Processing-Induced Densification Governs Patterns and Rheological Behavior of Langmuir Polymer Films

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Self-assembly is an effective strategy to prepare films at fluid interfaces. Conventionally, the structure and properties of self-assembled films are tuned through molecular interactions, chemical modifications, and varying pH. Here, we show that the preparation pathway, specifically the solvent evaporation rate during Langmuir film formation from homogeneous dissolved solution, provides an alternative route for tuning patterns and rheological properties. Although such pathway-dependent behavior has been reported for spin-coated polymer films [1]. However, a quantitative relationship between preparation conditions and the properties of Langmuir polymer films has remained unexplored. To quantify the influence of preparation history, we systematically investigated films prepared with varying (i) solvent evaporation rates (E_v) and (ii) initial polymer concentrations (c_0) [2]. Films of identical thickness produced using different combinations of c_0 and E_v, exhibited significant variations in the *in-plane* compressibility modulus, highlighting the importance of preparation pathways. Although variations in c_0 and E_v produced similar patterns, their mechanical responses differed markedly: the maximum compressibility modulus scaled as $\varepsilon_{max} \sim c_0$, while exhibits contrast behavior with E_v, as $\varepsilon_{max} \sim 1/E_v$. To unify these observations, we introduce an effective parameter (Ξ) that combines the effects of c_0, E_v, and the polymer chain length (N). The compressibility moduli collapse onto a linear scaling with Ξ, demonstrating that slower preparation rates produce mechanically stiffer films. These findings establish the preparation pathway as a predictive parameter for controlling both pattern formation and the viscoelastic properties of ultrathin Langmuir polymer films.

References:

[1] S. Chandran et al., ACS Macro Lett., **6**, 1296 (2017)

[2] P. Mahawar et al., ACS Polym Au, **4**, 302, (2024)

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