Experimental Report

Proposal: **9-11-1645** **Council:** 10/2012

Title: Investigation of chain deformation"flattening" in polyelectrolyte multilayers upon adsorption at solid interfaces

This proposal is continuation of: 9-11-1599

Researh Area: Materials

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Samples: PSS
PAH
Silicon

Instrument	Req. Days	All. Days	From	To
FIGARO	9	8	26/02/2013	28/02/2013
			03/07/2013	08/07/2013

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.
Multilayer films composed of poly(allylamine) (PAH) and deuterated as well as non-deuterated poly(styrenesulfonate) (PSS) will be prepared with a varying number of non-deuterated layers between the deuterated layers. In the deuterated layers, the percentage of deuteration will be adjusted from about 20% to 50%. After having established the feasibility of GISANS measurements on this sample in the foregoing experiment, now, a systematic study on the lateral polymer conformation is proposed under varying preparation conditions.

Multilayer films composed of poly(allylamine hydrochloryde) (PAH) and a mixture of deuterated as well as non-deuterated poly(styrenesulfonate) (PSS) and one film composed of poly(N,N-diallyl-N,N-dimethyl ammonium chloride) (PDADMAC) and a mixture of deuterated as well as non-deuterated PSS were measured by GISANS on the FIGARO instrument.

These films were prepared on silicon wafers by dipping with the LbL (Layer-by-Layer) method in the polyelectrolyte solutions, which consist of $3x10^{-3}$ monomol/L of PSS and $3x10^{-3}$ monomol/L of PAH in 2 M of NaCl salt solutions for the (PSS-PAH) films and of 10^{-3} monomol/L of PSS and 10^{-3} monomol/L of PDADMAC in 50mM of acetate, 0.2 M of NaCl salt, pH=5.6 solutions for the (PSS-PDADMAC) film. The solutions of PSS were mixture of 50% deuterated – 50% non-deuterated PSS and 30% deuterated – 70% non-deutrerated PSS for the (PSS-PAH) films and mixture of 50% deuterated – 50% non-deuterated PSS for the (PSS-PDADMAC) film. The films had an amount of 40 to 70 layer pairs which correspond to thicknesses from 300 to 500 nm.

These 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 1.3*10 mm^2 and 6.667*10 mm^2.

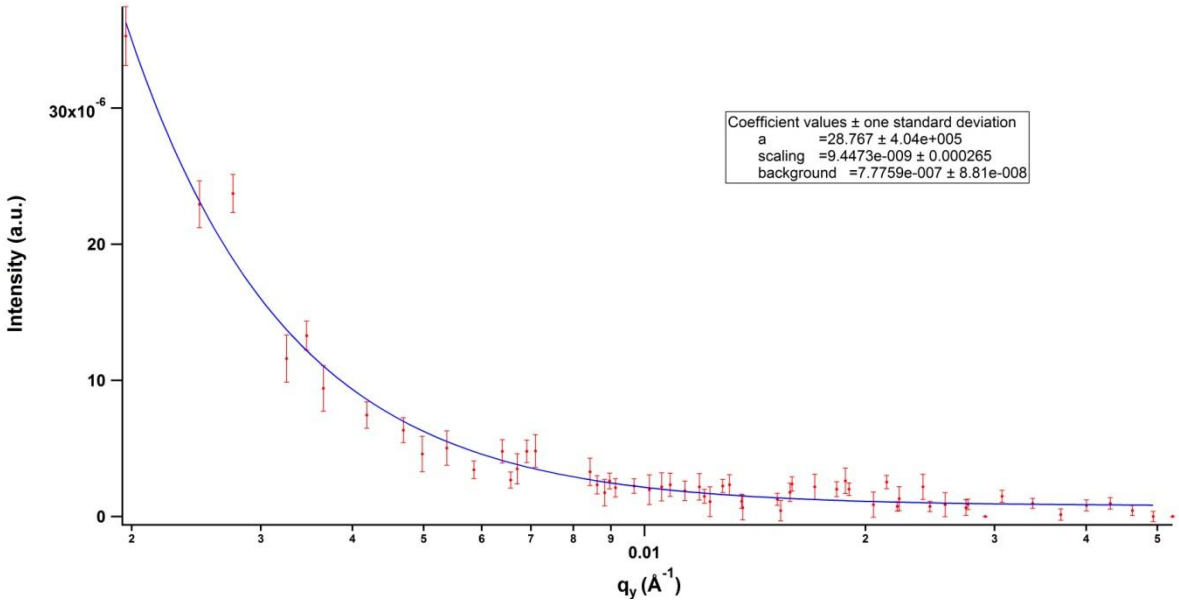

Fig. 1 : q_y cut of the GISANS signal at the Yoneda peak (red crosses) for the 50% deuterated PSS sample as explained in the text. The curve is composed of the superposition of the data for the wavelenght 5 Å, 7 Å and 9 Å (red points). The blue line is the theoretical model.

A considerable simplification of the problem can be achieved when confining the data analysis to the scattering in q_y direction at the Yoneda peak [1]. The scattering is governed by the evanescent wave in this case which is parallel to the surface. Therefore the scattering comes mostly from 'bulk' scattering of a thin layer at the surface and the surface reflectivity signal is suppressed. In this case the form factor of the sample can be observed directly.
Therefore we perfomed intensity cuts along the q_y axis at the Yoneda peak as it was introduced by Stamm and co-workers [1]. The cut performed at different wavelength (cf. Figure 1). Contrary to Stamm who used a Debye function, we use the high q limit:
$I = \frac{12}{q^2 a^2}$ with I the intensity, q the scattering vector and a the pair correlation length.

Then we can determine the in-plane radius of gyration of a PSS chain by using :

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

We can't be more precise than a few nanometers with this analysis.

We have determine than the radii of gyration of a PSS chain for the three samples are comprised between 22.5 nm and 24.5 nm. So we can conclude two things :

- We have the same result, with the same quality of data, for 30% and 50% deuterated PSS.
- We have the same radius of PSS chains for different deposition condition (different polycation and solvent).

Finally, by using this results in addition with reflectometry (experiment 9-12-335 on SUPER-ADAM), which allows us to determine the size of a polymer chain perpendicular to the surface, we can determine the conformation of a polymer chain. In the two (PSS-PAH) cases, we have a smaller radius perpendicular to the surface than a radius parallel to the surface, which mean that we have flattened coil conformation.

[1] Kraus J, Müller-Buschbaum P, Kuhlmann T, Schubert DW, Stamm M *Europhys.Lett.* **2000**, 49, 210.