# In situ & Real-time Characterization of Bio-mimetic Thin Films: Neutron Reflectivity Study

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## 1. Introduction

A sound understanding of the interfacial behavior of polyelectrolytes is necessary for numerous applications of thin film coating, particularly those involving biomimetic membranes[1], stabilization of colloids[2], electronic materials[3], and cell adhesion for biomedical applictions[4]. A variety of external parameters, such as salt concentration in the subphase[5], pH[6], nature of the adsorbing surface[7], temperature[8], and solvents[9] can be easily used to control and tune the interfacial properties of polyelectrolytes.

Adsorption characteristics of polyelectrolytes on various surfaces have been extensively reported.[10] The nature of the adsorbed layer was found to be dependent on the strength of the charge interaction between the polymer chain and the surface. For example, the adsorbed layer can be thin or form a brush-like structure. An air-water[11] interface has been the preferred choice of many researchers, due to its neutrality, its strong surface attraction for polymers, and its smooth surface, which provides free conformational movement of the polymer chains. The strong surface attraction of this interface is caused by the low surface energy of most of the organic polymers relative to the surface tension of water. Problems encountered due to the lack of interaction of the neutral surface (air) with the electrostatic part of polymer were solved by hydrophobically modifying the polyelectrolytes.

In this presentation, we will show a detailed study on the structure of Langmuir monolayers of sulfonated polystyrene with a low level of sufonation (3~35%) at the air/water interface. To get the exact depth profile, *in situ* neutron reflectivity (NR) was performed at the air/water interface. With the 35% charged polymer, the highly stretched brush was observed, while only localized thin layer was observed for the polymers with less than 24 % of sulfonation. The combined study of NR and ∏-A isotherms provides basic structural information as a function of sulfonation level including (a) how the ionomer molecules are adjusting their configurations when the layers are compressed, (b) whether the charged segments are indeed localized within the films

## 2. Instrumentation and Experimental

### 2.1 Instrumentation

Specular neutron reflectivity was performed on a NG7 horizontal liquid spectrometer at the Center for Neutron Research (National Institute of Standards and Technology, Gaithersburg) using a wavelength λ of 4.76Å. A mini Langmuir trough was mounted on the sample height elevator of the liquid spectrometer so that *in-situ* isotherms measurements could be made concurrent with the neutron measurements. The isotherms carried out under neutron exposure were very similar to those measured previously. The horizontal slits were set to 30 mm. A one-dimensional position sensitive detector (PSD) having the 255 channels oriented perpendicular to the sample surface enables one to simultaneously record both a specular intensity and an incoherent background scattering. The reflected intensity was obtained by integrating the peak channels. The measured intensity has been then converted to the absolute reflectivity by normalization with the detector/monitor ratio below the critical angle, where total external reflection occurs.

The specular reflectivity was measured as a function of scattering wave-vector transfer $q_z=4\pi/\lambda\sin(\theta)$, where $\theta$ is the incident angle.
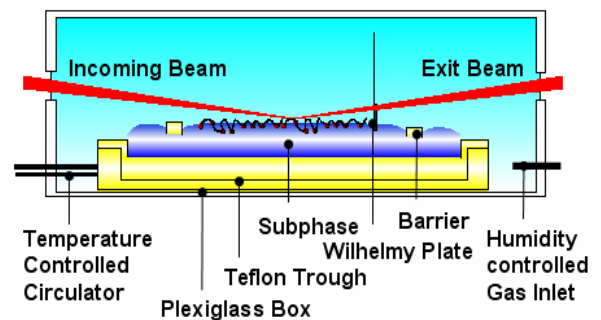


Figure 1. Schematic of neutron reflectivity setup at the air/water interface

### 2.2 Analysis

To explain the general behavior according to the film thickness $d$ and the roughnesses ($\sigma$), the Born approximation can be used. The reflectivity $R_F(q_z)$ is given by

$$R(q_z) \propto R_F \left| \int \frac{dSLD(z)}{dz} \exp(-iq_z z) \right|^2$$

where $R_F$ is the Fresnel reflectivity at an infinitely sharp interface, which can be approximated by $(q_c/q_z)^4$ at high $q_z$ region. $dSLD(z)/d(z)$ is the gradient of *SLD* of the sample along the surface normal. The sharp interfaces are smeared by rms roughness, $\sigma$,

which is given by convoluting the infinitely sharp profile with a Gaussian smoothing function. Refractive index (n) of medium is given in terms of the *SLD* by $n=1-\lambda^2 SLD/2\pi$, where $\lambda$ is the wavelength of the neutron beam. The refractive indices of "deuterated" PSSA are quite different from the subphase media, i.e., pure water.

