Experimental Report

Proposal: **9-10-1269** **Council:** 4/2012

Title: Multilayers built by layer-by-layer self assembly onto vesicles.

This proposal is a new proposal

Researh Area: Soft condensed matter

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Samples: dioctadecyldimethylammonium bromide
dioleoylphosphatidylcholine
poly(styrenesulfonate, sodium salt)
poly(allylaminehydrochloride)
polystyrene latex nanoparticles

Instrument	Req. Days	All. Days	From	To
D11	0	2	30/04/2013	02/05/2013

Abstract:

The structure of polyelectrolyte and nanoparticle-polyelectrolyte multilayers constructed onto vesicles will be studied by Small Angle Neutron Scattering. This is an exploratory investigation and our first goal is to compare the structure of multilayers built onto fluid and curved interfaces (vesicles) with the structure of polyelectrolyte multilayers supported on solid flat substrates which are well studied. As far as we are aware, polyelectrolyte multilayers has not been built onto vesicles up to now (there is a very recent paper on vesicles decorated with one layer of polyelectrolyte, Soft Matter 201) and obviously these systems have not been studied previously neither by Light, X-Ray or Neutron scattering techniques.

Report: Multi-layers built onto vesicles.

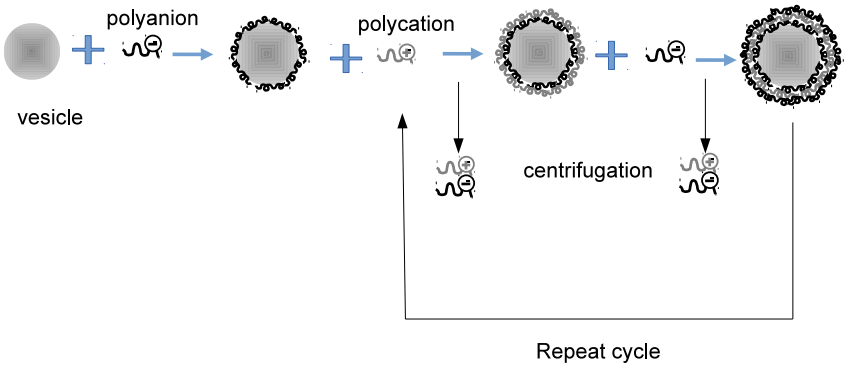
August 6, 2013

1 Aim of the Experiment

The structure of polyelectrolyte multilayers constructed onto vesicles were studied by Small Angle Neutron Scattering on D11. This was an exploratory investigation and our first goal was to obtain information on the multilayer thickness and internal structure.

2 System

Our system is composed of micro-capsules obtained by polyelectrolytes adsorption onto the external surface of vesicles. To do so we use the layer by layer technique: the vesicles, in an aqueous (H2O, D2O or mixtures) dispersion, are mixed first with an aqueous solution of a polyanion. After about 15 minutes, a solution of a polycation is added. After other 15 minutes, the excess of the polycation-polyanion complex is eliminated by centrifugation. The vesicles with the first bilayer so obtained are then recovered and the process is repeated to obtain the desired number of layers (see figure).



3 Samples

Vesicles: The vesicles were obtained by extrusion from mixtures of a cationic surfactant dioctadecyl-dimethylammonium bromide (DODAB) and the lipid dioleoylphosphatidylcholine (DOPC). The mean vesicle radius, measured by dynamic light scattering, was 40 nm. For SANS the samples were prepared in D2O, H2O and in mixtures of D2O/H2O.

Multilayers capsules: The polyelectrolytes used were poly-(styrenesulfonate, sodium salt), PSS and poly-(allylaminehydrochloride), PAH in a sequence: vesicle-(PSS-PAH)n. In D2O we have prepared 4 samples with n = 1, 2, 3 and 4. We have tried also the same systems prepared with deutereted PSS in water and in mixtures of H2O/D2O in order to match the PAH (85H:15D) and the deutereted PSSd (30H:70D).

