ESRF	**Experiment title:** **ASAXS study of flexible cylindrical magnetic core-shell polymer brushes**	**Experiment number**: SC-2025
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Shifts: 12	**Local contact(s):** Dr. Peter Boesecke	
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Report:

In this experiment we are evaluating the overall shape of flexible polyelectrolytes having cylindrical shape using ASAXS technique. The central question is the distribution of the counterions around the macroion. Due to the eletric field of the macroion a certain fraction of the counterions are expected to be condensed to the macroion. In particular we tried to understand polychelates of a amphiphilic brush with poly(acrylic acid) core and poly(n-buthyl acrylate) shell having iron counterions. An atomic force micrograph picture and a sketch of the investigated system is shown in Fig. 1.

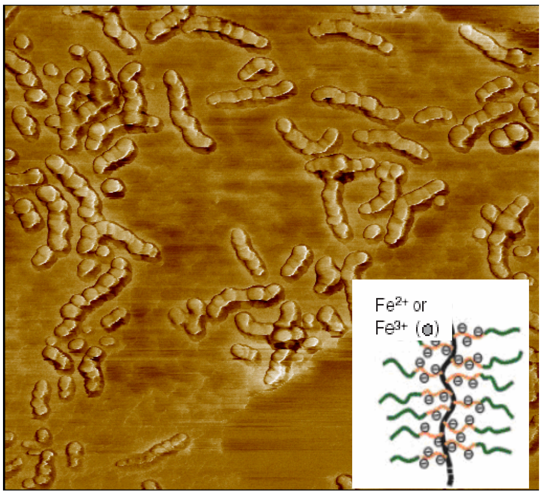

Fig. 1: Schematic illustration and AFM image of cylindrical magnetic nanowires.

ASAXS technique combines conventional SAXS with the effect of anormalous dispersion. When the wavelength of incident radiation approach the absorption edge an element the scattering factor f 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.

Based on the work of Stuhrmann [1] and on our recent work [2,3], the ASAXS-intensity can 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 is the Fourier-transform *v(q)* of the distribution of the counterions [2,3].

The macroion of the polyelectrolyte brush does not exhibit any resonance near the energy employed for the ASAXS studies, since it consists of elements as carbon and hydrogen. Therefore in contrast to the scattering of the counterions the contribution of the macroion to the measured scattering intensity stays constant in the range of energies used in our experiments. For ASAXS the intensity *I(q)* is measured at seven energies immediately below and above the edge of the counter ions (edge: 7112 eV) at two detector positions (4.2 m and 0.5 m). Unfortunately, a limited solubility (5 g/L in mixture of methanol /chloroform) led to a low ASAXS effect which created difficulties in the course of the analysis of the data. Hence, we first studied dry samples. Fig. 2 shows the scattering intensities of a dried brush at three different energies of the incident beam. The ASAXS analysis showed no ASAXS effect for $q<0.3$ nm^{-1}, therefore we show a plot for $q>0.3$ nm^{-1}. In the inset the intensity far away from the edge is given and the range of ASAXS effect is marked. From Fig. 2, it is evident that the scattering intensities are lowered as the absorption edge of the counterion iron is approached. As one can see, the ASAXS effect is very low.
The variation of *I(q)* with *f'* is used to decompose *I(q)* for $q>0.3$ nm^{-1} according to eq. 1. The result is given in Fig. 3. The small discrepancies may be attributed to statistical error. For $q>0.3$ nm^{-1} the shape of the partial scattering of the counterions $v^2(q)$ is similar to the scattering of the whole particle *I(q)*. Evaluation of the AFM picture shown in Fig. 1 leads to the assumption that the formfactor of magnetic nanowires can be described using the model of flexible cylinders or a pearl necklace model (chain of spheres separated by a given distance). In pearl necklace model the blob size due to iron ions is expected to be about a few nanometer in diameter. Model calculations using the model of flexible cylinders based on parameters found in AFM (contour length about