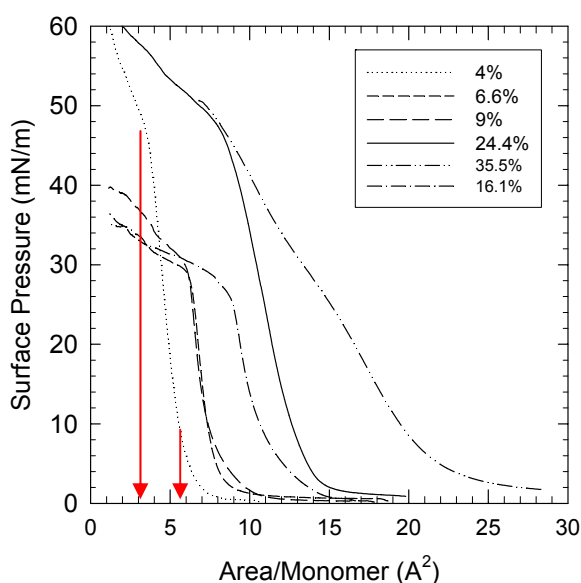## 3. Results and Discussion



Figure 2. Surface isotherms of polyelectrolytes as a function of degree of sulfonation

The inception of a plateau signifies the point at which the charge effect comes in picture and leads the surface activities, i.e., submerging or packing of polymer chains. From Figure 2, PSSA with 4% and 5% of degree of sulfonation show the highest plateau (~ 45mN/m) and collapse pressure (~ 65mN/m), indicating that they are highly compressible. The unique feature of PSSA of 35% is its broad transition, which we also considered a plateau. The transition pressure is slightly lower (from ~ 15mN/m to ~35mN/m) than the plateau region of PSSA 6%-16%, and lowest among all the PSSA used. However, the isotherm occurs at the highest mean molecular area, indicating dominance of the electrostatic interactions over the hydrophobic interactions. Hence, the molecules are highly expanded.

The neutron reflectivity of 35% sulfonated membrane shows a strong indication of brush-like submersion into the subphase. The bottom layer is fully extended and the data can be best fitted with a parabolic brush-like layer, which is approximately > 60 Å long. The upper layer, however, remains 20 Å thick. We used the brush-like profile given by $SLD_2(1-(z/t_2)^2)$, where $SLD_2$ and $d_2$ are the scattering length density at the interface of the upper and bottom layer, respectively, and $d_2$ is the thickness cutoff for the bottom layer. This sudden transition was in fact highly reversible, as observed in the hysteresis curves in Figure 2d. These

results confirm that the polyelectrolytes chains with ion contents > 35% are submerged in the water subphase with increasing surface pressure, due to the strong repulsive interaction, when the polyelectrolyte chains are compressed into a small area at the air-water interface.

## 4. Summary

The Langmuir monolayers of randomly charged PSSA*x* with various degrees of sulfonation (*x*) ranging from 4% up to 35% were studied. The randomly charged PSSA were found to be amphiphilic and stable, though greatly dependent on the charge percentage used at the air-water interface. We found three specific regimes for the range of polyelectrolytes (4%-35%) used for the study. For PSSA 35% neither hysteresis nor the formation of micellar structures was observed. Neutron reflectivity data showed that a brush transition occurs upon compression at smaller areas, by submersion of the chains into the water subphase. We placed PSSA 35% in the *polyelectrolyte* regime, due to the dominance of the electrostatic interactions over the hydrophobic interactions.

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