# Experimental report

15/09/2016

**Proposal:** **9-12-455**

**Council:** 4/2016

**Title:** One-step formation of polymer-surfactant multilayers studied by neutron reflectometry

**Research area:** Soft condensed matter

**This proposal is a new proposal**

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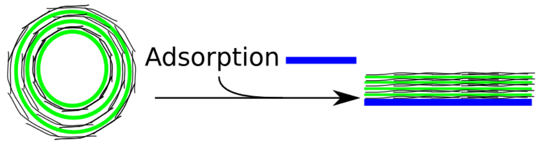
**Samples:** $C_{11}H_{23}COO(CH_2CH_2O)_{4.5}CH_2COOH$
Chitosan $(C_6H_{11}NO_4)_n$

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D17 | 3 | 3 | 03/06/2016 | 06/06/2016 |

## Abstract:

In this proposal, we plan a comprehensive structural investigation of well-ordered polyelectrolyte - surfactant multilayers formed upon adsorption of multilamellar vesicles on silicon wafers. The vesicles are spontaneously formed in bulk solution when dodecyl oligoethyleneoxide carboxylic acid C12E4.5CH2COOH is admixed to the biopolycation chitosan in acidic conditions (pH = 4). The number of layers of the multilamellaer vesicles directly depends the mixing ratio of the components, and affects the thickness and composition of the formed film. With respect to conventional polymer-based coatings, this novel functionalization route stands out for its simplicity, whereby the film thickness and composition can be determined by the mixing ratio of the components in the bulk solution.

**Introduction:** With the performed experiments, we aimed at demonstrating the formation of well-structured polyelectrolyte-surfactant multilayers, formed in a one-step adsorption of preformed complexes in bulk solution, as schematically depicted on the left. In particular, the substrates were coated with complexes of chitosan and $C_{12}E_{4.5}CH_2COOH$ or $C_{18:1}E_5CH_2COOH$, which were shown to form multilayered vesicles, with a well-defined number of layers, depending on the solution composition[1].



**NR-Experiments:** Polyelectrolyte-surfactant coatings were prepared by spin-coating polymer-surfactant solutions on a 5x5 cm^2 silicon blocks, previously cleaned and hydrophylized by UV-Ozone treatment. Complexes were prepared at various chitosan to $C_{12}E_{4.5}CH_2COOH$ or $C_{18:1}E_5CH_2COOH$ mixing ratio. In both solutions multiwalled vesicles are present, as verified by small-angle neutron scattering (SANS).

Experiments were performed on D17 in Time-of-flight mode, using three different angles and covering a q-range from 0.08 to 0.25 $A^{-1}$. The reflectivity profiles were recorded at different humidity conditions, from 0 to 80 %RH with D2O in the gas phase, thereby controlling the chemical potential of water in the system and therefore the level of hydration of the hydrophilic part of the layer. An exemplary set of reflectivity profiles is given in Figure 1.

The increase of relative humidity has strong effects on the reflectivity profiles, namely:

- The critical angle shifts towards higher q.
- A Bragg peak appears and moves to smaller scattering vectors.
- The fringes resulting from the two periodicities in the system becomes narrower as humidity is increased, indicating the increase of the thickness within the periodic unit.

These features support the hypothesis of the formation of multilayered coating, with separated hydrophobic (the surfactant tails) and hydrophilic (the polyelectrolyte and the ethoxylated surfactant headgroup) part, where the hydrophilic layers swell with increasing relative humidity.

