynamics, (5) BAM images, (6) full-Q, structural analysis: fitting and parameters, and (7) mid-Q, structural dynamics analysis: fitting. See DOI: https://doi.org/10.1039/d2cc03766a
important pre-requisite of studying this system was that extended structures formed upon film compression were stable with time, allowing them to be characterized directly, and making them robust to potential applications. PLL was chosen over other polypeptides because in the bulk SDS can induce rigid in-plane interactions in a β-sheet conformation. This pre-requisite was met, as ellipsometry data comparing compressed spread films of the NaPSS/DTAB and PLL/SDS systems show that only the latter type of film is stable (Fig. 1A).

Our methodology is to form a film by dispensing aqueous droplets containing PLL/SDS aggregates onto the water surface of a Langmuir trough and use barriers to control its surface area. The spreading solutions comprise 100 ppm PLL and 0.80 mM SDS, which self-assemble to form negatively charged aggregates as characterized by zeta potential (ESI,† Section S1), chosen simply because aggregates charged with excess surfactant are effective in forming extended structures for the NaPSS/DTAB system. Several reflectometry techniques are applied to complement in situ measurements of the surface pressure, Π. Ellipsometry is used to measure the phase shift from the presence of the film, dΔ, which is related to the total amount of interfacial material per unit area.† Brewster angle microscopy (BAM) is used to image the lateral morphology on the μm-scale. Three implementations of neutron reflectometry (NR) are applied to resolve the film composition and structure. First is the recently-developed low-Qz analysis (0.01–0.03 Å⁻¹), where Qz is the momentum transfer normal to the interface, to resolve the surface excesses of PLL and SDS during three compression/expansion cycles. Second is the full-Qz analysis (0.01–0.25 Å⁻¹) to resolve the interfacial structure at a high film compression state. Third is a novel mid-Qz analysis (0.02–0.12 Å⁻¹) to resolve the structural dynamics during one cycle. Full details about the materials and methods used are provided (ESI,† Section S2).

The dynamics of PLL/SDS spread films were first examined by combining measurements of Π with the low-Qz analysis of NR, ellipsometry and BAM. First, the Π–A film response over three cycles is shown (Fig. 1B). Film compression initially results in a continuous increase in Π, attributed to enhanced molecular interactions with an increasing number of surfactant molecules per unit area in what we term the ‘surface monolayer’, i.e., a layer of surfactant in contact with air (hydrophobic driving force) with hydrated polyelectrolyte bound to the headgroups (electrostatic driving force). Upon further compression, beyond state iii, Π remains constant at ~28 mN m⁻¹, which is attributed to collapse of the surface monolayer, i.e. expulsion of material either to bound extended structures or the bulk. Expansion of the film is characterized by a large hysteresis in Π, the presence of a pseudo-plateau and a final value of Π close to the initial one, consistent with reincorporation of material back into the surface monolayer yet with a kinetic barrier.

The low-Qz analysis of NR was applied to provide the surface excesses of PLL and SDS (Fig. 1C). An explanation of the fitting procedure is provided (ESI,† Section S3). In comparison with the value 0.1 mól m⁻² at the collapse, upon further compression 0.1 mól m⁻² continually rises to exceed this value. This observation demonstrates that the material expelled from the surface monolayer beyond the collapse remains bound in the form of extended structures rather than being lost to the bulk. From 0.1 mól m⁻² at the maximum compression state measured, and with the assumption that 0.1 mól m⁻² in the surface monolayer does not increase by further compression of the film after the collapse, it may be noted that 27% of the SDS would be in the extended structures; we will return to this point later. Moreover, despite the large hysteresis in Π, there is no hysteresis in Γ, indicating that there are equivalent amounts of material in the film at corresponding...
surface areas during compression or expansion, which suggests that the hysteresis is attributed to a kinetic barrier for the transfer of material from the extended structures to the surface monolayer. These results are supported qualitatively in values of d1 recorded over successive cycles using ellipsometry (ESI,† Section S4). Lastly, the film composition over successive cycles is generally similar, hinting at their robustness to potential applications.

Next, we applied BAM to visualize the films (Fig. 1D). While prior to the collapse, images i, ii and iii are uniform with increasing brightness, images iv and v after exhibit discrete regions on the μm-scale that grow in number during compression, which we have reproduced in higher resolution combined with analysis of their coverage (ESI,† Section S5). The regions are attributed to discrete extended structures in contact with the surface monolayer and disappear in image vi upon expansion due to transfer of material back to the surface monolayer resulting in a homogeneous film once again.

