



	Experiment title: Investigation of spherical polyelectrolyte brushes by ASAXS	Experiment number: SC- 787
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Shifts: 8	Local contact(s): Dr. Theyencheri Narayanan	<i>Received at ESRF:</i>

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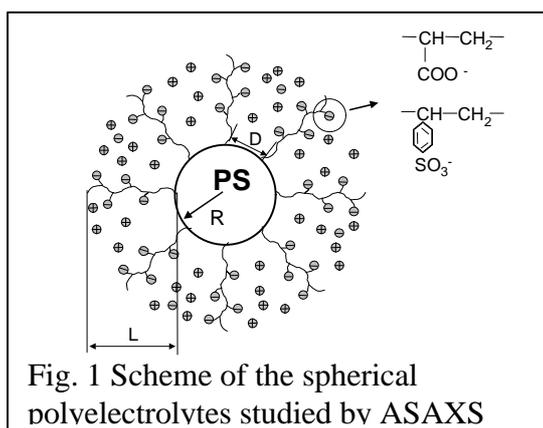
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Report:

We have studied the chain conformation and the distribution of counterions of spherical polyelectrolyte brushes. These systems consist of a solid poly(styrene) (PS) core with chemically bound linear poly(acrylic acid) (PAA) chains on the surface as depicted in fig.1 [1-2]. The central issue in the field of polyelectrolytes is the distribution of the counterions around the macroion. This



is closely related to the conformation of the polyelectrolyte chains and to the correlations between counterions and the macroion.

We examined four systems differing in the length of the PAA-chains. For two of the system we also varied the pH of the solvent. First we measured the sample with normal counterions (H^+) to receive information about the macroion and the confirmation of the polyelectrolyte chains. Then we used the same system with Rubidium-counterions to perform anomalous small-angle X-ray scattering experiments (ASAXS). In the energy-range around the k-

edge of rubidium ($E=15.199eV$), the scattering factor of the macroion stays constant while the scattering factor of the counterions is changing rapidly. Each serie was measured at 15 different energies, changing from 12460eV to 15200eV, e.g. from far below too slightly behind the edge of the counterions. To monitor exactly the energy, the transmission of the sample was measured simultaneously to the scattering intensity. The following results are shown for the system with the longest chains. It contains more Rb-counterions than systems with shorter chains so that it possesses the most pronounced effect by changing the energy.

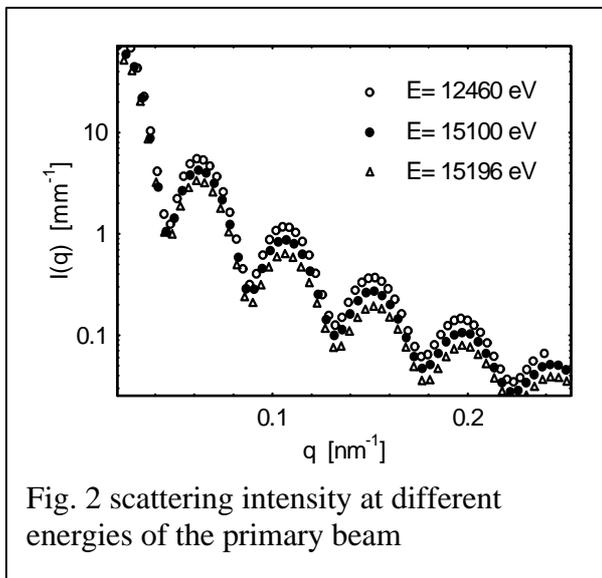


Fig. 2 scattering intensity at different energies of the primary beam

Fig 2. shows the first result of the measurement: The scattering intensity changes remarkably for the same sample when changing the energy of the primary beam.

Near the adsorption edge, the scattering factor becomes a complex quantity $f = f_0 + f'(E) + i f''(E)$. Hence, one can split the scattering intensity into three terms [3]:

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

Model calculations [3] show that the self-term of the counterions, $v^2(q)$, is negligible compared to the both other terms. If one subtracts two energies from each other, the constant term $F_0^2(q)$ (contains the contribution of the macroion and the constant part f_0 of the counterions) should vanish. The remaining cross term should scale with the difference of the f' -values. Fig. 3 demonstrate this behaviour for the experimental data for three different pairs of energies. Calculating of this behavior is a test for the model calculations saying $v^2(q)$ is negligible and a test for the absolute intensities if the scattering experiment.