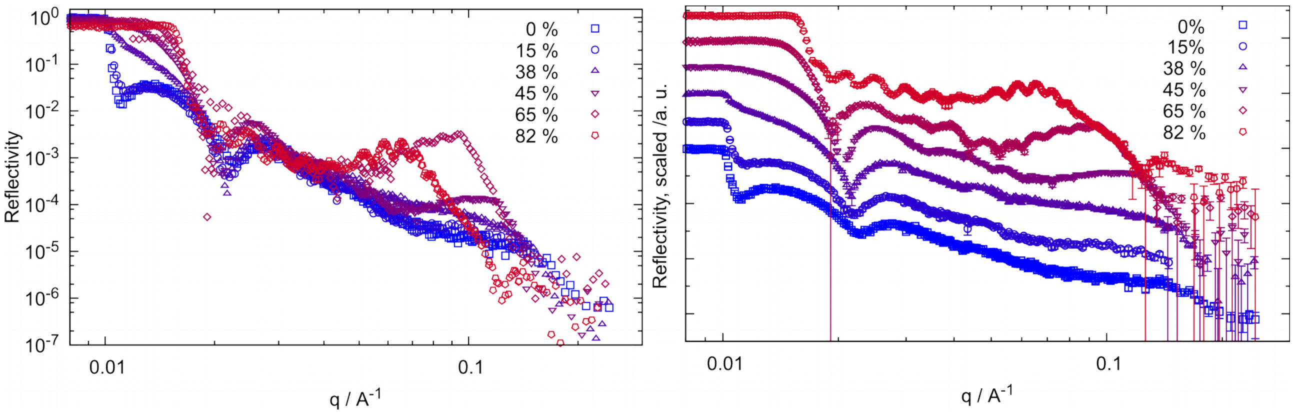
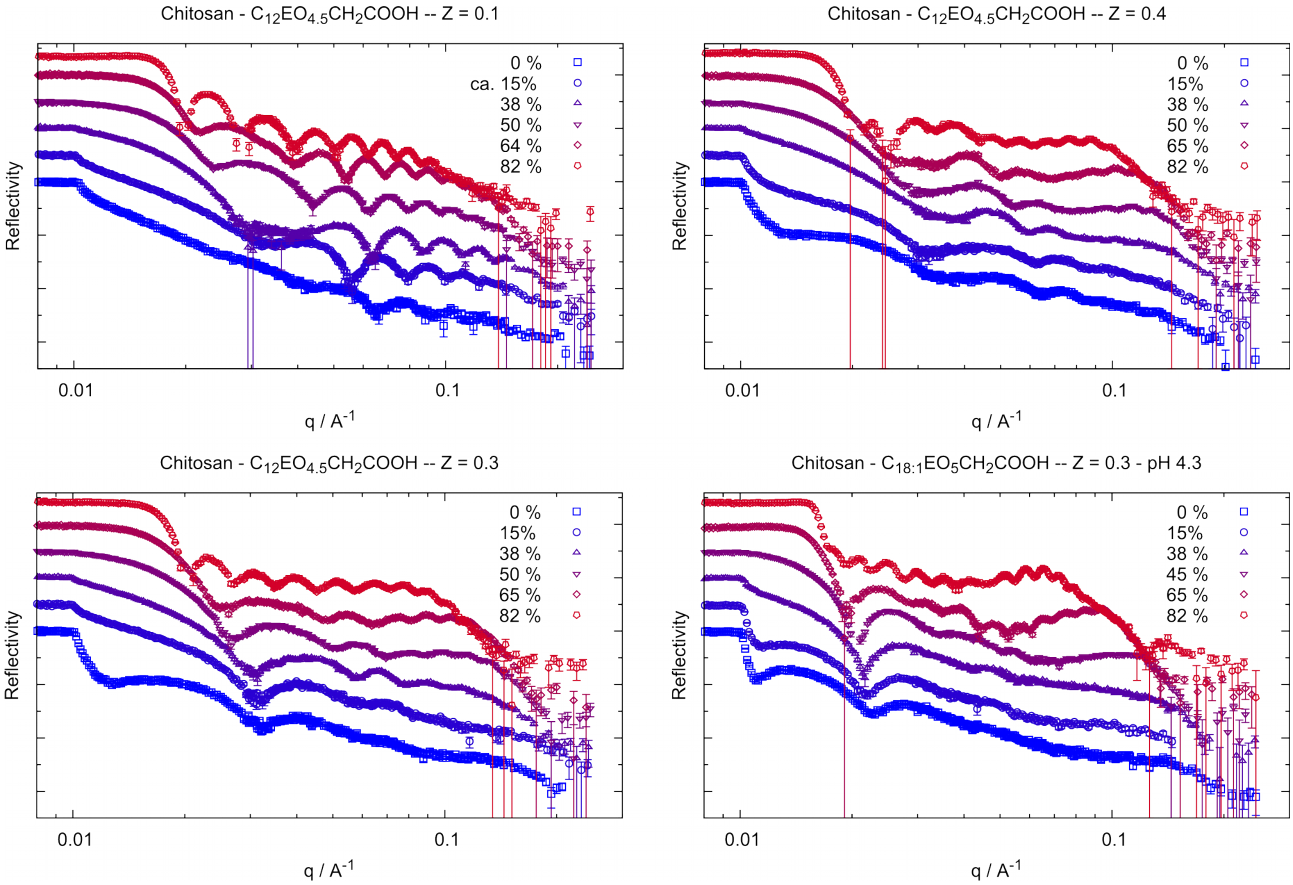


