



Experiment title: Hierarchical interpolyelectrolyte complex formation

Experiment number:
sc3941

Beamline: ID02	Date of experiment: from: 21.11.2014 to: 24.11.2014	Date of report: 19.02.2015
Shifts: 6	Local contact(s): Gudrun Lotze	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Plamper, Felix

Dähling, Claudia*

Gelissen, Arjan*

Steinschulte, Alexander*

Jung, Andre*

Richtering, Walter

Report:

The aim of the experiment was to investigate the aggregation pathway of oppositely charged polyelectrolytes. By use of bis-hydrophilic, ionic/non-ionic polymers, a hierarchical co- and self-assembly process is anticipated. Preliminary experiments indicated that two distinct processes take place at different time scales. In a first step, the oppositely-charged polyelectrolytes allegedly co-assemble to small interpolyelectrolyte complex particles (containing only one bis-hydrophilic molecule per particle). Secondly, these small particles self-assemble further to different micellar morphologies (vesicles, rods). Theoretical calculations indicate that the final morphology of the self- and co-assembled interpolyelectrolyte complexes (IPECs) depend on the arm number of the bis-hydrophilic (ionic/non-ionic) miktoarm star polymer. By mixing different ratios of a bis-hydrophilic (ionic/non-ionic) miktoarm star and a bis-hydrophilic (ionic/non-ionic) diblock copolymer before IPEC formation we can influence the morphology of the IPECs in a similar way. The different final morphologies were also investigated in this beam time. Finally, we investigated IPEC formation with thermosensitive polyanionic diblock copolymer (consisting of (poly(N-isopropylacryl amide) (PNIPAM) and poly(vinyl sulfonate) (PVS)) below and above the transition temperature of a thermoresponsive polyelectrolyte diblock copolymer.

Results

By mixing different ratios of cationic miktoarm stars (based on quaternized poly(dimethylaminoethyl methacrylate) qPDMAEMA and poly(ethylene oxide) PEO with an average of 4.3 qPDMAEMA arms) PEO₁₁₄-(qPDMAEMA₃₉)_{4,3} and cationic diblock copolymers PEO₁₁₄-*b*-qPDMAEMA₄₅ prior to the IPEC formation with poly(styrene sulfonate) PSS we obtained different self-assembled morphologies. These were investigated in a static experiment using a flow cell. We showed that it is possible to create by this rather simple method spherical micelles, cylindrical micelles and vesicles (see fig. 1). The different mixing ratios are named in this report by the average arm number of qPDMAEMA per PEO chain (the diblock is therefore

