Experimental Report

28/10/2013

Proposal:	**9-11-1559**	**Council:**	10/2011
Title:	Understanding the non-uniform compression of polyelectrolyte multilayers.		

This proposal is continuation of: 9-11-1481

Researh Area: Soft condensed matter

Main proposer: **DE VOS Wiebe**

Experimental Team:
PRESCOTT Stuart
RICHARDSON Robert M.
MEARS Laura
DE VOS Wiebe
ABBOTT Stephen

Local Contact: BARKER Robert

Samples:
poly(allylamine hydrochloride)
deuterated poly(styrene sulfonate)
poly(ethylene imine)
poly(styrene sulfonate)

Instrument	Req. Days	All. Days	From	To
D17	3	3	30/11/2012	03/12/2012

Abstract:

We have recently developed a unique surface force style apparatus that allows direct measurements of the structure of polymer layers under compression using neutron reflection. We have used this setup to investigate polyelectrolyte multilayers (PEMs) under compression. We could show very clearly that the mechanical properties of these layers depend very much on the final layer being the positively charged PAH or the negatively charged PSSA. Even more interesting was the observation that the PAH terminated layer was compressed in a very non-uniform way: compressed water was preferentially expelled from the inner part of the layer, while the outer part retained all its water. On the other hand, the PSSA terminated layer behaved very uniformly under compression. We propose to continue our investigation on this topic specifically to understand this non-uniform behaviour. For this we will investigate a PEM that takes up a much higher amount of water: the non-uniform compression will either be much more pronounced, or it will only show up when most of the water is pushed out of the layers. In addition we will look at the effect of ionic strength on the non-uniform behaviour.

Title: Understanding the non-uniform compression of polyelectrolyte multilayers

Experiment: 9-11-1559 Dates: 30/11/2012 - 03/12/2012 Instrument: D17
Team: W.M. de Vos, S.B. Abbott, L.L.E. Mears, S.W. Prescott, R.M. Richardson
Local contact: R. Barker

Abstract

We have continued our investigations into understanding the origin of the non-uniform compression and 'odd-even' hydration effect in polyelectrolyte multilayers (PEM's). Using our unique sample environment, which combines a surface force type apparatus with neutron reflectivity, we have characterised the hydration under compression of PAH/PSS multilayer stacks with 11 and 47 bi-layers, with each of the polymers used as the final terminating layer. In addition, we also consider the case whereby we compress two oppositely terminated PEM stacks together to investigate a system with a neutral surface charge. With no confining pressure, PAH terminated samples are swelled by 20±1% (volume) with H_2O. A compression of 5 bars reduces this hydration to 10±1%. PSS terminated stacks are approximately 5% more hydrated that their equivalent PAH terminated samples both with and without a confining pressure. In PSS terminated stacks this hydration is generally uniformly distributed throughout the sample, however for PAH layers under compression a larger hydration is observed in the layers closest to the surface. This uneven hydration is more noticeable in thinner PEM stacks. When oppositely terminated PEM's are compressed together we observe almost complete dehydration at the interface between the two PEM's. Using this data we are developing a model that describes the hydration of this PEM system using a description of internal charges influenced by the charge species of the final adsorbed layer.

Introduction

The PEM system we consider consists of repeating alternate layers of poly(allylamine hydrochloride), PAH, and poly(styrene sulfonate), PSS. These layers are of particular interest as they are a suitable method to change surface properties [1] and are also of interest as possible capsules for drug delivery [2]. A previous experiment of ours investigated the compression of similar PEM's with 23 bi-layers when hydrated with demineralised water and a 0.1 M NaCl solution [3, 4]. The aim of this experiment was to extend the range of parameters investigated to include the sample thickness, the effect of fabricating a sample with a 0.1M NaCl – 2g/l PAH/PSS solution, and to investigate the effects of bringing oppositely surface charged PEM's together. The latter being an example of the new types of system that can be investigated with our apparatus.

Our recently developed apparatus combines a surface force type apparatus with neutron reflection using a silicon block and a flexible Melinex membrane [5]. Surface contact is achieved by inflating the membrane against the silicon surface, with molecular contact achievable over a large surface area as the membrane is able to deform over any trapped dust or long range (>1mm) surface roughness. The applied force is then controlled by the pressure used to inflate this membrane, allowing us to study PEM systems under compression.

The PEM layers were prepared with a spin-assisted layer-by-layer approach [4]. To assist in determining the distribution of hydration within the sample we selectively replace 3 PSSA layers with deuterated PSSA to split the sample into 4 equal sections. The selective deuteration results in Bragg peaks that allow for a clear determination of the structure of the multilayer. Three pairs of PEM's with 11, 23 and 47 bi-layers were adsorbed onto separate Si blocks, however one of each pair did not have the final PAH layer adsorbed onto it and the 23 bi-layer samples were created using a salty solution. In addition, a 21 bi-layer PAH terminated sample was also created on a Si block. This last sample was compressed with a Melinex sheet that had been coated with a 2 bi-layer PSSA terminated PEM.

