Experimental report

09/11/2018

Proposal: **9-11-1888** **Council:** 4/2018

Title: Contrast variation study of block copolymer micelles consiting of twonegatively charged polyelectrolytes

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Nico Oliver CARL**

Experimental team: Wenke MUELLER
Nico Oliver CARL

Local contacts: Ralf SCHWEINS

Samples: C3H3NaO2
C3D3NaO2

Instrument	Requested days	Allocated days	From	To
D11	4	3	07/09/2018	10/09/2018

Abstract:

Polyelectrolytes are widely used in industrial processes as anti-scaling agents, for waste water treatment or as rheology modifier in cement. They also serve as model system for natural polyelectrolytes such as proteins. The specific interaction of the charged polymer chain with oppositely charged species such as surfactants or ions is the basis for many of those applications and the industrial relevance of polyelectrolytes.

Previous works on two different negatively charged polyelectrolytes showed that the interaction with multivalent cations such as Ca2+ or Ba2+ strongly depends on the chemical nature of the anionic moiety. We use this cation selectivity to self-assemble a block copolymer consisting of both polymers into well-defined micelles (c.f. figure 1B). The block copolymer shows interesting properties such as a combination of lower and upper critical solution temperature or pH responsivity. Our work aims towards a better understanding of the specific interaction of multivalent cations with polyelectrolytes but also towards the design of new responsive and schizophrenic self-assembled systems.

Experimental Report 9-11-1888

Contrast variation study of block copolymer micelles consisting of two negatively charged polyelectrolytes

Experimental team: Nico Carl, Ralf Schweins

Data of the experiment: 07.09.-10.09.2018

Introduction

The aim of this experiment was to investigate the structure of block copolymer micelles with contrast variation. The block copolymers of interest consist of two negatively charged polyelectrolytes: polyacrylic acid (PAA) and polystyrene sulfonate (PSS). In the presence of multivalent cations such as Ca^{2+} this type of polymers form micelles. One main question was which block forms the hydrophobic core of the micelles and which block the hydrophilic corona. By deuteration of the PAA block it is possible to create a large difference in scattering length densities between PAA and PSS block.

Samples and technique

During the experiment, we investigated three different polymers all of them with similar molecular weight (~100 kg/mol): PSS_5-*b*-h_3PAA_{95} (block ratio 5:95), PSS_5-*b*-d_3PAA_{95} (block ratio 5:95) and PSS_{50}-*b*-d_3PAA_{50} (block ratio 50:50). d_3PAA and h_3PAA describes deuterated polyacrylic acid and hydrogenated polyacrylic acid, respectively.

For the contrast variation experiment, the micelles were prepared at the same polymer and Ca^{2+} concentration in six different H_2O/D_2O ratios.

In order to get an additional contrast and to guarantee that changing H_2O/D_2O ratio does not influence the micelle structure, SAXS profiles (figure 4A, ID02, ESRF) were acquired for all samples and contrasts.

Results and discussion

Figure 1, 2 and 3 show the SANS profiles acquired during the beamtime. Figure 4A shows the SAXS profiles for the sample PSS_5-*b*-d_3PAA_{95}. The solid lines represent simultaneous fit of all contrasts and the SAXS profiles to the model of polydisperse block copolymer with self-avoiding chains in the corona (Svaneborg, C., & Pedersen, J. S. (2002). Macromolecules, 35(3), 1028–1037).

For the two asymmetric polymers (PSS_5-*b*-h_3PAA_{95} and PSS_5-*b*-d_3PAA_{95}) we found, that changing from light to heavy water has an influence of the aggregation number (and therefore the position of the first form factor oscillations). Therefore, we attributed a separate aggregation number to each contrast. The aggregation numbers from PSS_5-*b*-d_3PAA_{95} as a function of D_2O content are shown in figure 4B. We used these aggregation numbers to normalize the coherent forward scattering from SANS. The square root of these reduced intensities are shown as a function of D_2O content in figure 4C. The points follow a linear trend and indicate that the match point of this particular sample occurs at 125 % D_2O.

The analysis of the data clearly shows that PAA complexed by Ca^{2+} forms the core of the corona, whereas PSS chains are located in the corona of the micelle.