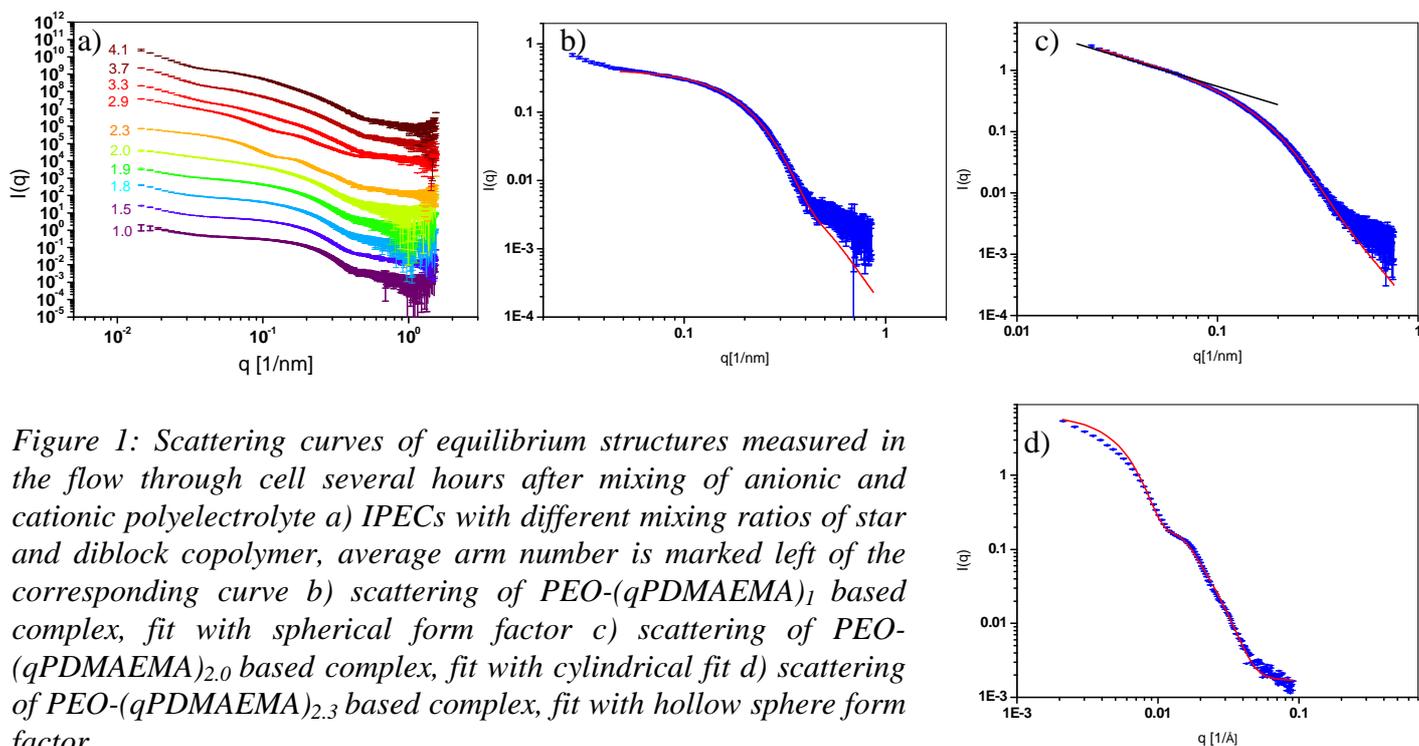
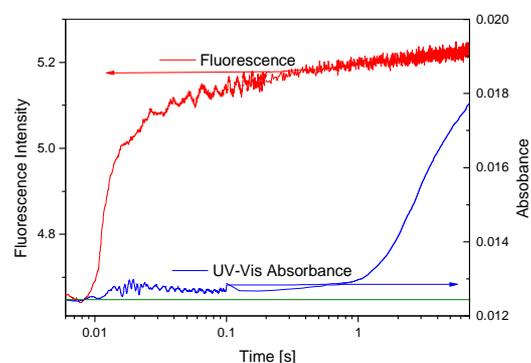


Figure 1: Scattering curves of equilibrium structures measured in the flow through cell several hours after mixing of anionic and cationic polyelectrolyte a) IPECs with different mixing ratios of star and diblock copolymer, average arm number is marked left of the corresponding curve b) scattering of PEO-(qPDMAEMA)₁ based complex, fit with spherical form factor c) scattering of PEO-(qPDMAEMA)_{2.0} based complex, fit with cylindrical fit d) scattering of PEO-(qPDMAEMA)_{2.3} based complex, fit with hollow sphere form factor

named PEO-(qPDMAEMA)₁ and a 1:1 mixture of the diblock and the miktoarm star PEO-(qPDMAEMA)_{2.7}. For PEO-(qPDMAEMA)₁ and PEO-(qPDMAEMA)_{1.5} the scattering shows the presence of mainly spherical micelles. The scattering of PEO-(qPDMAEMA)_{1.8} and PEO-(qPDMAEMA)_{1.9} shows a mixed phase consisting of spherical and cylindrical micelles. PEO-(qPDMAEMA)_{2.0} can be fitted with a pure cylindrical model. Above PEO-(qPDMAEMA)_{2.3} is the scattering dominated by vesicles. Hence, one can easily create different self-assembled morphologies by changing the average respective arm number without the need to synthesize different star polymers.

