	Experiment title: **Study of Polyelectrolytes by ASAXS**	**Experiment number**: SC-1029
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Shifts: 12	**Local contact(s)**: Dr. D.Pontoni Dr. T.Narayanan	

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Report: We report a comprehensive ASAXS-study of polyelectrolytes in solution, which we have further investigated in our long-term project (SC1144). Polyelectrolytes consist of macroions and counterions. A central question in this field is the spatial distribution of the counterions around the macroion. The strong electric field of the macroion leads to marked correlation of the counterions with the macroion. In particular, a certain fraction of the counterions will be “condensed” to the macroion. Scattering methods as e.g. small-angle X-ray scattering are ideally suited to investigate the correlation of the counterions to the macroion in a quantitative fashion and hence to furnish the decisive information for a comprehensive testing of current theoretical models of polyelectrolytes.

Rod-like Polyelectrolytes: Rod-like polyelectrolytes as depicted in Fig. 1 are model compounds for linear polyelectrolytes. In our earlier studies by ASAXS [1-2] we have demonstrated that this method allows us to determine the counterion distribution around the cylindrical macroion. We have used rigid rod-like polyelectrolytes composed of a poly(para-phenylene) backbone and side groups with bromine counterions affixed to it. In these studies, we were able to successfully demonstrate that the ASAXS-data leads to three partial intensities in a numerically self-consistent fashion. In particular, the scattering intensity that is solely due to the cloud of the counterions was determined and compared to the prediction of the Poisson-Boltzmann cell model. A quantitative agreement was found between experimental and theoretical predictions [3].

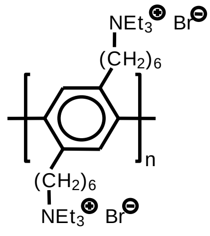

Fig1. Scheme of rod-like polyelectrolytes

ASAXS Theory: ASAXS as applied to polyelectrolyte systems, near the absorption edge the scattering factor f of the counterions becomes a complex quantity: $f = f_0 + f' + i\, f''$ where f_0 is the energy-independent scattering factor. The factor f_0 is identical to the number of electrons in the respective ion. The quantities f' and f'' are the real and the imaginary part of the resonant part of f, and i is the imaginary unit. Fig.1 displays the two quantities as function of energy for Bromine ions. Hence, f' decreases considerably in the immediate vicinity of the edge which in turn leads to a decrease of the scattering factor f of the Br-ions. In our experiments we have studied polyelectrolyte systems bearing Bromine counterions, the absorption edges of these counterions could be easily reached by synchroton radiation.

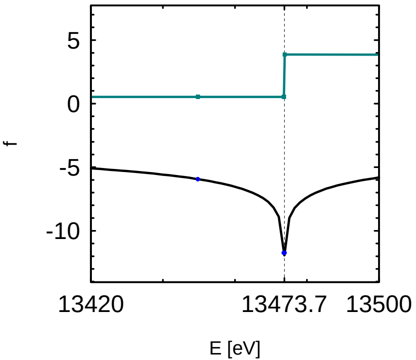

Fig:1 depicts the Dispersion of Br near the K-edge: The real part f' and the imaginary part f'' as function of energy.

Based on the earlier work of Stuhrmann [5], the ASAXS-intensity may be split into three terms :

$$I(q) = F_0^2(q) + 2f'(E)F_0(q)v(q) + [f'(E)^2 + f''(E)^2]v^2(q) \qquad (1)$$

The first term is the intensity measured far below the edge as measured by conventional SAXS. The second term is the cross-term of the non-resonant amplitude and the third term, also know as the self-term is the Fourier-transform *v(q)* of the distribution of the counterions.

