Study of the Layer-by-Layer assembly of PDADMAC/PAA multilayer films as function of pH

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Polyelectrolyte multilayers (PEMs) fabricated by means of the Layer-by-Layer (LBL) technique are a good example of nanostructured polymer films that can be easily applied for surface modification and device fabrication [1].

PEMs are fabricated by the alternative assembly of polycations and polyanions on charged surfaces that is mainly driven by electrostatic interactions [2]. The stepwise assembly protocol allows obtaining structures with controllable composition at the nanoscale level in the growing direction, which can include multiple functionalities like proteins, nanoparticles, growth factors, lipids, etc. [3].

In this work we studied the assembly of poly(diallyl dimethyl ammonium chloride) (PDADMAC) and poly(acrylic acid) (PAA), which are a strong and a week polyelectrolyte respectively. The charge of PAA depends on the pH and increases with increasing pH [4] [5]. On the other hand, the charge of PDADMAC remains constant and is independent of the pH [6]. Since the main interaction in the build up of polyelectrolyte one would expect that the charging of PAA at high pH would favour the multilayer build up.

The assembly of PDADMAC and PAA in different pH ranging from 3 to 13 was followed in real time by means of the Quartz Microbalance with Dissipation (QCM-D) combined with ellipsometry. It was observed that at low pH, around 3, the assembly follows a supralinear trend and results in film thickness of 480nm. Surprisingly, with increasing the pH and the charge of PAA, the amount of assembled polymer diminishes what results in the film thickness of only 20nm.
In order to understand the interaction between PAA and PDADMAC and their behaviour at different pH, We applied Confocal Raman Microscopy (CRM) and Isothermal Titration Calorimetry (ITC) techniques. CRM allowed us to determine the stoichiometry between the polyelectrolytes and the degree of charge of PAA as a function of pH. By means of ITC it was possible to measure the heat of complexation of PDADMAC/PAA at different pH and establish the thermodynamic basis for the polycation-polyanion interaction.

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