

	Experiment title: Study of Polyelectrolytes by ASAXS	Experiment number: SC-1144
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Shifts:	Local contact(s): Dr. T. Narayanan	<i>Received at ESRF:</i>

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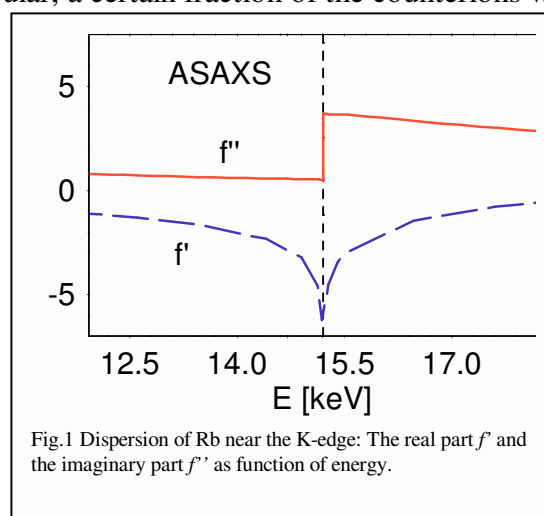
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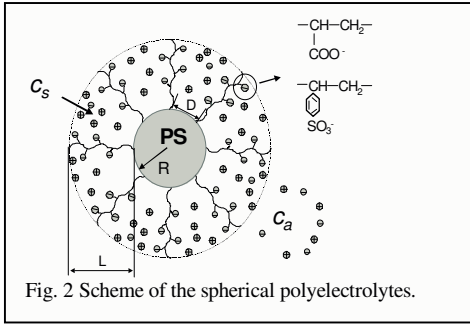
Report: We are at present working on a long-term project, which is a continuation of our earlier experiment (SC-1029), to study the polyelectrolytes in solution using ASAXS. A important question in this field is the spatial distribution of the counterions around the macroion. The strong electric field of the macroion leads to strong correlation of the counterions with the macroion. In particular, a certain fraction of the counterions will be “condensed” to the macroion. Earlier experiments (SC 787, SC-1029) have shown that small-angle X-ray scattering methods 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 [6].

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 Rubidium 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 Rubidium ions. In our

experiments we have studied polyelectrolyte systems bearing Rubidium (star polymers) or Strontium (brushes) counterions.



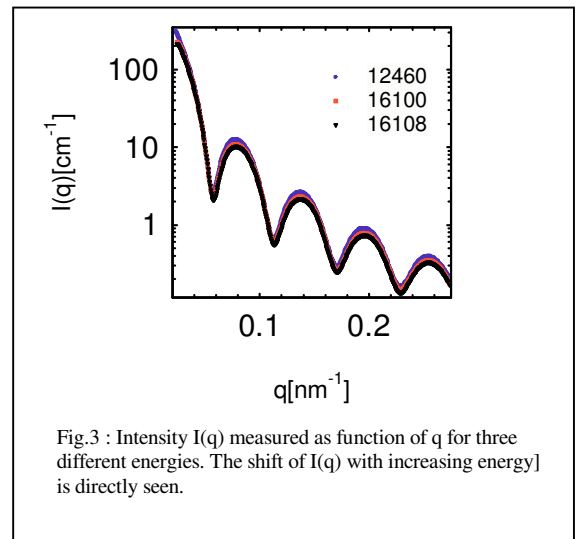
Based on the earlier work of Stuhrmann [2], the ASAXS-intensity may be split into three terms :

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

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 known as the self-term is the Fourier-transform $v(q)$ of the distribution of the counterions.

1. Spherical Systems: *Spherical polyelectrolyte brushes* [1-2] are shown in Fig. 2. The spherical polyelectrolyte brushes consist of a solid poly(styrene) core of ca. 100 nm diameter onto which long linear chains of poly(sodium styrene sulfonate) (NaPSS) are densely grafted. Such systems are defined as quenched polyelectrolyte brushes. The sodium counterions can be replaced by ions which can be ‘seen’ by synchrotron radiation by counterion replacement using ultrafiltration. In the following, we would present the results obtained from the ASAXS studies carried out on such systems bearing Strontium counterions.