From the analysis of the scattering data, we obtained several parameters:

- the aggregation number N_{agg}
- the radius of the core R_{core} and the corresponding standard deviation σ_{Rcore} of the distribution function
- the thickness of the corona and the radius of gyration of the chains in the corona R_g
- the molar volume $V_{m,Ca2+}$ of complexed Ca^{2+}
- the interaction parameter of the chains in the corona v
- the solvent volume fraction of the core $f_{solvent}$

Table 1 shows the fit parameters obtained from the data.

Nagg	**R_{core}**	**σ_{Rcore}/R_{core}**	**R_g**	**$V_{m,Ca2+}$**	**v**	**$f_{solvent}$**
PSS_5-*b*-h_3PAA_{95} (Nagg and core dimensions for 100% D_2O)						
116.8	22.3	0.11	2.1	0.190	0.0	0.83
PSS_5-*b*-d_3PAA_{95} (Nagg and core dimensions for 100% D_2O)						
125.9	23.7	0.10	2.1	0.177	0.0	0.85
PSS_{50}-*b*-d_3PAA_{50}						
19.1	8.8	0.07	9.5	0.198	1.2	0.85

Table1: Fit parameters resulting from the simultaneous analysis of the SANS and SAXS curves.

From table 1 it is obvious that the size and structure of PSS_5-*b*-h_3PAA_{95} are PSS_5-*b*-d_3PAA_{95} nearly identical. The main difference between the symmetric and asymmetric block copolymer are the aggregation numbers and the interaction parameter v. PSS_{50}-*b*-d_3PAA_{50} shows considerably smaller aggregation numbers.

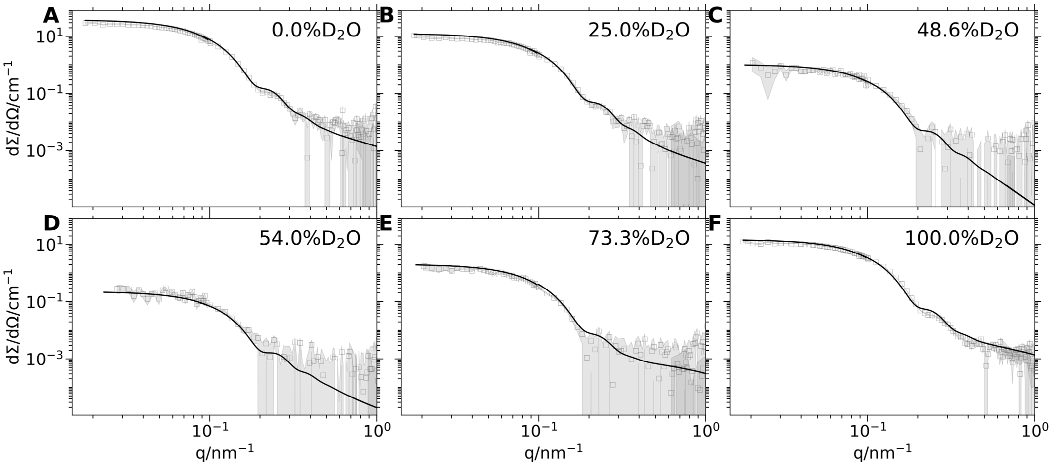

Figure 1: SANS profiles of PSS_5-*b*-h_3PAA_{95} micelles in 0.0%D_2O (**A**), 25.0%D_2O (**B**), 48.6%D_2O (**C**), 54.0%D_2O (**D**), 73.3%D_2O (**E**), 100.0%D_2O (**F**). The solid lines represent fits to the form factor of a polydisperse block copolymer micelle.

