Experimental Report

Proposal: **9-11-1684** **Council:** 4/2014

Title: Investigation of conformational changes of polyelectrolyte chains in LbL-films upon adsorption at solid interfaces

This proposal is continuation of: 9-11-1645

Researh Area: Soft condensed matter

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Samples: PSS-PAH-PMAA-PVP-Silicon

Instrument	Req. Days	All. Days	From	To
FIGARO	7	4	19/09/2014	23/09/2014
D11	0	2		

Abstract:

PEMs can be considered polyelectrolyte complexes at interfaces that are fabricated using Layer-by-Layer (LbL) assembly. Depending on various parameters, polyelectrolyte complexes in bulk possess either a "brush-like" or a "pancake" structure, it is not clear how structure formation in PEMs occurs through a stepwise assembly process. In contrast to polyelectrolyte behavior in solution, individual layers are thinner when deposited from salt free solutions and thicker when deposited at high salt concentrations. Our first GISANS measurements showed that the polyelectrolytes chains have a flattened coil conformation in films composed of poly(allylamine) (PAH) and poly(styrenesulfonate) (PSS) for one preparation condition. GISANS on films composed of different polymers under different preparation conditions will allow us to determine the conformation of the polyelectrolyte chains in each cases and, after enough measurement, to understand more the mechanism of deposition of the multilayer films.

Two multilayer films were measured by GISANS on the FIGARO instrument : one sample composed of poly(allylamine hydrochloryde) (PAH) and a mixture of deuterated as well as non-deuterated poly(styrenesulfonate) (PSS) and one composed of poly(4-vinyl-N-methylpyridinium) (PMeVP) and a mixture of deuterated as well as non-deuterated poly(methacrylic acid) (PMAA). Four multilayer films were measured by reflectometry on the FIGARO instrument : one sample composed of poly(allylamine hydrochloryde) (PAH) and deuterated as well as non-deuterated poly(styrenesulfonate) (PSS) and three composed of poly(4-vinyl-N-methylpyridinium) (PmeVP) and deuterated as well as non-deuterated poly(methacrylic acid) (PMAA).

These films were prepared on silicon wafers with the LbL (Layer-by-Layer) method. The (PSS-PAH) films were prepared with polyelectrolyte solutions consisting of $3x10^{-3}$ monomol/L of PSS or PAH in 2 M of NaCl salt solutions, the two by spraying with different angles. The (PMAA-PMeVP) films were prepared by dipping in polyelectrolyte solutions consisting of 10^{-2} monomol/L of PMAA or PMeVP in pure water. The films measured by reflectometry were composed of several repetitions of alternation of one deuterated layer pair with 1 to 4 non-deuterated layer pairs. The films mesured by GISANS had an amount of 4 layer pairs which correspond to a thickness of 1 µm for the (PMAA-PMeVP) film, with PMAA layers composed of a mixture of 30% deuterated – 70% non-deuterated PMAA, and an amount of 80 layer pairs which correspond to 400nm for the (PSS-PAH) film, with PSS layers composed of 30% deuterated – 70% non-deuterated PSS.

Two films were measured by GISANS on the FIGARO instrument. The data were collected at a fixed incident angle θ_z of 1° with a wavelength resolution $d\lambda/\lambda$ of 7%. We used collimation slits of 1.7*10 mm^2 and 6.667*10 mm^2.

Four films were measured by reflectometry on the FIGARO instrument. The data were collected at two incident angles of 0.622° and 2° with a wavelength resolution $d\lambda/\lambda$ of 0.82%. We used collimation slits of 0.216 mm for 0.622° and 0.7 mm for 2°, which leads to an angular resolution $\Delta\theta/\theta$ of 0.9%.

Figure 1 shows the reflectivity curve for one of the films and the fit done with Motofit. We can see the typical Bragg pics due to the layered structure and the alternation of deuterated and non-deuterated layers.

From the fit of the reflectivity curve, we can determine the internal structure of the film perpendicular to the surface (thicknesses, SLDs of the deuterated and non-deuterated parts and the roughnesses at the interfaces of the deuterated and non-deuterated parts) and, what is the most interesting for us, the average size of a PSS chain perpendicular to the surface.

Figure 2 shows the GISANS signal for the wavelength of 7 Å and 9 Å for the (PMAA-PMeVP) film. The curves follow an high q limit:

$I = \frac{12}{q^2 a^2}$ with I the intensity, q the scattering vector and a the pair correlation length.

After fitting the curves and calculating a, we will be able to determine the radius of gyration of a polymer chain in the film :

$R_G = a * \sqrt{\frac{N}{6}}$ with R_G the in-plane radius of gyration and N the number of monomeres in a polymer chain.