Figure 2: Turbidity and fluorescence stopped flow during formation of the miktoarm star complex with PSS: fluorescence trace is displayed in red and turbidity trace is displayed in blue



The formation of these IPECs was then investigated by a stopped flow experiment. Preliminary stopped flow experiments on the miktoarm star-PSS complex indicated a two-step, hierarchical assembly process. Hereby, we used a rhodamine-labelled, cationic miktoarm star, which interacts upon mixing with linear, short PSS. While the onset of a pronounced turbidity change is detected above 1 s, the fluorescence increases already within the first 100 ms period (Fig.2). The fluorescence signal is predominantly sensitive to the actual complexation, while the turbidity senses mainly the aggregation to larger structures. The stopped flow SAXS experiments were conducted on the miktoarm star (PEO-(qPDMAEMA)_{4.3}), on the diblock copolymer (PEO-(qPDMAEMA)₁) and on a star diblock mixture (PEO-(qPDMAEMA)_{2.3}). The scattering of the uncomplexed star mixtures and PSS as well as final structures (measured hours after mixing) were recorded and are shown in light grey (PSS), dark grey (star, diblock or star mixture) and black (final structures) in the corresponding graph in fig. 3. The stopped flow SAXS experiments show that the first step is too fast to be completely resolved. The scattering recorded in the steady state directly after the dead time shows already the first self-assembled structures (see fig 3).

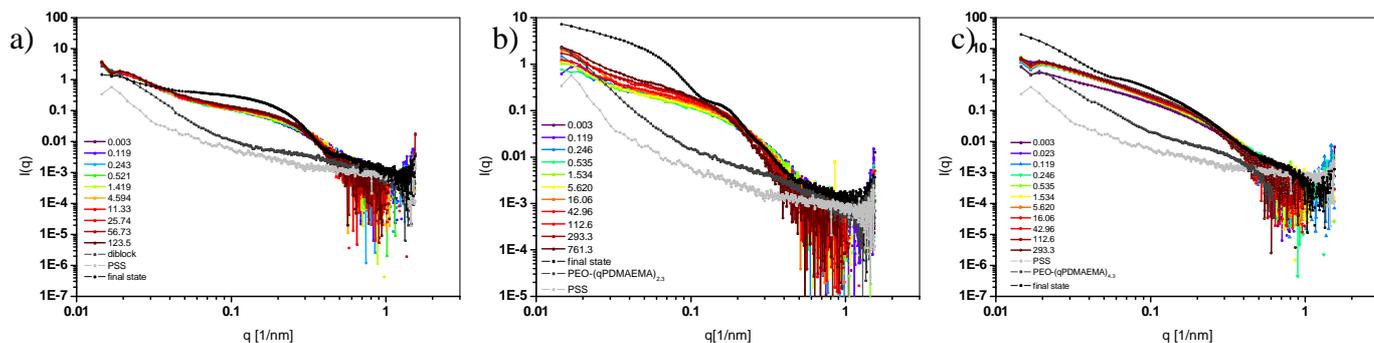


Figure 3: Scattering curves of stopped-flow experiment of a) the complexation of the diblock copolymer $\text{PEO}-(q\text{PDMAEMA})_1$ b) the complexation of the diblock star mixture $\text{PEO}-(q\text{PDMAEMA})_{2,3}$ c) the complexation of the miktoarm star $\text{PEO}-(q\text{PDMAEMA})_{4,3}$

There is only in case of the star complex ($\text{PEO}-(q\text{PDMAEMA})_{4,3}$) a change of the scattering in the first 100 ms (see fig 3c). This increase is probably contributed to an increase of concentration of the self-assembled structures and happens between 3 ms and 23 ms. Unfortunately, we did not record further information between 3 ms and 23 ms. The high increase in the first 10 ms of the fluorescence stopped flow experiments is therefore probably corresponding to the end of the first process. According to the turbidity measurements of the pure miktoarm star-PSS complex, aggregation to larger (and therefore strong scattering) structures at time > 1 s was expected. No prominent enough change in the scattering could be detected in the first 10 min in the observed q range. On the other hand, there is a relevant difference between the last scattering curve in the stopped flow and the final state (measured in the flow through cell several hours after mixing) detected. This change could lead to such a huge increase in turbidity. Therefore, one possible explanation for the different observations in the time resolved turbidity and SAXS patterns is given: the strong rise in turbidity after 1 s might be caused not directly by the formation of vesicles, but by a hierarchical supraaggregation of the vesicular entities to larger (temporary) aggregates (similar to loose aggregates in aqueous polymer solutions). A detection of the kinetics over longer time is necessary to obtain more information about the formation of the structures measured after longer mixing times in the flow through cell.