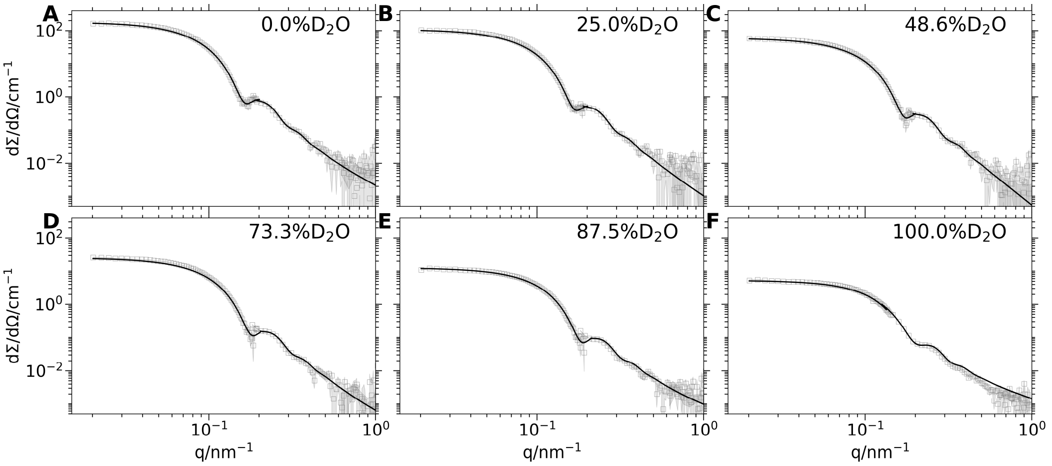

Figure 2: SANS profiles of PSS_5-*b*-d_3PAA_{95} micelles in 0.0%D_2O (**A**), 25.0%D_2O (**B**), 48.6%D_2O (**C**), 73.3%D_2O (**D**), 87.5%D_2O (**E**), 100.0%D_2O (**F**). The solid lines represent fits to the form factor of a polydisperse block copolymer micelle.

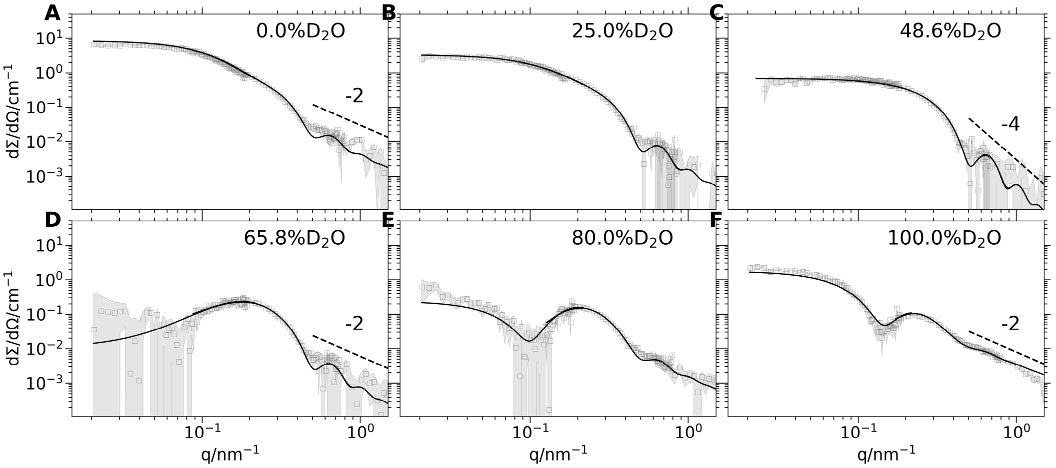

Figure 3: SANS profiles of PSS_{50}-*b*-d_3PAA_{50} micelles in 0.0%D_2O (**A**), 25.0%D_2O (**B**), 48.6%D_2O (**C**), 65.8%D_2O (**D**), 80.0%D_2O (**E**), 100.0%D_2O (**F**). The solid lines represent fits to the form factor of a polydisperse block copolymer micelle.

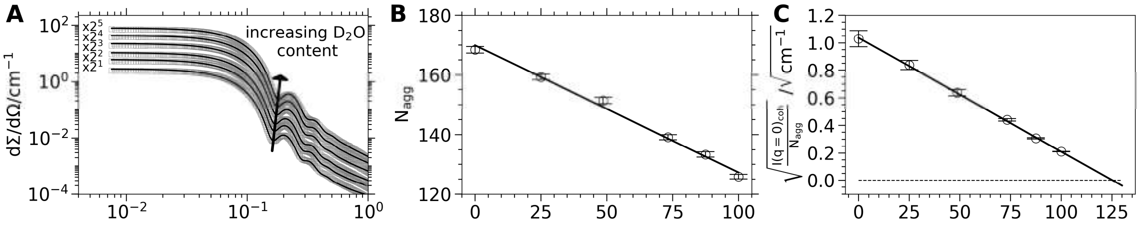

Figure 4: (**A**) SAXS profiles PSS_5-*b*-d_3PAA_{95} micelles in 0.0%, 25.0%, 48.6%, 73.3%, 87.5% and 100.0% D_2O. The solid lines represent fits to the form factor of a polydisperse block copolymer micelle. (**B**) Aggregation number of the micelles as a function of D_2O content. The solid line represents a linear fit to the data. (**C**) Coherent forward scattering normalized by aggregation number from SANS as a function of D_2O content. The solid line represents a linear fit to the data.