

Sr²⁺-Induced Collapse of Sodium Polyacrylate Chains as Assessed by Anomalous Small-Angle X-ray Scattering

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The present contribution deals with the conformation of the sodium salt of polyacrylic acid (NaPA) in aqueous solutions with 0.01 M NaCl and pH 9. NaCl was added in order to screen the electrostatic interaction between dissociated carboxylate groups, which leads to a coiled chain conformation of the polyanions. In contradiction to Na⁺, Sr²⁺ binds specifically and more tightly to the carboxylate groups. This interaction neutralizes the polyanions to a large extent, and due to the hydrophobic nature of the backbone, leads to a collapse of the polyelectrolyte chains. Theoretical work on this shrinking process, based on scaling arguments and Monte Carlo simulations propose that polyelectrolyte structure passes elongated intermediates like cigars or pearl necklaces [1,2] before reaching the spherical shape. However, these conformations have not yet been observed experimentally. If a large fraction of the carboxylate sites is occupied by Sr²⁺ ions, the spacial distribution of the Sr²⁺ ions should reflect the monomer density distribution within the collapsing chain and anomalous small angle X-ray scattering (ASAXS) may be a well-suited experimental technique to study the correlation of the macroion with its counterions [3].

First, a stock solution of NaPA (supplier: Polysciences, Eppelheim, Germany) was prepared in bidistilled water with 0.01 M NaCl and pH 9. After 3 days, this solution was combined with a SrCl₂ solution with pH 9 and 2[Sr²⁺]+[Na⁺]=0.01M [4]. The Sr²⁺ content thereby is set to 1.5 mM. In order to approach the precipitation limit, several polymer concentrations were produced by diluting with a solution with 1.5 mM SrCl₂, pH 9 and 2[Sr²⁺]+[Na⁺]=0.01M, i.e. with a constant concentration of cationic charges. Preliminary measurements using combined static and dynamic light scattering (ALV 5000E CGS) allowed us to get first information on the shape of the polymer chains in dependence on the ratio of 2[Sr²⁺]/[NaPA]. Finally, two samples differing in the polymer concentration were chosen: P4KE corresponds to [NaPA] = 3.61 mM, i.e. 2[Sr²⁺]/[NaPA] = 0.42, P4KU2 corresponds to [NaPA] = 3.25 mM, i.e. 2[Sr²⁺]/[NaPA] = 0.46 which is close to the border line of phase separation. Compared to coiled chains in Sr²⁺-free solutions, the polyanion dimensions of both samples are significantly shrunken. The two samples as well as the solvent (containing the same amount of Sr²⁺) were filled into capillaries from Hilgenberg GmbH, Malsfeld, Germany. The capillaries are made of borosilicate glass with an inner diameter of 4 mm and a wall thickness of 0.05 mm. The inner diameter of 4 mm is nearly the optimal size for the energy range of the Sr-K edge at 16.105 keV. The capillaries were closed with a pipette plug fixed by two component quick setting adhesive.

ASAXS measurements were performed at the JUSIFA beamline at HASYLAB, DESY Hamburg in the energy range of the K-absorption edge of Strontium at 16.105 keV. The energy dependence of the small angle X-ray scattering near the K-absorption edge of Sr is used to separate the scattering due specifically to the Sr-ions.

In Figure 1 the scattering curves of NaPA-chains at [NaPA]=3.61 mM (P4KE) obtained from SAXS measurements are shown. The total as well as the separated scattering curve follows a power law of $d\sigma/d\Omega \sim q^{-\alpha}$. The exponent α is close to 2 for both curves, indicating a coil like behavior [5]. However, it is worth mentioning that the separated curve reveals undulations which points to the occurrence of spherical subdomains as would be expected for a pearl necklace [2].

The scattering curves (total and separated in Figure 2) of a second sample (P4KU2) with a smaller concentration of NaPA ([NaPA] = 3.25 mM), but the same SrCl₂ content as P4KE show a different behavior. However, the separated scattering curve (red) obtained from SAXS measurements at the two energies 15.507 and 16.105 keV exhibits a similar characteristic for $q > 0.02 \text{ 1/\AA}$ with

pronounced maxima, minima and shoulders indicating a scattering function, which again seems to be influenced by correlation effects between rather monodisperse subdomains within the collapsing chains. The total scattering curve (black) measured at 15.507 keV shows several shoulders and is compatible with the form factor of a polydisperse sphere with the polydispersity inherent in the original NaPA-sample. Possibly the NaPA coil collapses to a sphere whereby the structure of pearl-like subdomains is preserved.

Thereby the measurements clearly reveal significant contributions from non-uniformly distributed Sr-counterions imaging the monomer distribution.

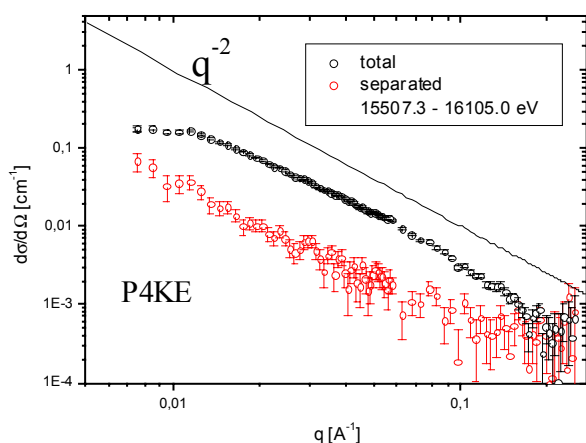


Figure 1: ASAXS measurements of the collapsed NaPA chains ($[\text{NaPA}] = 3.61 \text{ mM}$; $2[\text{Sr}^{2+}]/[\text{NaPA}] = 0.46$) at the Sr-K-absorption edge at 16.105 keV. The black scattering curve represents the scattering from the polymer and the Sr^{2+} ions. The red scattering curve is the separated scattering curve of the Sr^{2+} ions.

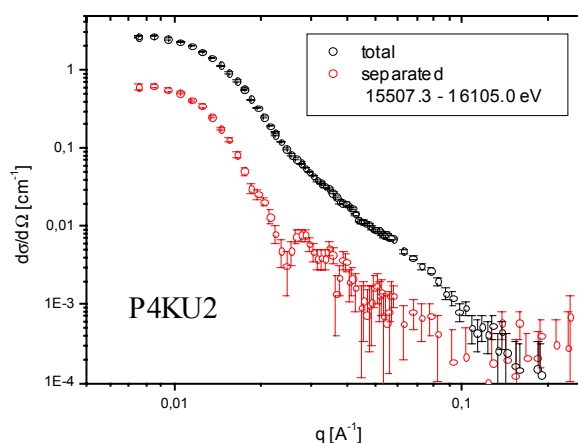


Figure 2: ASAXS measurements of the collapsed to sphere NaPA chains ($[\text{NaPA}] = 3.25 \text{ mM}$; $2[\text{Sr}^{2+}]/[\text{NaPA}] = 0.41$) at the Sr-K-absorption edge at 16.105 keV. The black scattering curve represents the scattering from the polymer and the counterions. The red scattering curve is the separated scattering curve of the Sr^{2+} ions.

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