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- fill in a separate form for each project or series of measurements.
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- 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:** Thermo-responsive poly ion complexes	**Experiment number**: SC-4270
Beamline:	**Date of experiment**: from: 17/06/2016 8:00 to: 20/06/2016 8:00	**Date of report**: 10/09/2016
Shifts:	**Local contact(s)**: Michael Sztucki	*Received at ESRF:*

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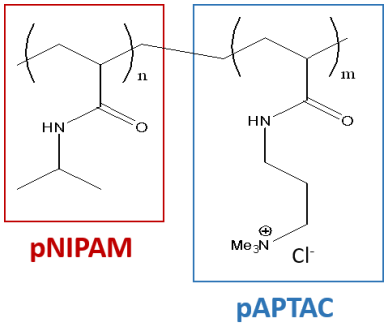
Report:

Scientific Background

Poly Ion Complex (PIC) micelles formed through the association of oppositely charged polymers and block-copolymers attract much interest due to their stimuli-responsive properties in aqueous solutions, i.e. pH, ionic strength [1,2]. When the block-copolymer contains a thermo-responsive group, PIC micelles can also undergo morphological transitions induced by temperature. One of the main advantages of PIC micelles is the easiness of preparation which does not require the use of an organic solvent as they are prepared directly in water. Their applications span from drug carriers, vectors for gene delivery to proton exchange membranes for fuel cells [1,2].



Scheme 1. Chemical structure of the used double hydrophilic block copolymers

We recently started the study of PIC morphologies formed from poly(3-acrylamidopropyltrimethylammonium chloride)-b-poly(N-isopropylacrylamide) (pAPTAC-b-pNIPAM), a double hydrophilic block-copolymer (DHBC) and poly(acrylic)acid (pAA) (Scheme 1).
At the same total molecular weight, 10k, two different block ratios have been already characterized by SLS and Zeta potential (ξ): pAPTACm-b-pNIPAMn (m = 1k, 5k and n = 9k, 5k) and pAAn n=2k. The experiments suggested a morphological transition above the pNIPAM Lower Critical Solution Temperature (LCST). However, these techniques do not allow distinguishing among the possible morphologies for the complexes and suffer from sample turbidity at high temperature.

Therefore, we aimed at **investigating the uptake of PAA during the PIC formation** and **elucidating the spatial distribution of the counter-ions**, localizing the position of the charged blocks in the aggregates. Besides, we wanted to **clarify the supposed transition.** At this purpose ASAXS is the technique of choice for polyions [3-5], preferred to SANS contrast matching technique which needs much synthetic effort.

Results

We studied Poly Ion Complexes of the following systems: (I) $pAPTABr_{5k}$-b-$pNIPAM_{5k}$/ $pAA_{2k,}$ (II) $pAPTABr_{1k}$-b-$pNIPAM_{9k}$/ pAA_{2k} and (III) $pAPTABr_{1k}$-b-$pNIPAM_{9k}$/ $pAA_{10k,}$ at pH 7 and four different mixing molar unit ratio, *R*, between the pAPTAC and the pAA ionizable groups (*R* = 0.5, 0.75, 1, 1.5). In order to have sufficient scattering contrast from the counterions , we used a polymer weight concentration of 1% and 5% for $pAPTABr_{5k}$-b-$pNIPAM_{5k}$ and $pAPTABr_{1k}$-b-$pNIPAM_{9k,}$ respectively. In addition, unlike planned in the proposal, the pH of pAA solutions was adjusted with a solution of RbOH in order to be able to follow also the pAA counterions during the PIC formation.
We performed ASAXS experiments at two different temperatures, 25°C and 45°C, in a wide q-range spanning from 0.0075 nm^{-1} up to 5.63 nm^{-1}. Besides, the intensity I(q) was measured at 20 different energies, below and above the edge of the counterions (Br^- 13480 eV Rb^+ 15200 eV). The macroions of the polymer skeleton do not exhibit any resonance near the energies used in the experiment, while the counter ions do. For this reason the scattering contribution coming from the macroions is constant, the differences in the spectra should be attributed to the Br and Rb counter ions condensed around the polymer skeleton.
Figure 1 shows the spectra registered for the PIC $pAPTABr_{5k}$-b-$pNIPAM_{5k}$/ pAA_{2k} with R=0.5, 1 and 1.5 at T=25°C. A ASAXS effect was successfully detected in the high-q region of the spectra and it decreases going from R=0.5 to R=1, while it is completely absent for R=1.5. In the low-*q* region, the scattering intensity profiles as a function of the incident energy overlap, indicating that no Br^- is located in the outer part of the nano-object and all the pAPTAC is then confined inside the nano-objetc. On the other side, $pAPTABr_{1k}$-b-$pNIPAM_{9k}$/pAA_{2k} and $pAPTABr_{1k}$-b-$pNIPAM_{9k}$/ pAA_{10k} show no change of scattered intensity when varying the energy is observed in all the investigated q range (**Figure 2**). No ASAXS effect is observed for Rb^+ at 25°C, as it could be expected due probably to the fact that the pAA chains involved in the nano-object formation lose most of their counter-ions which are replaced by amine groups in pAPTAC (data not shown).