Analysis of Rod-like polyelectrolytes:

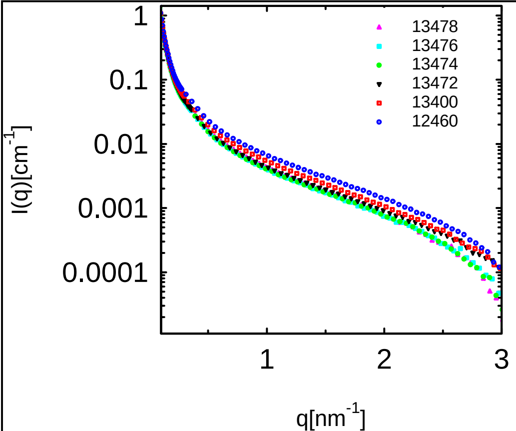

Fig 2: shows: Intensity I(q) measured as function of q for different energies of the incident beam.

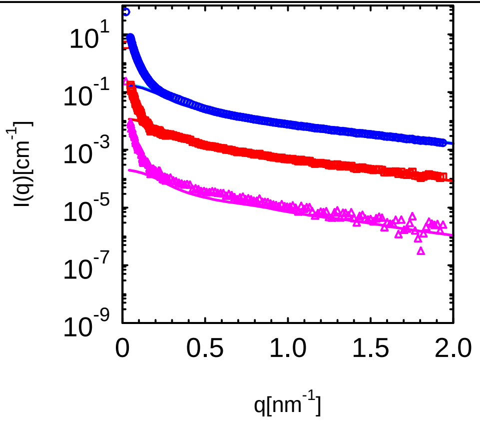

Fig 3: shows the partial intensities obtained by ASAXS are plotted against q. The solid lines mark the prediction of the cell model.

The polyelectrolyte (Fig. 1) was synthesized and purified as described recently [6-7]. ASAXS experiments were carried out on rod-like polyelectrolytes having two bromine counterions per repeating unit, the K-edge of which can easily be reached (E = 13473.7 eV), the degree of polymerization Pn=53. Dilute polyelectrolyte solutions (7.0 g/L) were used and hence the effect of structure factor could be discarded at higher angles. Fig. 2 demonstrates that reasonable data were obtained up to $q \approx 3nm^{-1}$. The shift of $I(q)$ towards smaller values as the absorption edge was approached, as predicted by Eq.1 was indeed observed for rod-like polyelectrolytes as well. Fig. 3 shows the decomposition of the ASAXS-intensities measured at different energies of the incident beam according to Eq. 1. The latter partial intensity named self-term is the most interesting result because it is the scattering intensity of cloud of counterions only. All previous evaluations of ASAXS-data proceeded by subtracting the first, non-resonant term from the experimental data. The non-resonant term could in principle be obtained through measurements far below the edge. Model calculations furthermore showed that the third partial intensity is small as compared to the cross term. Hence, this term was disregarded in previous ASAXS-studies of polyelectrolytes. Eq. 1 is a quadratic form in terms of the scattering factor f' if f'' is disregarded. This approximation is justified for data below the edge were f'' is rather small indeed. In Fig. 3 the uppermost intensity (circles) corresponds to the conventional SAXS-intensity measured far below the edge. The lowermost intensity is the self-term of of Eq.1 and the intensity in between marks the cross-term. As expected from previous model calculations, the intensities exhibit a very similar dependence on q. The self-term which is much smaller than the non-resonant term or the cross term can be obtained up to

$q = 2.5\ nm^{-1}$. This term provides the most valuable information of the ASAXS-experiment. It refers to the scattering intensity that would result from a system in which the macroion is totally matched. The three partial intensities displayed in Fig. 3 now serve for an unambiguous test of the cell model. Since the polyelectrolyte has already been studied by conventional SAXS, all parameters can be taken from this work. Hence, the charge parameter ξ is 3.3 and the comparison with the cell model can be done. Fig. 3 shows that good agreement is reached for all three partial intensities. All ratios between the intensities as well as their dependence on q are captured by the cell model. The self-term is slightly underestimated but the small differences seen are hardly beyond the experimental uncertainty [3].

There is a small discrepancy between theory and experiment at small q-values, this upturn has been seen in the solution of flexible polyelectrolyte solutions. The publication of the full analysis of this data was selected as a hot article (http://www.rsc.org/is/journals/current/pccp/hotarticles.htm).

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