Diffusion of Star Polyelectrolytes in Ultrathin Coatings: a Neutron Reflectivity Study

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Assembly of polymers lies at the heart of synthetic biological matter and the materials used in drug delivery[1], photonics[2] and energy storage.[3,4] When exposed to different environmental stimuli (pH, salt concentration, electrochemical alteration, etc.), assembled polymers adjust via molecular motions, and these new structures may alter a material's physical properties and performance. Layer-by-layer (LbL) ultrathin polymer films epitomize such assembled functional materials, currently finding application as versatile drug delivery and antifouling coatings.[1,5,6] Achieving controlled, multistage delivery of drugs or maximizing the efficiency of antifouling coatings requires precise control of film layering *i.e*., molecular localization either within the film or at the film surface. One of the best non-invasive methods to explore film layering and polymer mobility in LbL films is neutron reflectivity (NR), which we have done at the Spallation Neutron Source Liquids Reflectometer at Oak Ridge National Laboratory.

In this *Science Snapshot*, we highlight our recent results of film stratification and polyelectrolyte diffusion in star-polymer-containing LbL films using neutron reflectivity.[7,8] In these studies, we explored the effect of polymer branching on molecular diffusivity triggered by exposing the LbL film to salt solutions. As salt ions weaken electrostatic bonding between poly(carboxylic) acids (e.g., linear or n-arm star poly(methacrylic acids), *L*PMAA and nPMAA, respectively) and a linear polycation, molecular mobility of all components is enhanced. While the effect of salt concentration on polymer diffusivity can be studied by *in-situ* ellipsometry[7] and fluorescence recovery after photobleaching,[8] neutron reflectivity provides unique information on the impact of such diffusivity on film stratification. In our experiments, we used a deuterated polycation to create neutron contrast within LbL films and observed changes in internal roughness (film stratification) as salt ions promoted enhanced molecular diffusivity. Our results showed that as-deposited films containing star polyelectrolytes were less well stratified compared to films composed of linear polymers. However, this difference in internal stratification could be due to either molecular mobility or result from enhanced external roughness of star containing films.[7] Exposure of the assembled LbL films to salt solutions allowed us to differentiate between these two possible contributions and directly observe enhanced molecular diffusivity of assembled polymers. **Figure 1** shows that exposure of star-containing LbL films (the inset of Fig. 1 depicts 8 arms, abbreviated 8PMAA) to salt solutions caused rapid intermixing of polymers perpendicular to the substrate that was much faster than the rate of intermixing in films containing a linear counterpart of the star polymer, *L*PMAA. Collecting data as a function of exposure time to the salt solution allowed us to determine polymer diffusion coefficients using a limited-source diffusion model. The diffusion coefficients of polycations in star-containing LbL films were up to one order of magnitude larger than those of all-linear LbL films. We attribute this enhanced diffusion in star-

containing multilayers to a lower density of ionic contacts and a fundamentally different diffusion mechanism relative to linear polymers.

In summary, neutron reflectivity studies with star-containing LbL films enabled, we believe for the first time, quantifying molecular diffusivity in star-containing LbL films and demonstrating the greater mobility of star polyelectrolytes in multilayer assemblies. These results add to a fundamental framework for development of novel smart coatings with controlled properties for biomedical, marine and optical applications.

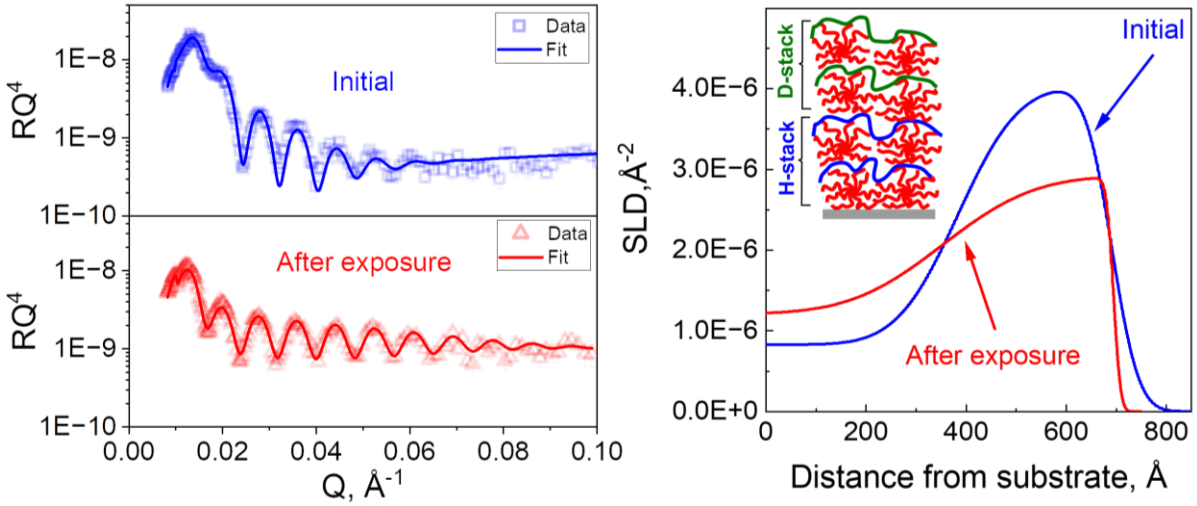

Fig. 1. (A) Neutron reflectivity data (plotted as RQ^4 to enhance small features) and (B) the corresponding neutron scattering length density (SLD – related to neutron refractive index) profiles for 8PMAA/(*h*QPC/8PMAA)$_3$(*d*QPC/8PMAA)$_3$ LbL films deposited at pH 6 before and after 45-min exposure to 0.25 M NaCl solutions. Inset shows the LbL film design used in the study; red stars represent 8-arm PMAA (8PMAA), blue lines – hydrogenated polycation (*h*QPC), and green lines – deuterated polycation (*d*QPC). Reprinted (adapted) with permission from Ref. 8. Copyright 2023 American Chemical Society.

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