*Fig. 1: Reflectivity profiles obtained from a coating prepared from chitosan – C18:1E5CH2COOH solution, with mixing ratio Z = 0.3 and pH = 4.3, obtained at different values of relative humidity of D2O. On the left the data are reported in absolute scale, on the right the curves are shifted for improved visibility.*


Chitosan - $C_{12}EO_{4.5}CH_2COOH$ -- Z = 0.1

Chitosan - $C_{12}EO_{4.5}CH_2COOH$ -- Z = 0.4

Chitosan - $C_{12}EO_{4.5}CH_2COOH$ -- Z = 0.3

Chitosan - $C_{18:1}EO_5CH_2COOH$ -- Z = 0.3 - pH 4.3

*Fig. 2: Reflectivity curves obtained from coatings prepared from complexes of chitosan - C12E4.5CH2COOH at pH 4.0 at different mixing ratios Z, or from chitosan – C18:1E5CH2COOH complexes formed at pH 4.3 and Z = 0.3. Curves are scaled for improved visibility.*

The structural information and swelling behavior can be deduced from the change observed in the reflectivity profiles: the shift of the critical angle is due to the enhanced internal contrast due to D2O uptake on the hydrophilic part; the smaller q separation between the minima of the fringes indicates a larger total thickness; the broadening and shift of the Bragg peak is explained by the increased contrast between the hydrated hydrophilic, domains and the hydropobic ones. Similar profiles and structural features are obtained also for the other prepared coatings, with the samples with less surfactant content showing a less marked Bragg-peak (see Fig. 2). Preliminary data analysis has been carried out to give a quantitative description of the scattering patterns. The first approach consists in assuming a perfectly ordered layer, where the thicknesses of the hydrophilic and hydrophobic domains are determined by the molecular architecture. The only variable in the series of swelling curves is the amount of water in the coating. A dedicated plugin was written for the software Aurore [2]. This approach however does not lead to successful results (see Fig. 3). The number of layers N of the multilayer assembly can be estimated as N = $d_{tot}/d_{layer}$, where $d_{tot}$ is the total thickness of the layer obtained from the Kiessig fringes, and $d_{layer}$ from the Bragg peak position. In particular, for the coating prepared from a chitosan – $C_{18:1}E_5CH_2COOH$ solution at a RH of ca. 80% (reported in Fig.1), we obtain a layer thickness of ca. 8 nm, in good agreement with the thickness determined in bulk solution by small-angle neutron scattering (SANS) and a total layer thickness of 80 nm, leading to a value of N = 10 (note that each single layer is composed by four sublayers: chitosan, hydrophilic domain of surfactant, hydrophobic domain, and the hydrophilic