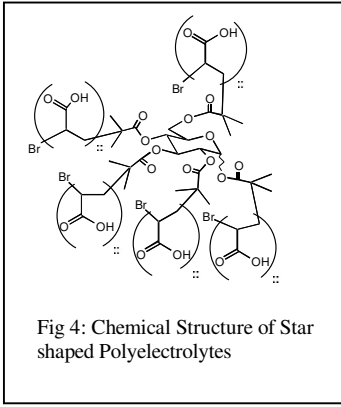
Analysis of spherical polyelectrolyte brushes: The macroion which is composed of polystyrene does not show any resonance near the energy employed for the ASAXS studies, since it consists of elements like Carbon and Hydrogen. Therefore the contribution of the macroion to the measured scattering intensity stays constant in the range of energies used in our experiments. ASAXS-investigation that probe the intensity $I(q)$ immediately below the edge and above the edge elucidate the variation of $I(q)$ due to the change of f . The entire spherical polyelectrolyte brush can now be described by two spatial distributions: i) the electron density of the macroion and ii) the spatial distribution of the counterions $v(r)$ having spherical symmetry. Fig. 3 shows the scattering intensities at three different energies of the incident beam obtained for spherical polyelectrolyte brushes. From Fig. 3, it is evident that the scattering intensities are lowered as the absorption edge of the counterion ion is approached.



In our previous experimental results obtained by ASAXS (proposal SC-787) on the spherical polyelectrolyte brushes bearing univalent Rubidium counterions, we had demonstrated that the counterions are strongly confined within the brush [7]. It was obviously interesting to study the behavior of divalent counterions, since very little has been known about such systems. In our experiments, we investigated the polyelectrolyte quenched brushes. The sodium counterions of these brushes were then replaced by divalent Strontium counterions by ultrafiltration, the absorption edge of these counterions can be reached by synchrotron radiation (Sr^{2+} 16104.6 eV). In these studies we are able to determine all the three partial intensities for the quenched brush systems bearing Strontium counterions. In Fig 4. the uppermost term (circles) corresponds to the conventional SAXS-intensity measured far below the edge. The term in the middle corresponds to the cross-term and the lowermost term is the so-called self-term obtained for spherical polyelectrolyte brushes with Strontium counterions according to Eq. 1. From the analysis of the data obtained for divalent counterions, it is clear that the Strontium ions too, as compared with the Rubidium ions decorate the polyelectrolyte chains and are strongly confined within the brushes. This results also confirm that using synchrotron radiation reliable and consistent ASAXS data can be obtained, and that the results obtained are in consistence with the theoretical predictions.

2. Star branched Polyelectrolytes: We present our preliminary results on star branched polyelectrolytes.

Here we have used star branched polyelectrolytes as shown in Fig 4, which consists of arms of poly(acrylic acid) (PAA), with varying number of arms and degree of polymerization, the polyelectrolyte is formed by titrating the polyacid with RbOH solution, as in the case of spherical polyelectrolyte brushes [1]. A series of SAXS and ASAXS experiments were carried out on star branched polyelectrolytes at different concentrations and varying degrees of dissociation.



Analysis of Star branched polyelectrolytes: Recent studies on Star branched polyelectrolytes have shown that the salt-free solutions of these polyelectrolytes, show an ordering phenomenon in the vicinity of the overlap volume fraction ϕ^* [4-5], with the ordering phenomenon decreasing for lower and higher volume fractions away from ϕ^* . In our experiments, we analysed star branched

polyelectrolytes using SAXS and ASAXS. Fig 3. shows the SAXS results obtained for star-shaped polyelectrolytes comprising of 21-arms and a degree of polymerization, $P_n=60$, $\alpha=0.7$. It is evident from Fig . 5, that some sort of an ordering phenomenon is observed in the vicinity of the overlap concentration, which then vanishes on either side of the overlap volume fraction ($\phi^* \sim 0.44$ vol.%).

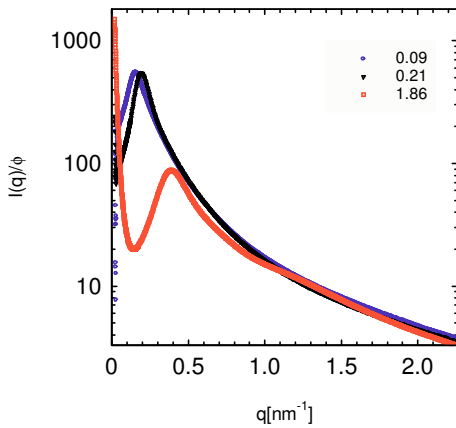


Fig 5: shows the SAXS scattering intensities as a function of q at Different volume fractions (vol %)

The shift of q_{max} towards higher q -values as a function of increased concentration, is due to the decrease in the interparticle distance between the polyelectrolyte chains. Fig 6. shows the scattering intensities at five different energies of the incident beam obtained for a 21-arm star with $P_n=60$. Like predicted by theory the scattering intensities are lowered as the absorptions edge of the counter ion is approached.

