EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Probing the phase diagram of PolyIon Complex Micelles using small angle x-ray scattering	**Experiment number**: sc5245
Beamline: ID02	**Date of experiment**: from: 26/08/2022 to: 29/08/2022	**Date of report**:
Shifts: 9	**Local contact(s)**: William	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Institut Charles Gerhardt de Montpellier, UMR5253 : Corine Gérardin, Nathalie Marcotte, Anu Vashishtha

Laboratoire de Synthèse et Fonctionnalisation des Céramiques, UMR3080 : Julien Schmitt, Swapneel Thakkar

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Laboratoire Charles Coulomb, UMR5221 : Martin In

Report:

PolyIon Complex (PIC) micelles are formed by electrostatic complexation between a double hydrophilic block copolymer (DHBC) which present one block charged and a micellisation agent of opposite charge. The charge of the DHBC or the micellisation agent is pH sensitive, hence pH is used to control the micellisation of these objects. They hence a found a promising application as templating agents for the synthesis of mesoporous silica: by forming the micelles during the material synthesis, before breaking the micelles by pH variation and freeing the porosity. This method has the advantage to functionalise in one step the material, as the DHBC (remaining in the silica walls) is used as templating agent but also functionalisation agent.

To use these PIC micelles for material formation, it is highly needed to study their phase diagram in suspension, at different pHs and temperature. We hence studied different groups of DHBC and micellisation agents, namely PAPEO-b-PAA (comb like poly ethylene oxide – b – poly acrylic acid) or PAPEO-b-PSS (poly styrene sulfonate) as DHBC and oligochitosan (2500 or 7500 g/mol) or neomycin as micellisation agent (13 series). The phase diagrams were studied at pHs 4.5, 5.5 or 6.5; where micelles are formed thanks to electrostatic complexation, and at 20, 40 and 60°C. Figure 1 present one of the phase diagram, measured at a sample detector distance of 1.5 m (measurements at 31 m were also done but the data are still under treatment), with concentration ranging from 0.1 to 50 wt%

From the data, one can see the increase of micelle-micelle repulsion with concentration, first fitted using a hard sphere repulsion model. We have observed from the data treatment that the strength of the repulsion decreases with temperature, probably as the amount of water within the micelles core decreases and hence their overall volume fraction decrease. We also observed clear mesophases when neomycin is used as micellisation agent, while samples with oligochitosan still exhibit a broad peak even at 50 wt%. We are currently fitting the data obtained.

