Molecular Ordering in Layer-by-Layer (LbL) Polyelectrolytes Films Studied by Nonlinear Optical Spectroscopy

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Nanostructured Layer-by-Layer (LbL) films produced by electrostatic self-assembly of alternating cationic and anionic polyelectrolytes are finding many useful applications as biosensors and in optoelectronics [1]. They have the advantage of allowing nanometer control of film thickness and composition by selecting the appropriate adsorbing species and tuning the experimental conditions for adsorption (concentration, pH, ionic strength, etc). However, for optimizing their applications a thorough structural characterization of the films is often needed, but difficult to obtain with traditional techniques. Here we use Sum-Frequency Vibrational Spectroscopy [2], a nonlinear optical technique that probes the vibrational spectrum of interfaces and is sensitive to molecular orientational order, to investigate at the molecular level the adsorption and structure of polymeric LbL films. In particular, this technique allows probing *in situ* the surface charge density during polyelectrolyte adsorption *via* its effect on the water vibrational spectrum within the electric double layer. We present results on LbL films of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) adsorbed onto fused silica substrates, probing the influence of both pH and ionic strength on film structure. *In situ* measurements show that the polymer chains are quite disordered, as no signal from the polymer backbone can be distinguished. However, polymer adsorption is confirmed by changes in the vibrational spectra of surface water molecules that are induced by the interfacial electric field. Through phase-measurements of the surface nonlinear response, we can confirm the charge inversion at interface after the adsorption of each polyelectrolyte layer. *Ex situ* measurements show that the films are very homogeneous and ordered when dried by slow water evaporation, but become highly inhomogeneous on the millimeter length scale if dried by nitrogen flow [3]. We can also observe that the orientational order of each polyelectrolyte layer is modified by the adsorption of subsequent layers. Increasing the ionic strength of the polyelectrolyte solutions leads to a reduced orientational order of the adsorbed layers due to screening of the electrostatic interactions. These results have direct implications to LbL device performance.

Keywords: Layer-by-Layer films, polyelectrolytes, vibrational spectroscopy, sum-frequency generation.

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[1] O. N. OLIVEIRA JR., J.-A. HE, V. ZUCOLOTTO, S. BALASUBRAMANIAN, L. LI, H. S. NALWA, J. KUMAR, and S. K. TRIPATHY, *Handbook of Polyelectrolytes and Their Applications*, edited by S. K. Tripathy, J. Kumar and H. S. Nalwa, *Volume 1: Polyelectrolyte-Based Multilayers, Self-Assemblies and Nanoestructures*, 2001.

[2] P. B. MIRANDA and Y. R. SHEN, *Journal of Physical Chemistry B* **103**, 3292 (1999).

[3] H. S. SILVA, T. M. UEHARA, K. BERGAMASKI and P. B. MIRANDA, *Journal of Nanoscience and Nanotechnology* (in press).

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