

Anomalous Small-Angle X-ray Scattering Study of poly(p-phenylene)-Polyelectrolyte with Bromine Counterions

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Between polyelectrolytes and their dissociated counterions in solution a correlation is forming due to the strong electric field. The exact distribution of the counterions around the macroion is still under discussion. Anomalous small-angle X-ray scattering (ASAXS) is a well-suited technique to analyze the distribution of the counterions [1,2]. If the energy E of the incident X-ray beam is changed in the vicinity of the absorption edge of the counterions their scattering contributions change accordingly. Therefrom, structural information about the distribution of the counterions can be obtained.

The synthesis of stiff-chain polyelectrolytes was carried out using the method developed by Rehahn et.al. [3], having degree of polymerisation ($P_n=53$). These stiff-chain polyelectrolytes were then cleaned using ultra-filtration and dried for storage. Fresh samples were prepared just before measurements using Millipore water (conductivity $0.4\mu\text{S}/\text{cm}$) as solvent. The salt-free solutions have been confined in capillaries of 4.1 mm diameter. ASAXS measurements were performed at the JUSIFA-beamline, at HASYLAB, DESY Hamburg in the energy range of the K-absorption edge of Br at 13473 eV. The scattering curves are calibrated into macroscopic scattering cross sections in units of cross section per unit volume.

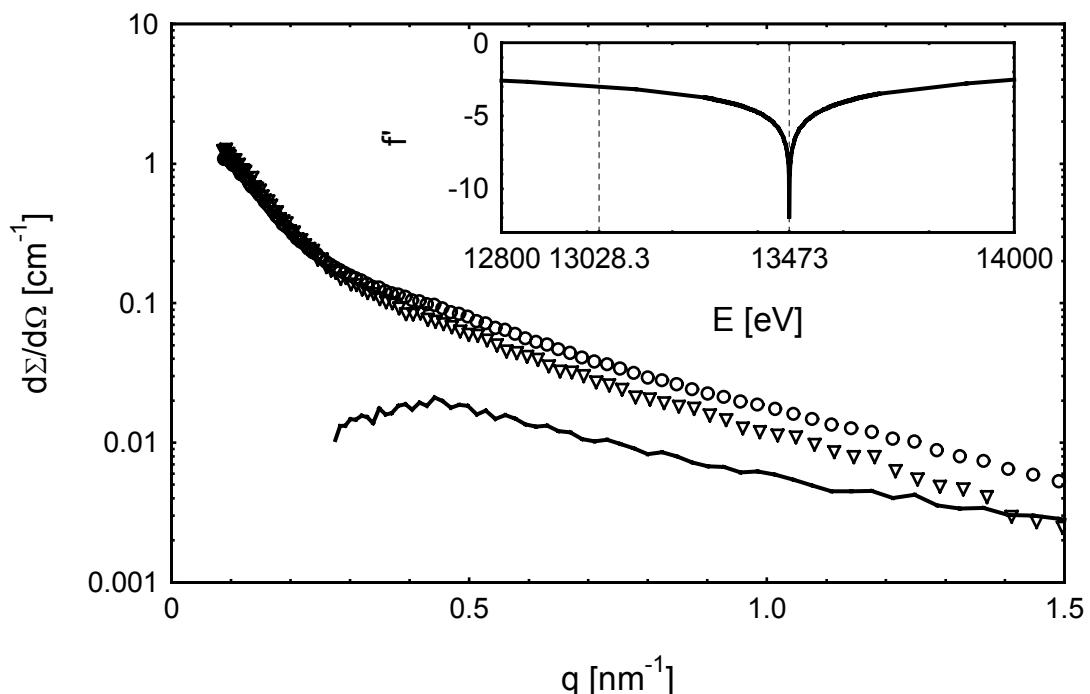


Figure 1: Scattering curve of the stiff-chain-polyelectrolyte with Br-counterions measured at two different energies: ○ at energy of 13028 eV, e.g. -445eV from the edge, ▽ at energy of 13473 eV, e.g. at the edge. The line shows the difference of the two scattering intensities. The inset shows the energy dependence of the scattering factor f' of bromide. The used intensities are marked with dashed lines.

In Figure 1 the scattering curves obtained from SAXS measurements at two different energies is shown. One energy far below the edge (-445 eV) and the other directly at the absorption edge. The inset shows the used intensities compared to the atomic scattering factor f^* of bromide. The scattering intensities reveal a significant energy dependence when approaching the energy of the K-absorption edge. The scattering intensity in the q-range between 0.4 and 2 nm⁻² is reduced when approaching the K-absorption edge of Br giving clear evidence of correlation between the counterions and the macroions. The solid line shows the difference between the two scattering intensities which is also resolved in good statistics. This difference is given by the crossterm of the energy-dependent scattering amplitude of the counterions and the constant amplitude of the backbone of the polyelectrolytes and therefore includes independent informations about the macroion and the counterions [4]. Further evaluations are in progress.

References

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