4 Results

In what follows we present the experimental results. In all cases we have used to fit the data the core shell(sphere) Model,

$$P(q) = \frac{scale}{Vs}\left[3Vc(\rho_c - \rho_s)\frac{sin(qr_c) - qr_c cos(qr_c)}{(qr_c)^3} + 3Vs(\rho_s - \rho_{solv})\frac{sin(qr_s) - qrcos(qr_s)}{(qr_s)^3}\right]^2 + bkg \qquad (1)$$

4.1 in D2O

For the systems in D2O all the results were fitted using the core-shell model with one layer (see figure from 1 to 3).

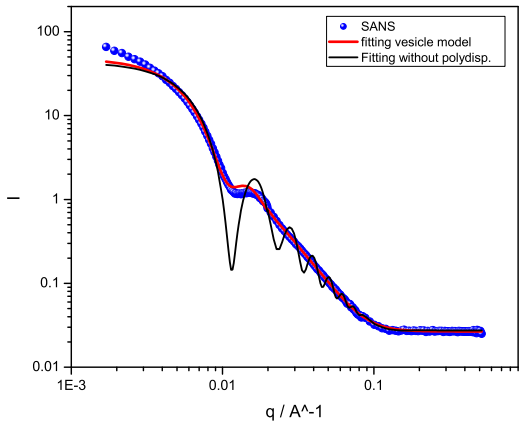


Figure 1: Dispersion of vesicles in D2O.

From the fitting, the vesicle internal radius is $228 \pm 4\mathring{A}$ and the shell thickness is $39 \pm 3\mathring{A}$ with a radius and shell polydispersity of 0.27 and 0.25 respectively.

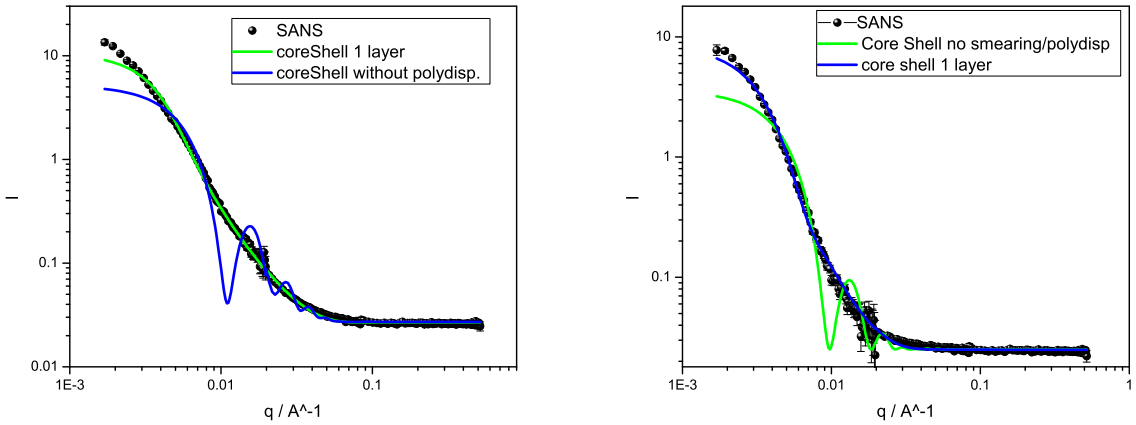


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Figure 2: Dispersion of micro-capsules with (a) 1 bilayer; (b) 2 bilayers

For the micro-capsules with 1 to 4 bilayers the experimental curves are shown in figures 2 and 3, and the fitting parameters are summarized in the following table.

bilayers	bkg	core sld	radius	shell sld	solvent sld	thickness
1	0.0268	6.38e-6	229±25	5.91e-6	6.18e-6	77 ±1
2	0.025	6e-8	225±30	5.91e-6	6.1e-6	140 ±6
3	0.0266	6.18e-6	200±15	6.1e-6	6.18e-6	200 ±8
4	0.034	6.37e-6	200±12	6.3e-6	6.37e-6	280 ±9

4.2 in H2O and H2O/D2O mixtures

In figure 4 we show the results for one bilayer capsule with deutereted PSS: Vesicle-PAH-PSSd. We have used the core-shell model to fit the data considering first only one layer: vesicle-(lipids-PAH-PSSd) and then assuming two shells: vesicle-(lipids-PAH)-(PSSd), see table.

