Experimental report

14/09/2015

Proposal: **9-11-1701** **Council:** 4/2014

Title: Aluminium/Barium induced coil shrinking of Polystyrenesulfonate chains in dilute solution

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: D_2O
NaCl
$AlCl_3$
$BaCl_2$
sodium polystyrenesulfonate

Instrument	Requested days	Allocated days	From	To
D11	3	3	03/10/2014	06/10/2014

Abstract:

If aluminium or barium ions are added to an aqueous solution of sodium polystyrenesulfonate (NaPSS) the ions will induce coil shrinking. Once a critical limit of counterions per sulfonate groups is exceeded, aggregation and thereby precipitation of the polyelectrolyte chains sets in. Neutron scattering experiments on deuterated NaPSS are suggested to get information about the change in morphology of shrinking PSS chains, induced by the respective cations close to the phase boundary. The results are also expected to broaden our knowledge on the impact of specifically interacting metal cations on the shape of polyelectrolyte chains in dilute solutions.

Experimental Report 9-11-1701

Aluminium/Barium induced coil shrinking of Polystyrenesulfonate chains in dilute solution

Description of Experiment:

The present work investigates the impact of Ba^{2+} and Al^{3+} as specifically interacting cations (SIC) on the morphology of polystyrene sulfonate (NaPSS) chains in order to compare the results with those received earlier with anionic polyacrylate chains. For both AlPSS and BaPSS, the phase boundary in 0.1 M NaCl in D_2O was determined. Accordingly, different points in the phase diagram for each system were addressed by a gradual increase of the metal cation concentration, while the NaPSS (Mw 1500 kD) concentration stayed constant (Fig. 1). All solutions contain a concentration of 0.1 M of positive charges. This is achieved by introducing the specifically interacting cations via replacement of the corresponding amount of Na-ions in 0.1 M NaCl. After mixing the component solutions, the samples were shaken for at least one night. Successively, the samples were split. One part of each sample was filtered (pore size 0.2 µm) into a light scattering cell and the other part was filtered into a 5 mm Hellma cuvette for SANS. Characterization by light scattering before and during the SANS experiment enabled proof that the samples remained stable during the time of the SANS experiment. Two sets of samples were generated for BaPSS, which differed in the polymer concentration. For AlPSS just one set of samples was created. For the SANS experiments, the samples were measured at three different detector distances (1.2 m, 8 m, 34 m).

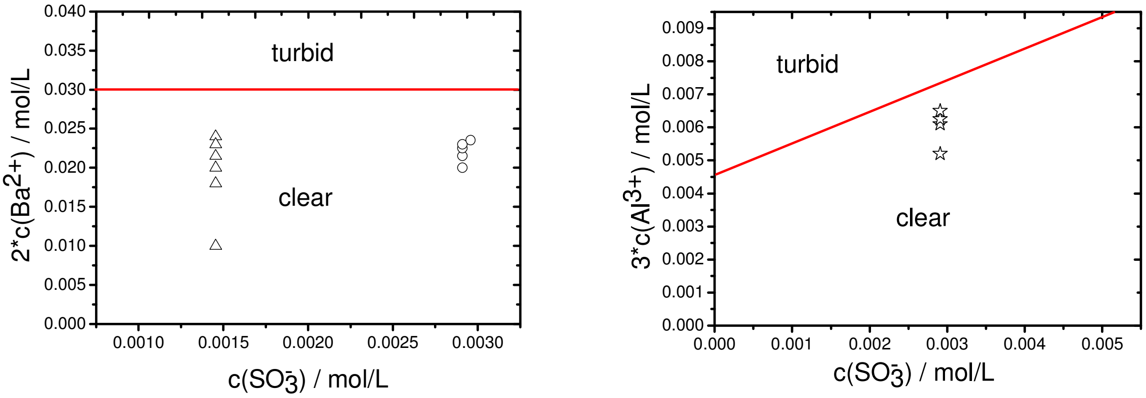


Fig. 1: Phasedigram of BaPSS (left) and AlPSS (right) in 0.1 M NaCl, dissolved in D_2O. The red line in both diagrams represents the respective phase boundary of the systems. The points represent the samples investigated by light and neutron scattering.