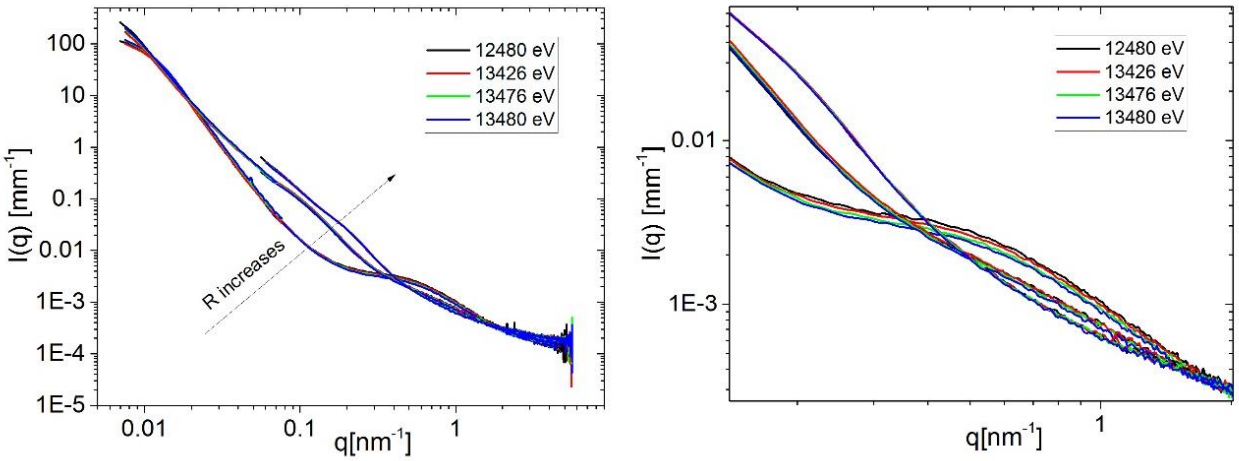


Figure 1 a) pAPTABr$_{5k}$-b-pNIPAM$_{5k}$/pAA$_{2k}$ at three different ratios R=0.5, 1 and 1.5 at T=25°C; **b)** zoom of the curve in a) in order to better show the ASAXS effect in the high q region

These results are in accordance with our preliminary structural investigations which indicate that the interior part of the aggregates is formed by pAPTAC complexed by pAA. The absence of Br^- ions in the core of the nano-objects in the case of pAPTABr$_{1k}$-b-pNIPAM$_{9k}$ could be ascribed to a different mechanism of PIC formation. In the case of pAPTABr$_{5k}$-b-pNIPAM$_{5k}$, the Br^- counter-ions of pAPTAC are progressively replaced by pAA while R increases. In the case of pAPTABr$_{1k}$-b-pNIPAM$_{9k}$ all the pAA present in solution replaces all the Br^- counter-ions to form object at the stoichiometric ratio even at low values of R.