Experimental Results

The first sets of experiments were to examine the 11 and 47 bi-layer samples. The experimental data and subsequent fits of the PSSA terminated samples are presented in figure 1. For the 11 bi-layer data set we have one Bragg peak and two Kiessig fringes, whereas for the significantly thicker 47 bi-layer sample we have up to 5 Bragg peaks and multiple fringes. Under a confining pressure these features shift to a higher Q value, indicating that the PEM is being compressed. The mechanism for this compression is to remove part of the water swelling the PEM layers as can be seen by the increased SLD observed at higher pressures in fig. 1c. The volume fraction of the water throughout the sample is determined by the fits and is found to be an almost uniform 25-26% at 0 bar. Appling 5 bar of pressure dehydrates the sample to about 13-15%. For the 11 bi-layer sample the dehydration is uniform; however, the 47 bi-layer sample demonstrates a linear 1.5% variation in the samples hydration with the higher hydration nearest to the surface, indicating a range to the effect of the charge of the final adsorbed layer. The exception is the final adsorbed layer, which due to the large surface charge has a hydration of 40% regardless of the confining pressure.

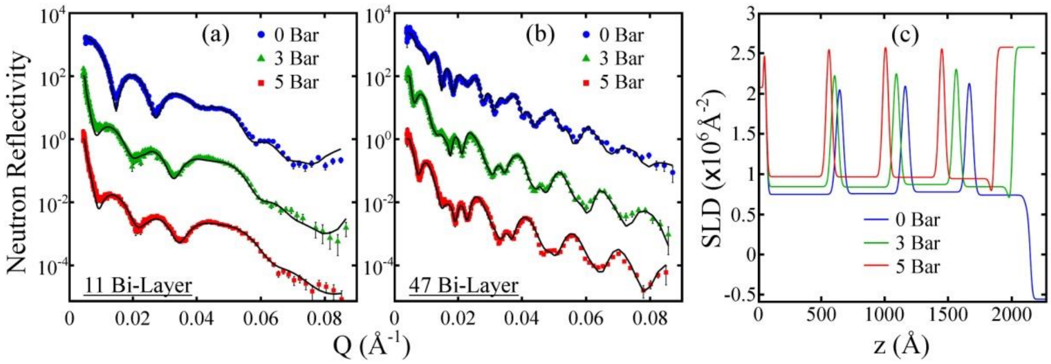

Figure 1: Neutron reflectivity data for a PSSA terminated PEM with (a) 11 bi-layers and (b) 47 bi-layers. (c) An example of the SLD profile for the fits presented in (a).

Similar data was also collected for the PAH terminated samples (not shown). In this instance the hydration was a uniform 20% at 0 bar and reduced to 10% at 5 bar. At 5 bar the hydration is non-uniform in the bi-layers adjacent to the final surface layer. This region has a noticeable increase in hydration, up to 30% for the 11 bi-layer PEM. These samples also showed a high hydration level of 40% in the final adsorbed layer regardless of confining pressure. The salt made 23 bi-layer samples showed at 0 bar an increased hydration compared to a non-salt made samples [4]; though at higher pressures there was no difference to that previously observed, with an exception of an increased dry layer thickness.

The most novel experiment compressed two oppositely surface charged PEM's together (data not shown). At 0 bar the sample behaves as a normal positively charged PAH terminated PEM. When contact is established with a negatively charged PSSA terminated PEM, the resulting charge neutralisation leads to a system where almost all (<3% at 3 bar) H_2O is extracted in the bi-layers near the interface. Surprisingly, the removal of the surface charge also allows a greater amount of water to be removed from the rest of the sample, resulting in a very non-uniform hydration profile in the sample. This result is very indicative of the important role the surface charge plays on the hydration behaviour of the whole structure.

Conclusions

When combined with our previous data, these results are being used to develop a model whereby the surface charge of the PEM influences the charge distribution within the rest of the PEM. The amount of charge is then directly linked to the hydration of the PEM when confined. This experiment also demonstrated a new type of system that can be examined with our unique set-up

1. G. Decher, *Science*, 277, 1232 (1997).
2. D.G. Shchukin, G.B. Sukhorukov, H. Möhwald, *Angew. Chem., Int. Ed*. 42, 4472 (2003).
3. W.M. de Vos, L.L.E. Mears, R.M. Richardson, S.W. Prescott, *Experimental report*, D17, 9-11-1481.
4. W.M. de Vos, L.L.E. Mears, R.M. Richardson, T. Cosgrove, R. Barker, S.W. Prescott, *Macromolecules*, 46, 1027 (2013)
5. W.M. de Vos, L.L.E. Mears, R.M. Richardson, T. Cosgrove, R.M. Dalgliesh, S.W. Prescott, *Rev. Sci. Instrum*., 83, 113903 (2012).