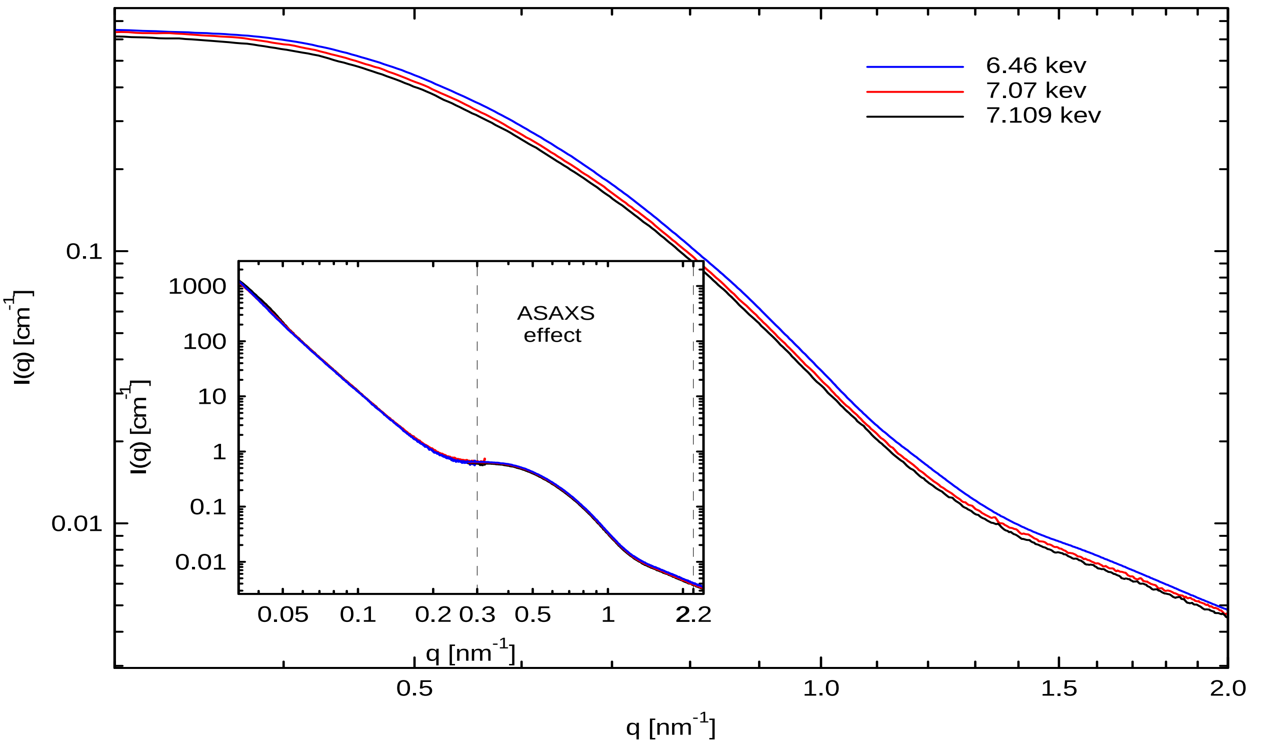

Fig. 2: Scattering intensities measured at different energies near K-edge of iron. Inset: Scattering intensity of magnetic cylindrical brushes far below the iron edge.