Results and Discussion:

Light scattering shows the expected trend of the polymer coil size with the Ba^{2+}/Al^{3+} concentration. While increasing the concentration of these SICs the radius of gyration (R_g) and the hydrodynamic radius (R_H) of the polyelectrolyte coils are shrinking. The SIC bind to the sulfonic groups of the polyelectrolyte and discharge the chains. This leads to a coil shrinking and once the level of SIC is high enough to aggregation and precipitation of the chains.

All SANS curves were merged with the respective light scattering curves (LS-SANS) in order to extend the scattering curve to lower q-values. Comparison of the LS-SANS curve of the sample with the highest (red curve in Fig. 3a) and the lowest amount of Al^{3+}-cations (black curve in Fig. 3a) overlay for the AlPSS system. Hence, AlPSS does not show any shape change at variable SIC concentration. The

Kratky-Plot of all four samples also overlay (Fig. 3b). Fits with the model of excluded volume chains to the joined LS-SANS curves gave nearly the same results as a Guinier analysis to the respective light scattering experiments for R_g (Tab.1).

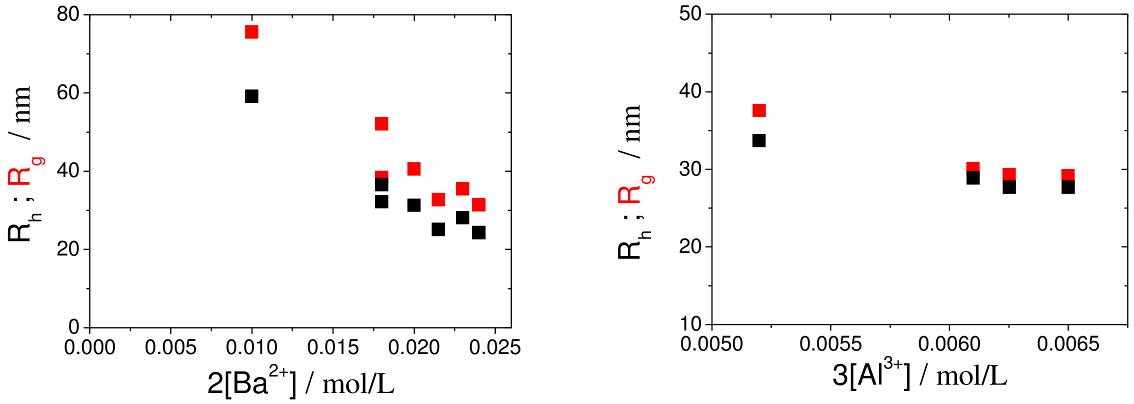


Fig. 2: Dependece of R_g and R_H of the polyelectrolyte coils on the SIC concentration from light scattering. The left hand figure is connected with the sample set in the BaPSS phase diagram indicated by the open triangles (Fig. 1). The right hand figure is connected with the sample set in the AlPSS phase diagram indicated by the open stars (Fig. 1).

Tab. 1: Comparison of experimental data and fits for the AlPSS system – Fig. 3a)

SAMPLE	Rg light scattering (*Guinier*)	Rg model fit to joined LS-SANS curve
Al-In (black curve Fig. 3a)	37.2 nm	37 nm
Al-VIIIn (red curve Fig. 3a)	29 nm	30.5 nm

In case of the BaPSS system the coil structure clearly depends on the Ba^{2+} concentration. By comparing the scattering curves recorded at the lowest and the highest concentration of Ba^{2+}-cations respectively, a change from a coil-like structure (black curve in Fig. 3c) to a more complex structure (red curve in Fig. 3c) is seen. In the Kratky-Plot a peak appears. The peak size increases with higher Ba^{2+}-concentrations (Fig. 3d). The scattering curve with the lowest concentration of Ba^{2+}-cations was fitted with the model of an *Excluded Volume Chain* (white line in 3c), while the curve with the highest concentration of Ba^{2+}-cations, was fitted with a *Pearl Necklace Model* (blue line in 3c) and a *Cylinder Model* (green line in 3c).

