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Orientation change of polyelectrolytes in linearly elongated polyelectrolyte multilayer measured by polarized UV spectroscopy

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HIGHLIGHTS

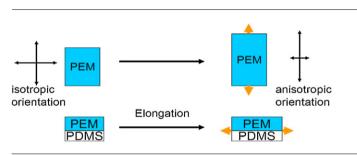
GRAPHICAL ABSTRACT

- ► The polyelectrolytes change their orientation upon elongation.
- The degree of orientation change depends on the ionic strength during preparation.
- The degree of directed local polarity depends on the preparation condition.
- The directed local polarity changes upon elongation.

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ABSTRACT

Supported polyelectrolyte multilayer (PEM) thin films produced by layer-by-layer self assembly, show interesting phenomena upon elongation and release like lithography-free surface structuring, controlled wettability, and stimuli-responsive nanovalves. To understand these effects, the structure and orientation change of PEM, when exposed to linear elongation were investigated by means of pyrene labeled polystyrenesulphonate and polarized UV spectroscopy. The samples were prepared either in solution containing 0.5 M NaCl or in salt free solutions, deposited on sheets of PDMS rubber and elongated laterally up to 10%. Our results show, that if the PEM is produced in the presence of salt the PEM contains a local polarity, depending on the orientation of molecules within the PEM. Upon elongation, the differences in oriented local polarity disappear. In the case of PEM prepared in salt free condition, the polarity within the PEM is independent of the molecular orientation. Upon elongation the orientation of dipole moment changes from isotropic to anisotropic. This effect is strongly enhanced by the presence of NaCl in the solutions from which the PEM were formed.

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1. Introduction

Polyelectrolytes (PE) are polymers containing electrolyte groups in their monomer blocks. Due to these electrolyte groups the PE interact due to electrostatic forces with each other, therefore they can be used to form polyelectrolyte multilayer (PEM) films, by utilizing layer-by-layer deposition (LbL) technique [1–3]. LbL assembly consists of sequential adsorption of polycation and polyanion layers onto oppositely charged surfaces [2]. The process is applied in a cyclic manner profiting from the surface charge overcompensation, which occurs while macromolecular species are adsorbed at the solid–liquid interface [1]. As a result the structure of PEM can be easily controlled on a molecular level [2]. PEM are films of usually less than 1 μ m thickness for different applications, ranging from chemo- or bio-sensors to coatings for medical implants, which enable cell adhesion and proliferation of injured tissues [4,5].

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