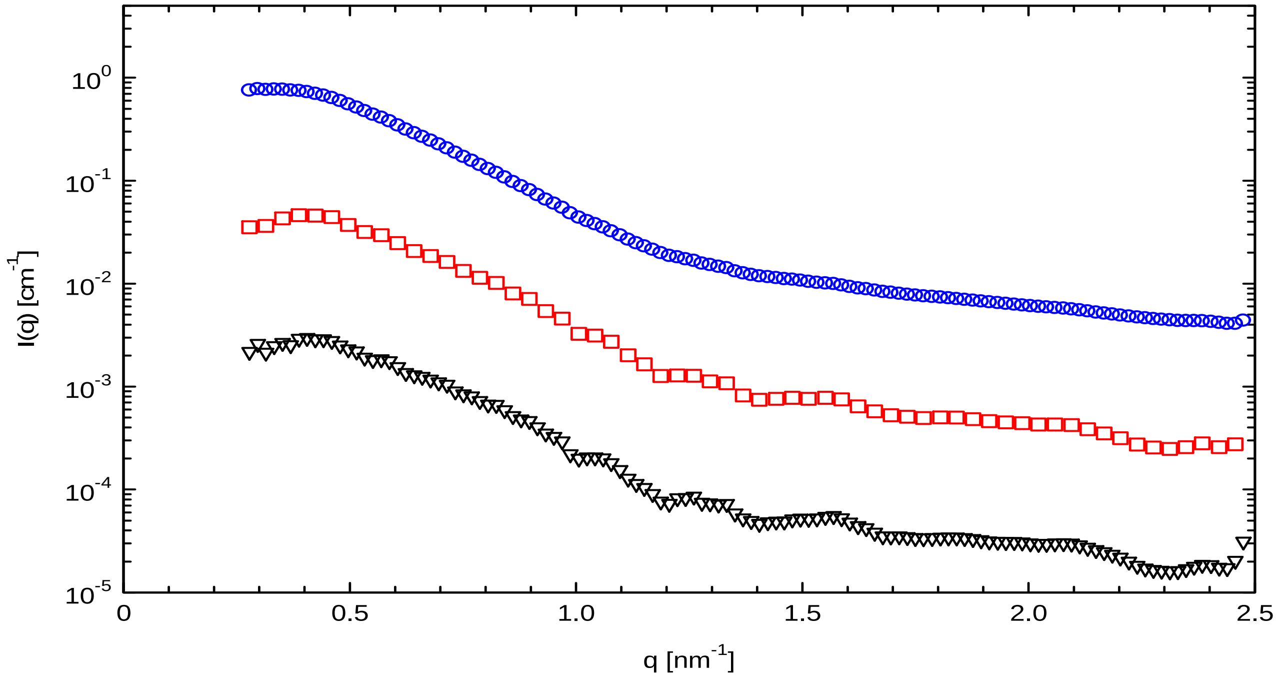

Fig. 3: Partial intensities obtained by decomposition of the intensity after equation 1. (blue: intensity measured far below the edge; red: cross term; black: self term).

380 nm, radius ca. 13 nm) do not describe the experimental data at all. In a first approximation the experimental data (and therefore partial scattering intensities due to the ASAXS effect) can be described for *q*>0.2 nm^{-1} using the model of connected spheres (radius 2.6 nm, polydispersity of 40% Gaussian distribution). Taking interparticular interactions into account allows a good description of the scattering pattern even for small *q* values. A more detailed analysis is currently under way.

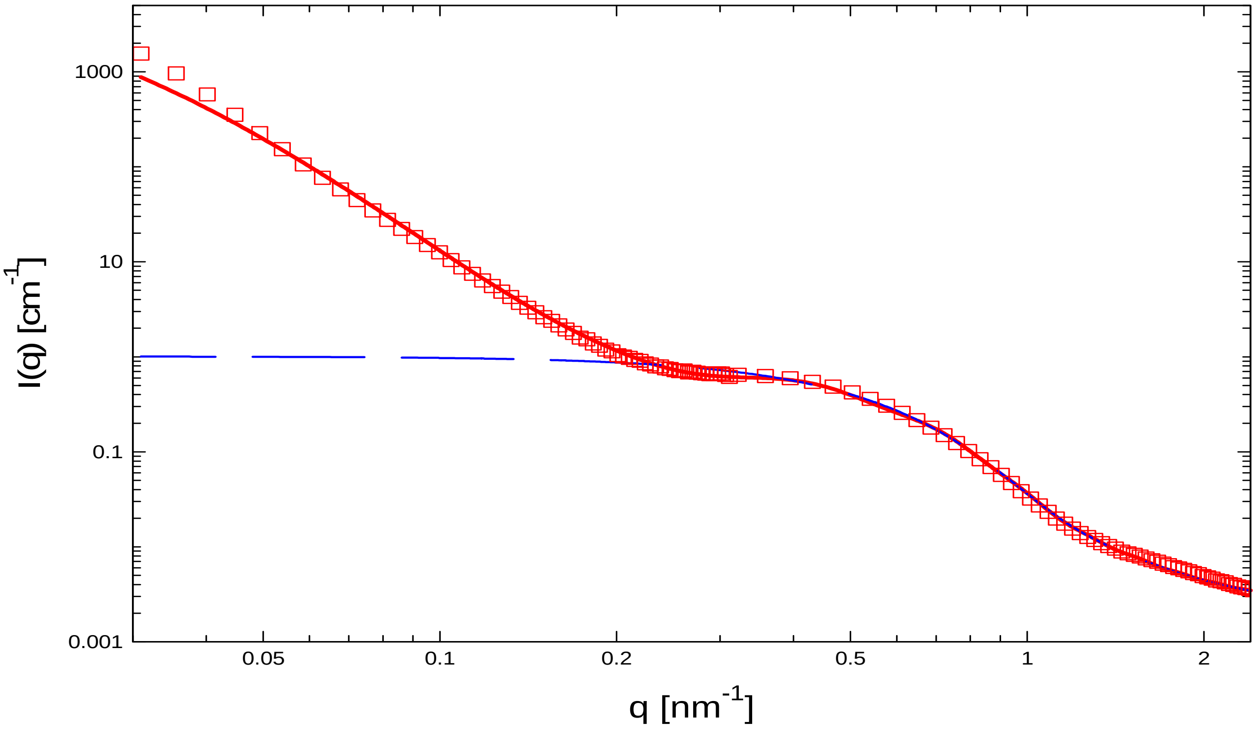

Fig. 4: Scattering intensity of a dries sample far away from the edge (symbols) in comparision to a formfactor of a sphere (blue dashed line). Taking interparticular interactions into account using the Baxter model leads to a good description (red solid line).

References

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