The fitting parameters are listed on the following table.

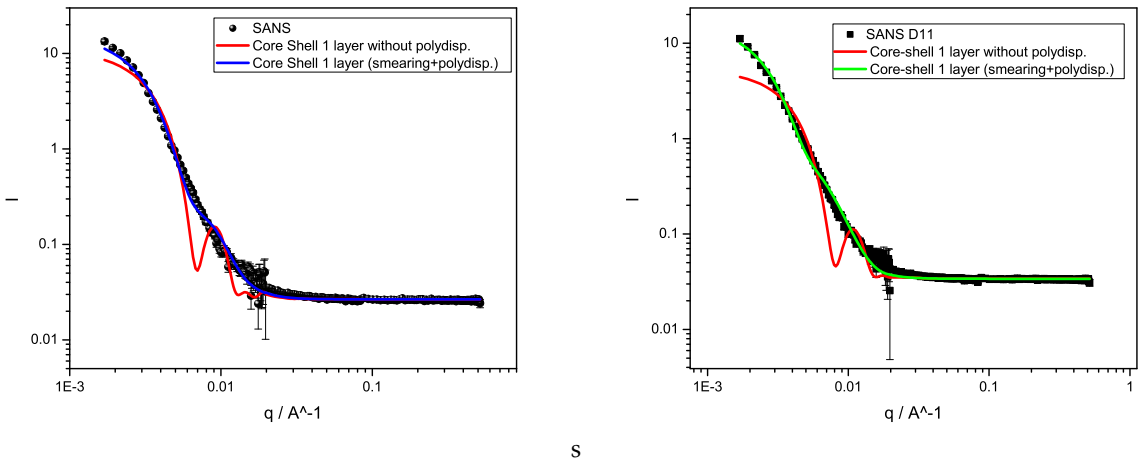

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Figure 3: Dispersion of micro-capsules with (a) 3 bilayer; (b) 4 bilayers

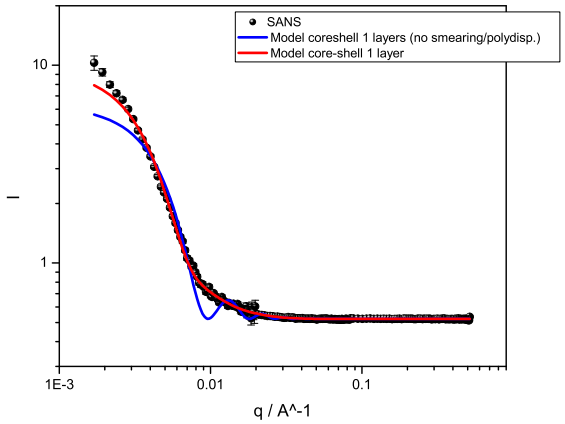

Figure 4: Vesicles with one bilayer composed of PAH and deutereted PSS in H2O.

Model	bkg	scale	sld solvent	sld shell2	thick shell2	sld shell 1	thick shell1	sld core	r core
1 shell	0.521	0.001	-5.6e-7	-	-	-2.79e-7	77.28 ± 24	-5.22e-7	220 ± 11
2 shells	0.521	1.14	-5.38e-7	-5.13e-7	70 ± 21	-5.56e-7	24 ± 4	-5.33e-7	209 ± 6

5 Problems

All samples prepared in H2O/D2O mixtures give very little intensities and it was impossible to obtain any usable data from them. During the experiments it was clear that the size polydispersity of vesicles as well as the polydispersity of the shell thickness of the micro-capsules obtained from them make difficult or impossible to obtain information on the internal structure of the layers.

6 Summary

Despite of all difficulties we have obtained valuable information about capsules size and the thickness of the multilayers (as a whole). The capsules have a core radius of about 22 nm and a shell thickness that increases in about 7 nm per layer. Due to the radius polydispersity of the vesicles and the shell thickness of the capsules, which produce the smearing of experimental curves, it was not possible to extract any detailed information about the internal structure of the multilayer.