A second implementation of NR exploiting the full $Q_z$-range allows us to resolve the extended structures of PLL/SDS films at maximum compression state v (Fig. 1B). Neutron reflectivity profiles in 4 isotopic contrasts with fits to a common interfacial model in stratified layers (Fig. 2A), and volume fraction ($V_f$) profiles (Fig. 2B) are shown. An explanation of the fitting procedure and a table of structural parameters is provided (ESI,† Section S6). A Kiessig fringe observed in data in the two isotopic contrasts that have the greatest scattering contrast between the surfactant chains and solvent, i.e., PLL with deuterated SDS in air contrast matched water (ACMW, 8.1% v/v D$_2$O in H$_2$O) and PLL with SDS in D$_2$O (purple arrow), reveal the presence of extended structures with surfactant present below the surface monolayer. The extended structure layer has a thickness of 21.8 ± 0.8 Å (almost twice that of the SDS monolayer), and a model also involving PLL in the layer did not improve the fit. We infer that the structures are either discrete patches of SDS bilayer wrapped by unresolved PLL or bound SDS hemimicelles. The amount of SDS present in the extended structure is 29 ± 1%, consistent with the 27 ± 1%

Fig. 2 (A) Neutron reflectivity profiles of a PLL/SDS spread film with deuterated SDS in D$_2$O (blue), SDS in D$_2$O (orange), deuterated SDS in ACMW (red), and SDS in ACMW (green); continuous lines show the model fits; purple arrow at $Q_z = 0.1$ Å$^{-1}$ indicates a Kiessig fringe symptomatic of the extended structure. (B) Corresponding volume fraction profiles of PLL (blue), SDS (red) and solvent (cyan).

Fig. 3 Neutron reflectivity profiles of a PLL/SDS spread film in D$_2$O at different compression states: (A) monolayer (ML) region and (B) extended structure (ES) region; states i–v are defined in Fig. 1B; solid lines show the simulated ML models and fitted ES models. (C) Variation of $π$ (black line) and fitted extended structure coverage (violet squares) with respect to the time; black and violet arrows indicate film collapse and the onset of extended structures, respectively; variation of area versus time is also shown.
The extended structures start to form (violet arrow) at the collapse (black arrow). The coverage increases with film compression beyond the collapse and decreases back down to 0% during the II pseudo-plateau upon expansion, indicating that the surfactant in the extended structures has been fully resupplied to the monolayer. While the increase in coverage of extended structures takes ~7 min, the reduction takes ~10 min, consistent with the kinetic barrier to resupply of material to the surface monolayer. Although NR has been used previously to resolve changes in film composition under surface area dynamic, this is the first time to the knowledge of the authors that it has been used to resolve changes in the extended structures of a dynamic air/water interface, and critically it highlights the unprecedented control gained over 2D versus 3D structures in P/S films, schematically illustrated (Fig. 4).

The PLL/SDS spread films studied in the present work are stable and reversible in their dynamics, which make them robust and amenable to transfer applications. The combination of the new film spreading approach with established deposition techniques may offer economic and environmental advantages as the amount of materials used and waste generated are low compared to other methods. As a result, 3D structures could be designed with controllable architecture and deposited onto solids for biomedical applications such as wound dressings, antimicrobial coatings or drug delivery applications.

Coupling of reflectometry techniques to a Langmuir trough has allowed us to elucidate the compositional and structural dynamics and directly characterize the extended structures in P/S spread films for the first time. This approach must now be urgently applied to other systems to understand in greater depth the physicochemical film properties, such as by tuning specific amino acid interactions with reference to different polypeptide conformations adopted in the bulk (e.g. α-helices by polyarginine/SDS versus β-sheets by PLL/SDS).

The mid-Qs structural dynamic application of NR showcased in this study opens the possibility to understand a wide variety of synthetic and biological systems that adopt 3D morphologies. Further applications of the method include, for example, particle-laden interfaces that present buckling or jamming phenomena, and lung surfactant models where the transfer of lipid between the surface monolayer and extended structures during respiration is vital for the stabilization of alveoli.

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Conflicts of interest

There are no conflicts of interest to declare.

References