Fig 7. shows the ASAXS data obtained for star shaped polyelectrolytes having 21-arms and degree of polymerization $P_n=60$, $\alpha=0.7$. As in the case of spherical polyelectrolyte brushes [1], we carried out the analysis of the ASAXS data for star-shaped polyelectrolytes in the similar fashion. All the three terms relating to Eq 1. can be extracted from this data as well. Fig 7. shows the three partial intensities as a function of q , for star-shaped polyelectrolytes. The uppermost term (circles) relates to the intensity measured far away from the absorption edge of Rubidium, the lowermost term is the self-term and relates to the counterions (triangles), and the intensity in between relates to the cross-term (squares).

The experimental data obtained for these systems, is currently being compared with the theoretical predictions by Jusufi et.al [3]. From our experiments, it was evident that the counterions decorate the macroions, as was found in the case of spherical polyelectrolyte brushes and rod-like polyelectrolytes (SC-1029). It is clear that ASAXS is indeed a very robust method to study the polyelectrolytes in solution, and to obtain the information regarding the distribution of counterions in solution. A detailed analysis of these results as compared with the computer simulations is currently under investigation.

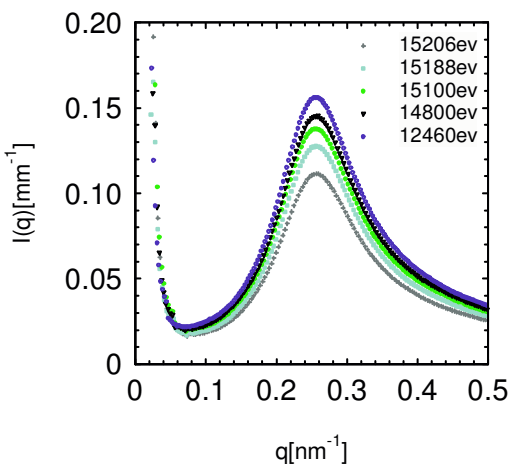
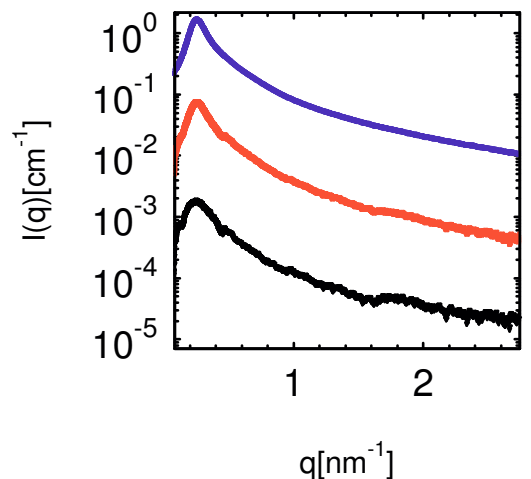


Fig 6 shows the scattering intensities at five different energies. The shift of the intensities $I(q)$ with the eneries is direct seen.

Fig 7: shows the three partial intensities as a function of q for Star Polyelectrolytes, with 21-arms and $P_n=60$.



References:

1. Dingenouts N, Merkle R, Guo X, Narayanan T, Goerigk G, Ballauff M, *J.Appl.Cryst.* (2003) 36:578
2. Stuhrmann HB (1985) *Adv Poly Sci* 67:123
3. Jusufi A, Likos C.N, Löwen H, *Phys Rev Letters* (2001) 88:018301
4. Heinrich M, Rawiso M, Zilliox J.G, Lesieur P, Simon J.P, *Eur Phys J E* (2002) 4:131
5. Moinard D, Taton D, Gnanou Y, Rochas C, Borsali R, *Macromol. Chem Phys* (2003) 204:89
6. Patel M, Rosenfeldt S, Ballauff M, Dingenouts N, Pontoni D, Narayanan T (2004) *Phys Chem Chem Phys* 6:2962
7. Dingenouts N, Patel M, Rosenfeldt S, Pontoni D, Narayanan T, Ballauff M, *Macromolecules*, accepted