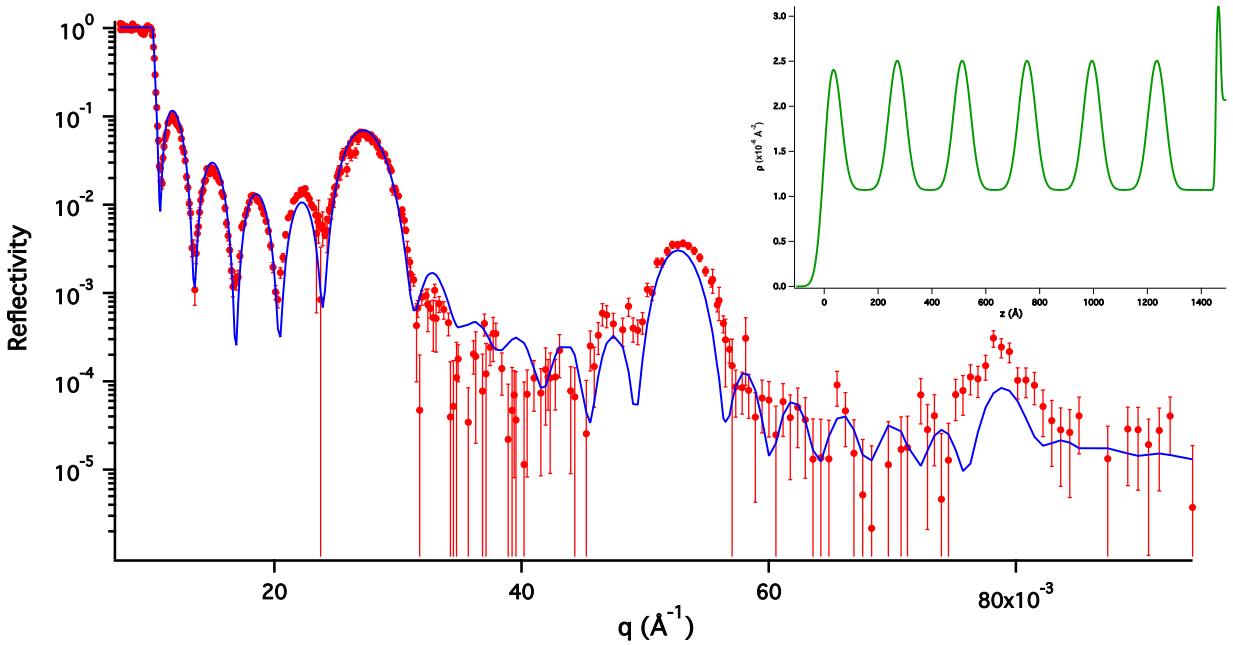

Fig. 1 : Reflectivity curve for one of the (PMAA-PMeVP) sample prepared by dipping. The red point represent the experimental the data, the blue line represent the fit.

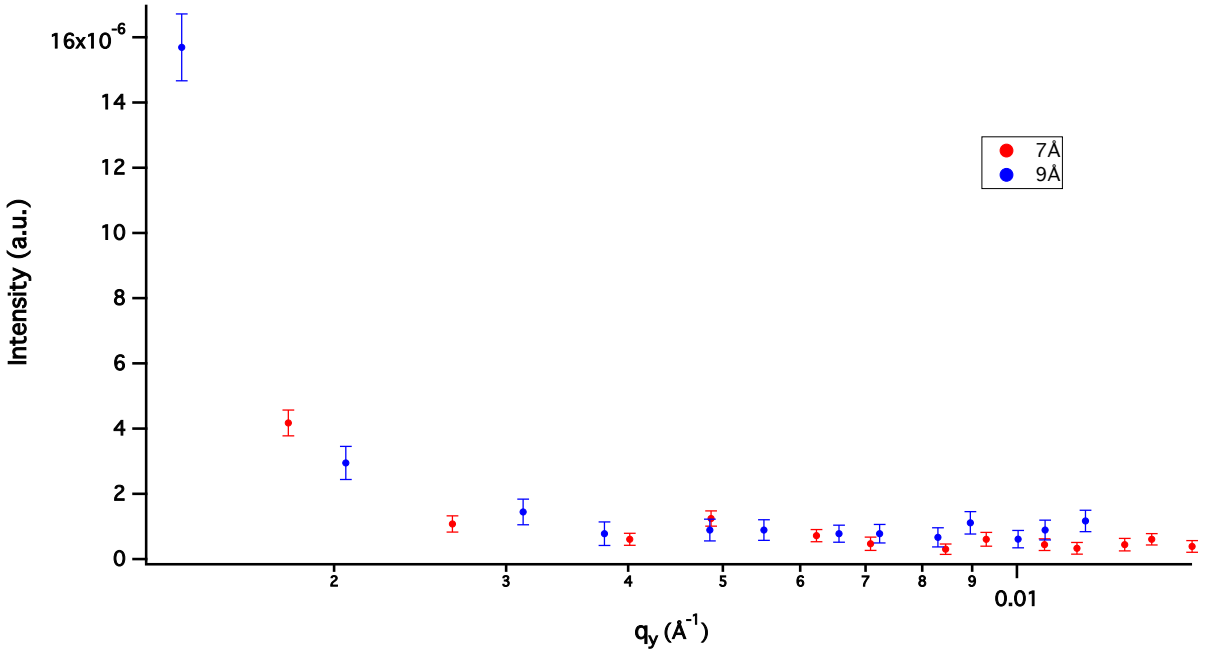

Fig. 2 : q_y cut of the GISANS signal at the Yoneda peak for the (PMAA-PMeVP) film. The curve is composed of the data for the wavelength of 7 Å (red points) and 9 Å (blue points).