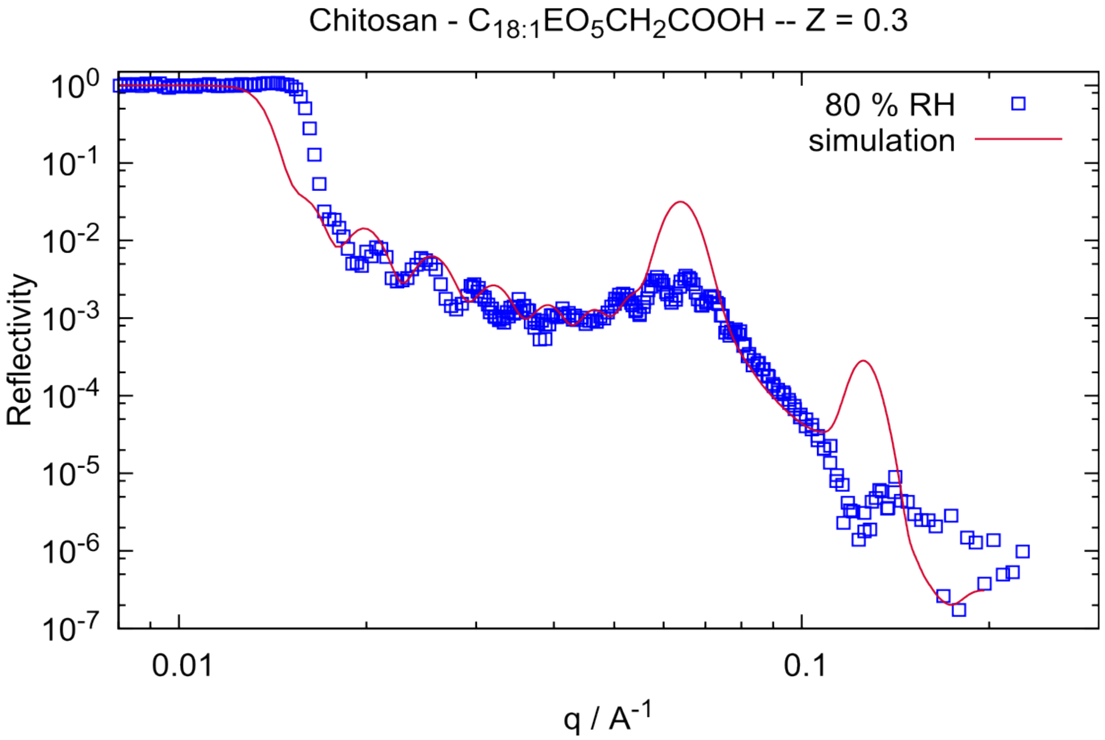


*Fig. 3 Reflectivity curve for coating prepared from a chitosan – C18:1E5CH2COOH complex solution, prepared with a mixing ratio of Z=0.3 (empty squares) and calculated relfectivity profile (full line). See text for further details.*

domain again). Tough the overall reflecticvity intensity, the Bragg peak position and the oscillation frequency are correctly predicted, significant deviation of the simulated reflecticvity profile and the experimental data are observed. In particular, the experimental critical angle is larger than the predicted one, i.e., the $D_2O$ content of the layer is underestimated. Moreover, the observed Bragg peak is less pronounced than the predicted one and the second order peak is completely absent. This observations lead to the hypothesis of the formation of a slightly disordered layer, with the presence of defects where $D_2O$ is accumulated.

**Summary:** The results demonstrate that a polymer-surfactant multilayer can be prepared by spin-coating multilayered vesicles from bulk solution onto a silicon block. The systems respond to variations in relative humidity with the selective swelling of the hydrophilic domains. Though the structure of the coating is close to the expected ordered multilayered polyelectrolyte-surfactant structure, it is likely that defects and misaligned domains are present (deduced from the weakly pronounced Bragg peak). The structural picture of these systems can be depicted by the sketch in Fig. 4.

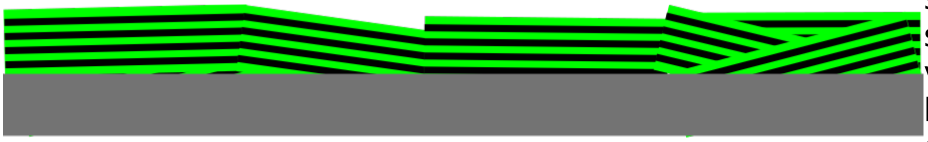


*Fig. 4: Schematic representation of probable structure of the coatings formed by polyelectrolyte surfactant multilayers.*

References

1. Chiappisi, L.; Prevost, S.; Grillo, I.; Gradzielski, M. Langmuir **2014**, 30, 10608–10616
2. Gerelli, Y. *J. Appl. Cryst.* **2016**, 49, 330–339.