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Polyanion Diffusion in Polyelectrolyte Multilayers

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Coatings of oppositely charged macromolecules (proteins, DNA, polyelectrolytes) are used for surface modification and functionalization. Yet, it remains a challenge to control the position and mobility of the molecules within the coating. As a model system, polyelectrolyte multilayers were used, which were prepared by the sequential adsorption of oppositely charged polyions. With neutron reflectivity, the diffusion constant of the polyanion PSS was measured. Two parameters were found to be important: (i) the conformation of the polyelectrolytes, which depends on the ion concentration in the deposition solution and (ii) the molecular weight of the polycation; the latter was the dominant parameter. Thus, the diffusion coefficient of PSS could be varied by five orders of magnitude; the observed scaling laws are consistent with sticky reptation.

An important question concerns the relationship between the polyelectrolyte composition in the multilayer and the deposition solution. Multilayers were prepared from binary mixtures of long deuterated PSS_{long} and short protonated PSS_{short}. A small amount of PSS_{long} in the deposition solution led to a disproportionate increase of PSS_{long} in the film, consistent with the higher diffusion coefficient of PSS_{short}. The results provide insight into the parameters which influence polyelectrolyte mobility and furthermore demonstrate how polyelectrolyte mobility influences film composition.

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