



	<b>Experiment title:</b> <b>Adsorbed Polyelectrolyte Layer at a Solid/Water Interface</b>	<b>Experiment number:</b> SC-387
<b>Beamline:</b>	<b>Date of experiment:</b> from: 10 <sup>th</sup> Dec to: 17 <sup>th</sup> Dec 1997	<b>Date of report:</b> 26 <sup>th</sup> Feb. 1998
<b>Shifts:</b>	<b>Local contact(s):</b> Oleg Konalov, Francois Rieutord	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

Olivier Theodoly\*, Thomas Waigh\*, Raymond Ober\*, Claudine Williams\*, Physique de Matière Condensée, CNRS URA 792, Collège de France, 11 place Marcelin Berthelot, F7523 1, Paris Cedex 05, France.

Jean Daillant\*, SPEC, Orme des Merisiers, CEA-Saclay, F91191 Gif-sur-Yvette Cedex, France.

**Report:**

The adsorption of polyelectrolytes on to surfaces is of vast industrial and technological importance. Applications vary from questions concerning the adhesion of milk proteins to milk bottles and dyes on 'clothes' fibres, to the stabilisation of colloids against flocculation. Randomly sulphonated polystyrenes (PSS) serve as an ideal model system to examine these phenomena since they may be synthesised with well defined degrees of polymerisation, charge content and hydrophobicity. The most striking feature of these highly charged polymers is that they can form an adsorbed layer on hydrophobic surfaces, unlike their hydrophilic counterparts. The aim of the experiment (SC-387) was to study the conformation of adsorbed polyelectrolytes at the *solid/aqueous interface* with high energy X-ray reflectivity.

The technique of X-ray reflectivity from polymers at the buried solid/liquid interface has not been previously tackled and it thus posed some unique problems. It was necessary to design a new liquid cell (figure 1) to allow the hydrophobic silanised silicon surfaces to be illuminated by the X-ray beam with a minimal loss of flux. Thin Kapton windows were used with the cylindrical teflon cell and the path length of the beam through the water was 24mm. The availability of high energy X-ray beams proved a great advantage of the beam line (ID13 compared to Troika). For example, the 20KeV beam used increased the transmitted signal by a factor of two when compared to an 18KeV beam. A further facet required by the liquid cell was the absence of ionic pollutants.

This required careful construction of the teflon housing so that the araldite water-tight seal was not in contact with the liquid reservoir and that the silicon wafers were immobilised using a vacuum pump. Great care was required to eradicate curvature of the wafer during pumping.

Normalisation of the resultant X-ray reflectivity profiles pose some additional questions. There is a currently unexplained loss of flux close to the critical edge. Analysis of the resultant curves was still possible using Patterson type correlation functions which allowed the calculation of polyelectrolyte film thickness with a relative insensitivity to the absolute normalisation. Film thickness are reduced with NaPSS compared to CsPSS which is currently ascribed to a change in the contrast mechanism i.e. the contribution of the polymer chain is more strongly weighted with the Na<sup>+</sup> cations.

An additional experimental observation was the existence of a density correlation length of c.a. 7nm perpendicular to the silanised surfaces into the bulk water. Whether this effect is a true hydrophobic density perturbation or an as yet unexplained experimental artifact is worthy of further study.

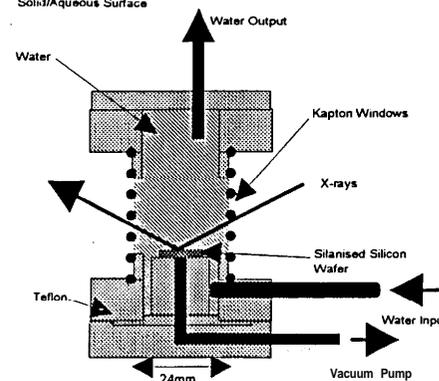
In addition to specular X-ray reflectivity experiments we probed the off-specular components with two PSS charge contents (Cs 35% and 55%) and measured an *in-plane correlation length* (Table 1). We currently ascribe this phenomena to the polyelectrolytes adopting a globular structure on the hydrophobic surface with the correlation length corresponding to the effect of inter-globular interference (fig. 2).

In conclusion high energy X-ray reflectivity is found to provide high resolution analysis of the conformation of adsorbed polyelectrolytes in water both perpendicular and parallel to a hydrophobic surface. Further detailed studies can be expected to provide yet more unique information on the rich variety of phenomena involved.

**Table 1 : Magnitudes of Film Thicknesses and In-plane Correlation Lengths for a Series of Adsorbed Polystyrenes with Varying Charge Contents.**

Sample with Percentage Charge Content (amount of added salt)	Film Thickness (Reflectivity, nm)	In Plane Correlation Length (Off-Specular, nm)
Cs 35% (CsCl=0M)	10.4	2
(CsCl=0.1M)	9	-
Cs 55% (CsCl=0M)	12	4
(CsCl=0.1M)	4	-
Na 55% (NaCl=0M)	4	-
(NaCl=0.1M)	2.4	-

**Figure 1 Construction of the Liquid Cell for Reflectivity Experiments at the Buried Solid/Aqueous Surface**



**Figure 2 Schematic Model for the Configuration of the Counter-ion Clouds. a) 35% and b) 55% sulphonations of polystyrene.**