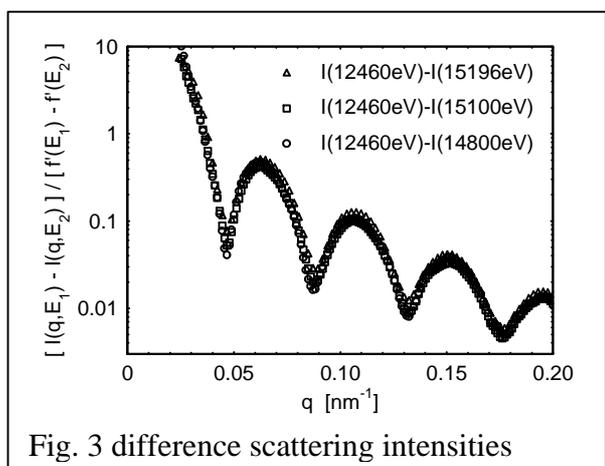


Fig. 3 difference scattering intensities

Eq. (1) shows that measuring at two energies gives the cross-term $F_0(q)v(q)$. On the other hand, measuring far below the edge where f' and f'' are negligible gives directly $F_0^2(q)$. Neglecting problems of polydispersity which is justified for the extremely small polydispersities of the samples examined here one can experimentally determine the scattering $v^2(q)$ of the counterions alone, just by calculating the square of the crossterm, divided through $F_0^2(q)$. Fig 4. shows the experimental result and a fit that describes both terms, $F_0^2(q)$ and $v^2(q)$. Therefore it was necessary to assume a similar scattering length density distribution for the polyelectrolytes and for the counterions as shown in the inset of fig.4.

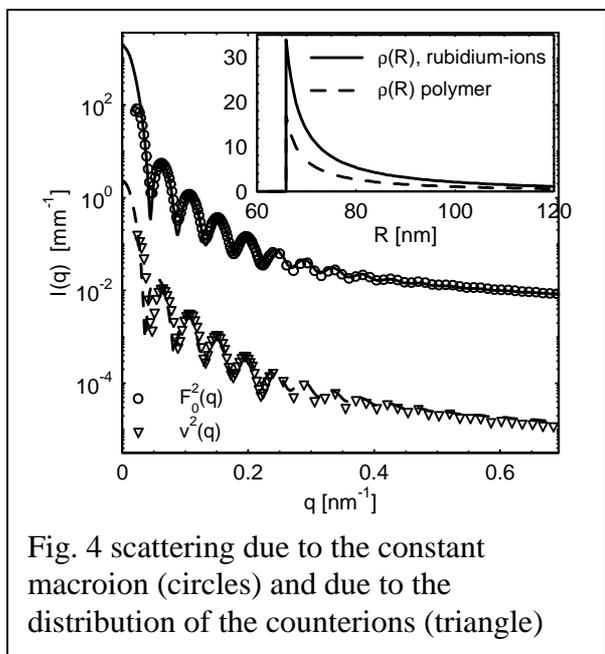


Fig. 4 scattering due to the constant macroion (circles) and due to the distribution of the counterions (triangle)

In conclusion: ASAXS gives the possibility to determine the scattering of the counterions alone. Hence, it is possible to distinguish between the distribution of polyelectrolytes and counterions by measuring only one system at different energies. In the present system the radial distribution of counterions and polyelectrolyte chains seems to be nearly the same which shows the strong correlation caused by the electrostatic interaction. A more detailed analysis and a first publication are in preparation.

1. Guo X, Ballauff M (2000) *Langmuir* **16**, 8719
2. Guo X, Ballauff M (2001) *Phys Rev E* **64**, 51406
3. De Robillard Q, Guo X, Dingenouts N, Ballauff M (2001) *Macromol Symp* **164**, 81