Title: Stretching of weak polyelectrolytes at the single-molecule level

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Date: June 2020

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Polyelectrolytes (PEs) are defined as polymers that are provided by an electric charge once they are dissolved in water. Polymers can be easily modified to make them sensitive to a variety of spurs. The spur can boost changes in many physical properties, such as pH, temperature, solvent and composition.

In the case of weak polyelectrolytes, the charge is in general a dynamical and fluctuating variable. This fact leads to the phenomenon of Charge Regulation (CR), which is defined as the ability of weak polyelectrolytes to modulate their ionization state when there is a presence of a physicochemical perturbation. CR is present in plenty of processes of biological, environmental and technological interest.

The objective of this work is to study the mechanical response of weak polyelectrolytes at the single-molecule level in order to undestand the relation between Charge Regulation (CR) and mechanical stretching. Concretely, the three weak polyelectrolytes that will be studied are polyacrylic acid, hylauronic acid and polyethylenimine. The mechanical response during stretching of weak polyelectrolytes under certain conditions has always being investigated and is an area that is still being studied. A technique that is often used in order to analyze such stretching is the single molecule force spectroscopy (SMFS) using an atomic force microscope (AFM) under environmental control. It can also be studied by computational simulations using Monte Carlo with the aim to analyze how the elasticity of the polyelectrolyte vary depending on the pH changes or the salt concentration.

For the nanomechanical AFM-SMFS characterization of the single polyelectrolyte, the AFM probe consists of a triangular or rectangular flexible cantilever equipped with a tip. The AFM tip is used to pick up and extend single macromolecules. The force is measured through detection

of the cantilever deflection. By the displacement of the piezo positioner, the chain extension of the macromolecules (polyelectrolytes included) can be assessed. For AFM-SMFS experiments, the sample molecules are physically or chemically adsorbed on flat surfaces like mica, glass, etc.

Finally, the experimental mesures obtained can be simultaneously compared to mechano-statistical teories, such as WLC or FJC and simulation Monte Carlo (MC) computational methods. In order to make this comparison much easier, a minimal model that captures the fundamental aspects present in the stretching of a weak linear polyelectrolyte is used. Additionally, MC simulations can also provide protonation and conformational properties.

Key words: weak polyelectrolyte, stretching techniques, polymer titration, charge regulation, AFM, SMFS, polyacrylic acid, hylauronic acid, polyethylenimine, Monte Carlo simulations, RIS, SB, SBRIS