This is especially true for the star diblock mixture ($\text{PEO}-(q\text{PDMAEMA})_{2,3}$) (see fig. 3b). Here one can observe an increase of intensity with time, while the first minimum shifts to lower q . It is possible to fit the stopped flow scattering of this sample with a cylindrical model. The fitting shows an increase in the diameter of the cylinder. The length is for all curves above 120 nm. Hence, it is therefore not possible to detect changes in the length as it is out of the detected q -range. The final state measured in the flow through after several hours of mixing shows a different scattering pattern. It is not possible to fit it with a cylindrical model, but with a hollow sphere model (see fig. 1d). Hence, a change in the structure on longer timescales can be seen.

The most intuitive stopped-flow scattering was observed for the diblock complex ($\text{PEO}-(q\text{PDMAEMA})_{1,0}$) (see fig. 3a). Here the fitted scattering profile just shows an increase in the size of the spherical micelle. Again, we observed larger structures in the final state but not a change in the morphology as observed for the $\text{PEO}-(q\text{PDMAEMA})_{2,3}$ and probably for the $\text{PEO}-(q\text{PDMAEMA})_{4,3}$ complex. These observations show that the first process of complexation and aggregation into small preliminary structures is too fast to be recorded by stopped-flow SAXS. But on larger timescales (larger than expected regarding the turbidity stopped flow) we can observe a change in morphology. This change is most dominant for mixtures of diblock and star which lead to structures on the edge to another morphology (e.g. $\text{PEO}-(q\text{PDMAEMA})_{2,3}$). Further investigations of this kinetics might give us new information about the formation of vesicles from worm-like micelles.

Additionally with poly(*N*-isopropyl acrylamide) PNIPAM, a thermosensitive compound was introduced to the interpolyelectrolyte complex (IPEC). The self-assembly of a cationic miktoarm star $\text{PEO}_{113}(q\text{PDMAEMA}_{18})_4$ and an anionic diblock copolymer $\text{PVS}_{31}\text{-}b\text{-PNIPAM}_{27}$, based on poly(vinyl sulfonate) PVS and PNIPAM, in 0.3 M NaCl solution was investigated. Two temperatures were used: a) below the LCST (20 °C) and b) above the LCST (60 °C) of the thermosensitive block. Below the LCST, the polyanion is in its unimeric state whereas above the LCST it forms micelles. Thus it is expected that the final IPEC morphologies differ.