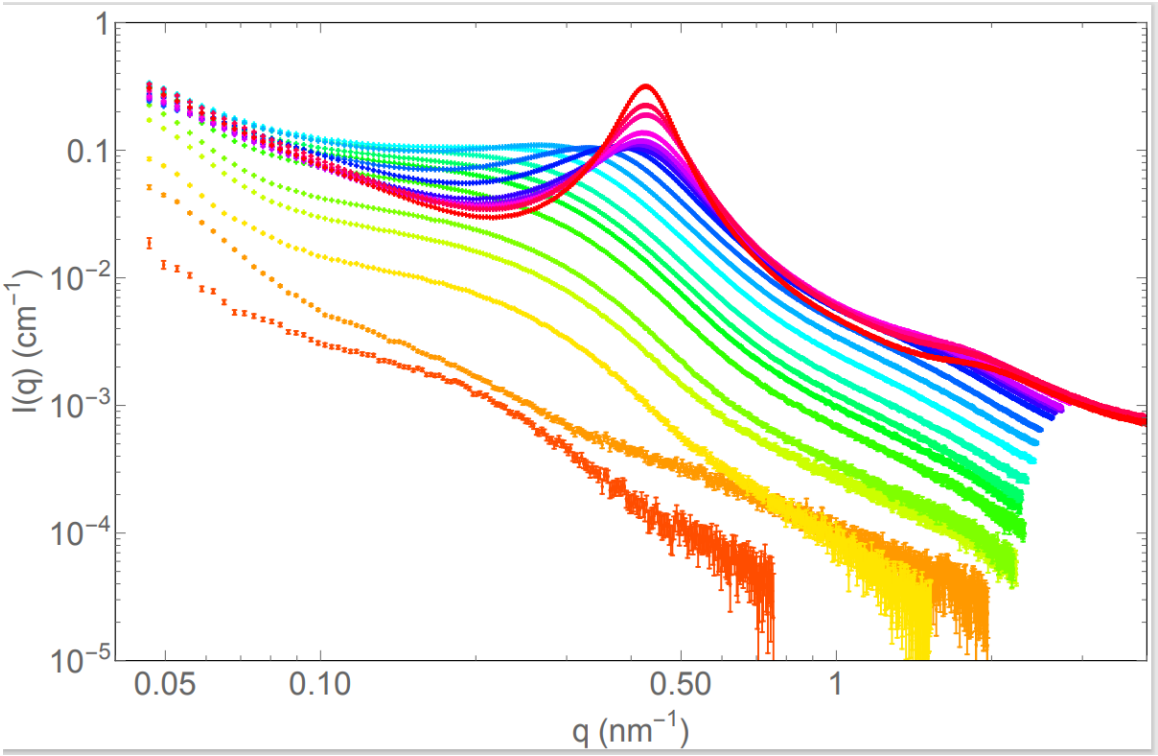

Figure 1 – Phase diagram of micelles made of PAPEO-b-PAA + oligochitosan 2500 g/mol at pH=5.5. Concentrations are ranging from 0.1 to 50 wt%

During this beamtime, as we were allocated 9 shifts, we carried also the experiments related to the beamtime application sc5246 “Probing the formation of mesoporous silica microspheres by a combination of SAXS and USAXS". Those silica microspheres are made using a combination of two DHBC: PAPEO-b-PAA and PAPEO-b-PAM (polyacrylamide). We expect the latter to stabilise the forming mesostructured particles and control the overall shape. We did ca. 10 kinetics including repeats, by using either neomycin or oligochitosan as micellisation agent, and by varying the ratio of PAPEO-b-PAA/PAPEO-b-PAM in the mixtures. The data are currently under treatment, but the signal associated to the microspheres could be seen in the USAXS regime (sample detector distance of 31 m).

Finally, we did some first tests of kinetics using a triple hydrophilic block copolymer (THBC) naming PAM-b-PAA-b-PAPEO; which allows forming mesoporous materials as 3D, 1D or even 0D depending on the synthesis conditions. As a proof of concept, we studied the synthesis of 1D particles (see Figure 2). It is clear from the pattern that we can see the emergence of a signal from the overall mesoporous objects in the ultra small angle regime (sample detector distance of 31 m).

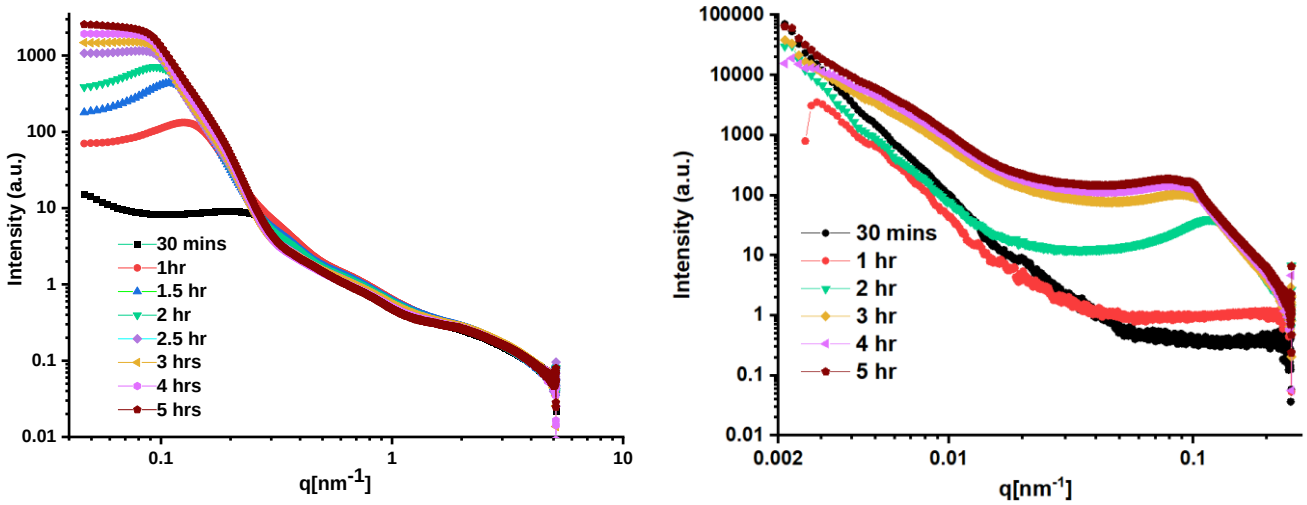

Figure 2 – (left) SAXS and (right) USAXS patterns for a kinetic of 1D particles made of 8wt% of THBC + oligochitson 2500 g/mol at pH 3.5

From this beamtime, we hence studied the complete phase diagrams of several PIC micelles, plus the synthesis of mesoporous microspheres using PIC micelles as templating agents. We expect to publish those results once the complete data analysis and data fitting is carried. The latter will require the modification of pre-existing models for the fitting of mesostructured microspheres. Finally, as a proof-of-concept for future measurements, we have studied the synthesis of 1D-mesostructured materials using a THBC.