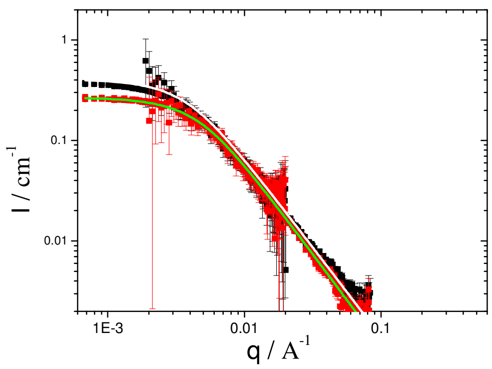
Tab. 2: Comparison of experimental data and fits in BaPSS system – Fig. 3c

SAMPLE	Rg light scattering (*Guinier*)	Rg model fit to joined LS-SANS curve
Ba 0.5n-modi (black curve Fig. 3c)	75.6 nm	66.2 nm
Ba VIIIn-modi (red curve Fig. 3c)	31 nm	22 nm

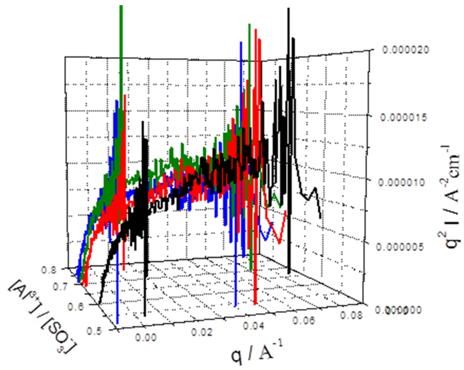
The fit with the *Excluded Volume Chain* gave good agreement with the LS-SANS curve and with the R_g results from the light scattering measurement in case of the BaPSS sample with the lowest Ba^{2+} content. In case of the curve with the highest concentration of Ba^{2+}-cations none of the models fits perfectly to the scattering curve. It is possible that the structure of the polystyrenesulfonate chain changes from a coil to a more potato- or cigar-like-structure. This would be similar to a mixture of a deformed-cylinder and perl-necklace-structure, where the spheres of the dumbbell are very close to each other. On the other hand it is also possible that the formfactor is influenced by a partial aggregation of the polyelectrolyte chains. In the light scattering measurements an increase of the molecular weight with increasing concentration of Ba^{2+}-cations was visible. The same trend was found for the maximum intensity in the SANS measurement, which increased slightly with increasing concentration of Ba^{2+}-cations (Fig. 3c).

In summary, the experiment provided new information on the behavior and structural changes of NaPSS chains in the presence of specifically interacting cations, which helps us to broaden our knowledge on polyelectrolyte – SIC systems.

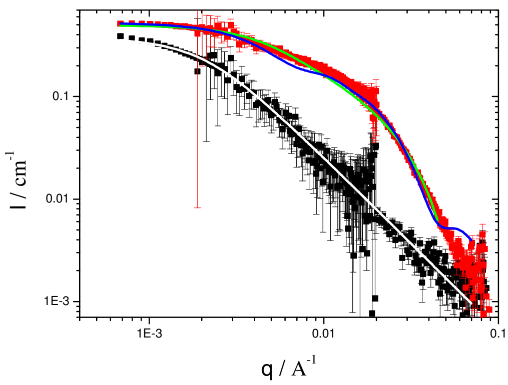
a)



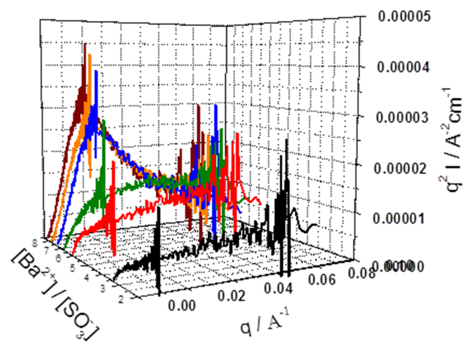
b)



c)



d)



<u>Fig. 3:</u> a) Scattering curve of the sample with the lowest (black curve) and highest (red curve) amount of Al^{3+}-cations and the respective fits b) Kratky plot of the set of samples form the AlPSS system - indicated by open stars in Fig. 1c) scattering curve of the samples with the lowest (black curve) and highest (red curve) amount of Ba^{2+}-cations and the respective fits (*Excluded Volume Chain* – white curve / *Cylinder* – green curve / *Pearl Necklace* – blue curve) d) Kratky plot of the set of samples from the BaPSS system – indicated by open triangles in Fig. 1