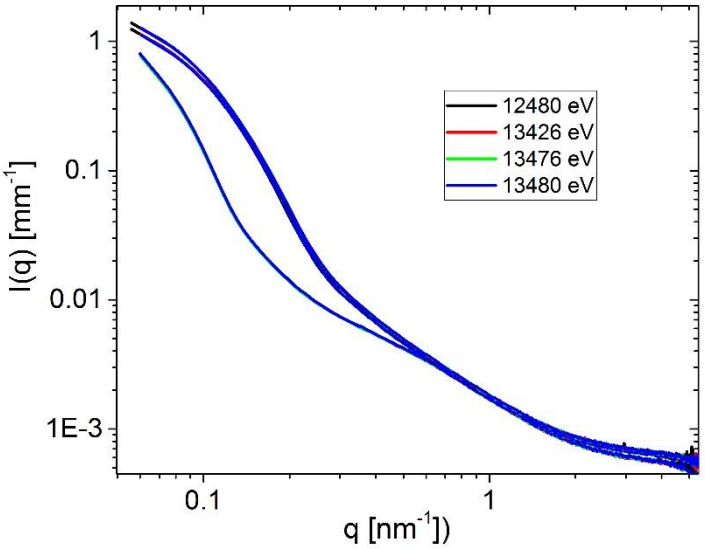


Figure 2. pAPTABr$_{1k}$-b-pNIPAM$_{9k}$/pAA$_{2k}$ at three different ratios R=0.5, 1 and 1.5 at T=25°C

In addition, we investigated the effect of temperature on the different samples. A change of the scattered intensity near the Br edge is still present in the case of pAPTABr$_{5k}$-b-pNIPAM$_{5k}$/pAA$_{2k}$ for R<1 (**Figure3**), but not for pAPTABr$_{1k}$-b-pNIPAM$_{9k}$/pAA$_{2k}$ (data not shown).

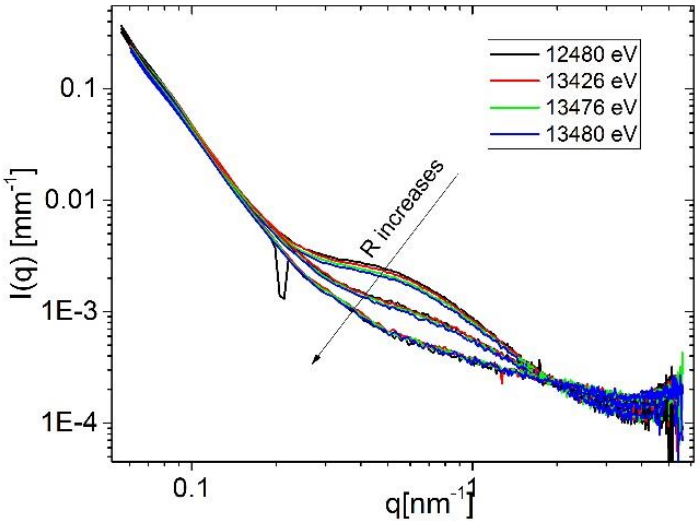


Figure 3. pAPTABr$_{5k}$-b-pNIPAM$_{5k}$/pAA$_{2k}$ at three different ratios R=0.5, 1 and 1.5 at T=45°C.

Also at high temperature, this ASAXS effect is observed in the high-q region of the spectra. This means that the pAPTAC chains stay in the interior of the object even above the hydrophilic/hydrophobic transition of the pNIPAM block. Nevertheless, the overall size of the nano-objects increases with temperature **(Figure 1** and **3)**, which would let us think that the hydrophobic pNiPAM at the exterior of the objects sticks making them grow.

Discussion and Conclusion

Currently, the data are still under exploitation. A structural model describing the overall scattering pattern for these hierarchical systems is under development.
On the qualitative level, our preliminary results at room temperature showed for the first time by means of ASAXS the presence of two different mechanisms of PICs formation: a non-cooperative one (pAPTABr$_{5k}$-b-pNIPAM$_{5k}$) where the Br^- counter-ions of pAPTAC are progressively replaced by pAA in the nano-objects; and a cooperative one (pAPTABr$_{1k}$-b-pNIPAM$_{9k}$) where nano-objects at the stoichiometric ratio are formed independently from the pAA content.
No ASAXS effect is present around the Rb edge, meaning that the pAA chains involved in the nano-object formation lose most of their counter-ions when they complex the amine groups in pAPTAC.

At high temperature, we observe an increase of the overall size of the objects whose interior is still formed by the pAPTAC block complexed to pAA. According to ξ potential measurements, the overall charge of the objects at high temperature is positive, so we would have expect a change of the scattered instensity when varying the energy around the Rb edge at low-q. This contradictory result needs to be investigated still in details.

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