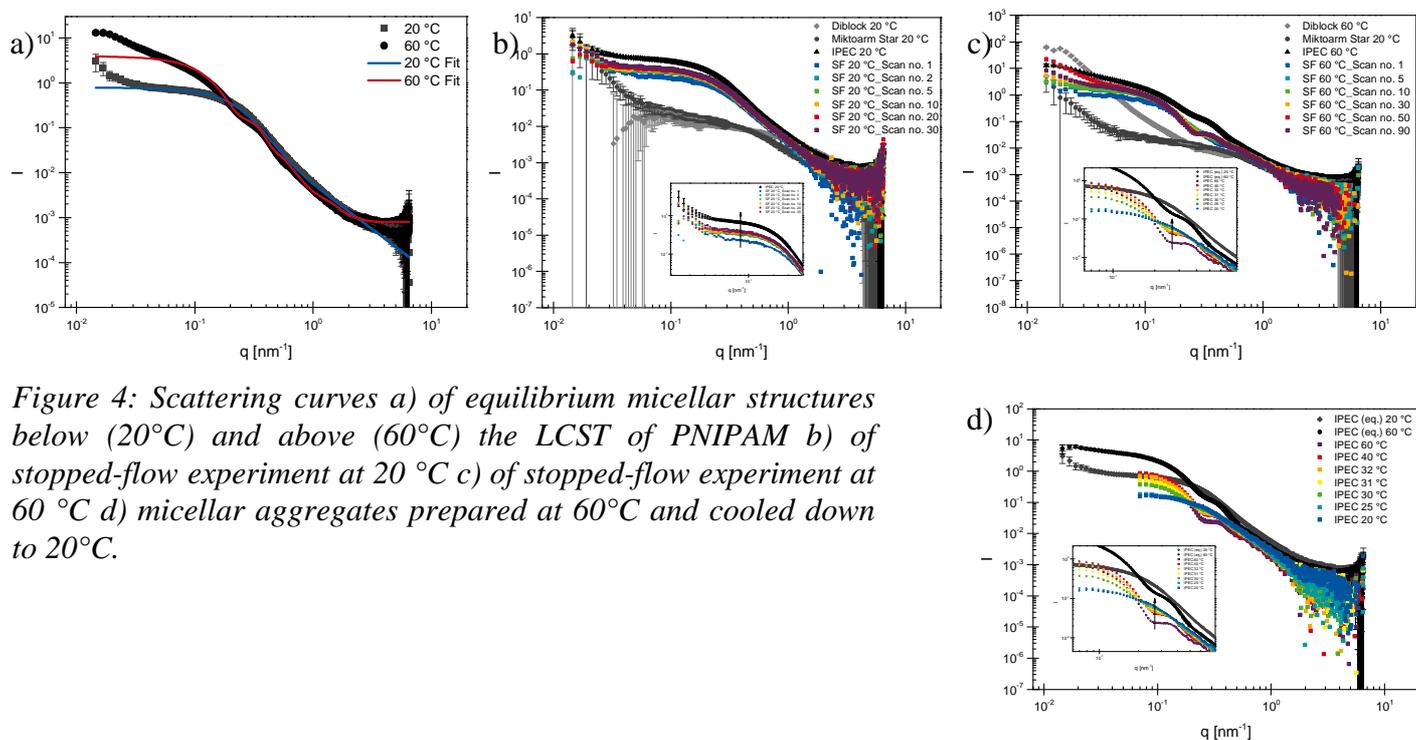


Figure 4: Scattering curves a) of equilibrium micellar structures below (20°C) and above (60°C) the LCST of PNIPAM b) of stopped-flow experiment at 20 °C c) of stopped-flow experiment at 60 °C d) micellar aggregates prepared at 60°C and cooled down to 20°C.

In order to get information on the equilibrium structures of the interpolyelectrolyte complex below and above the LCST, it was prepared 20 h before measuring at room temperature and 60 °C, respectively. For the latter case the solutions of the single components were preheated to 60°C and the complex dispersion was stored at 60°C until it was measured. The scattering curves obtained at 20 °C and 60 °C (see fig. 4a) show different shapes indicating that the micellar shapes differ. This satisfies the expectations as at 60 °C the thermosensitive diblock copolymer preforms micelles around which the interpolyelectrolyte complex is formed. Based on this the scattering curve at 60 °C was fitted with a core-shell-corona model (see 60 °C Fit, fig. 4a). At 20 °C, however, the thermosensitive compound is soluble in water. Thus the formation of core-corona micelles (see 20 °C Fit, fig. 4a) was expected with the polyelectrolytes building the core and with PEO and PNIPAM building the corona.

Further the assembly of the cationic miktoarm star and the anionic diblock copolymer was investigated with real time measurements by SAXS coupled to a stopped-flow device. The scattering curves obtained for the stopped-flow (SF) experiment at 20 °C are depicted in figure 4b). The curve shapes of all scans match with the one measured for the equilibrium structure (see IPEC 20 °C, fig. 4b). Hence the IPEC formation is faster than the dead time (0.017 s) of the experiment. The intensity, however, increases with time (see fig. 4b) indicating that the concentration of micelles increased.

For the stopped-flow measurements at 60°C all curves exhibit minima similar to the equilibrium curve (see fig. 4c). Again the IPEC formation was faster than the dead time (0.003 s). However, the minimum is shifted to smaller q -values (see fig. 4c) indicating that the size of the micelles increases with time.

After performing the stopped-flow experiment at 60 °C the setup was cooled down and SAXS measurements were run at different temperatures in order to see whether the micellar morphology built above the LCST of PNIPAM is preserved upon cooling to temperatures below the LCST. Figure 4d) clearly shows that the minimum present in the scattering curve at 60 °C (IPEC 60 °C) disappears when the temperature reaches the LCST of PNIPAM (32 °C). The scattering curves obtained at 25 °C and 20 °C are similar to that of the equilibrium structure at 20 °C (IPEC (eq.) 20 °C). These results proof that the micellar morphology rearranges upon cooling and that equilibrium structures are formed at all temperatures.