Experimental Report

13/02/2015

Proposal: **9-11-1694** **Council:** 4/2014

Title: Structural Properties of Water-soluble Bio-Polyelectrolyte/Block-Copolymer Complexes

This proposal is a new proposal

Researh Area: Chemistry

Main proposer: **GANAS Carolin**

Experimental Team: GANAS Carolin
CHIAPPISI Leonardo
HOFFMANN Ingo

Local Contact: GRILLO Isabelle

Samples: poly(ethylene glycol)-b-sodium polyacrylic acid / amino Cellulose

Instrument	Req. Days	All. Days	From	To
D11	0	2	08/11/2014	10/11/2014

Abstract:

Upon mixing of two polyelectrolytes with opposite charges inter-polyelectrolyte complexes (IPECs) can be formed. If an additional hydrophilic, but uncharged, block is present, these complexes are likely to be stable in solution, even at an equal charge ratio.

In this study a double hydrophilic blockcopolymer (polyethylene glycol-b-polyacrylic acid; PEG-b-PAA) is mixed with a bio-polyelectrolyte of opposite charge (amino modified cellulose) whereupon water soluble complexes are formed. In addition, small active molecules (drugs) can be incorporated into the core of the formed IPECs, protected by a water-soluble corona, which turns these systems into an interesting biocompatible delivery vehicle.

In our study we perform a systematic investigation of the effects of various parameters (bio-polymer structure, pH, mixing ratio) onto the structure of the complexes by application of static and dynamic light scattering (SLS, DLS) and small-angle neutron scattering (SANS). Combined with i.a. thermodynamic information from ITC and fluorescence correlation microscopy (FCS) (for drug solubilization/release), this knowledge will enable the design of tailored aggregates for delivery purposes.

Structural Properties of Water-soluble

Bio-Polyelectrolyte/Block-Copolymer Complexes

(Proposal No. 9-11-1694; 11.2014)

The aim of this beamtime was to investigate, the dependence of the complex formation between a double hydrophilic block copolymer and amino cellulose on the charge density along the backbone of amino cellulose. The system was varied from highly charged cellulose for DS = 2.76 to a less charged system at DS = 0.99. The SANS experiments were performed in the physiologically relevant pH range of 4 to 8 in NaCl solution. Furthermore the composition of the complexes (defined by the mixing ratio Z = [cationic]/[[anionic]) was varied, as well as the type of the cationic amino cellulose (as mentioned above), and the architecture of the double-hydrophilic copolymer PEG-b-PAA-Na (block lengths).

Here it shall be noted that our system is doubly pH sensitive, as both the polycation and polyanion react on the pH in the range of 4 to 8, which presumably is the reason for the pronounced pH dependence of the IPEC micelles.

Solutions were prepared with respect to the desired final concentration (ca- 0.4%wt total polymer content) and pH. Both components were mixed from an equal volume by adding the polycation containing solution to the polyanion containing solution.

Settings: D11: Wavelength 6A; Coll dist. 5.5m; 8m, 20.5m

1. 2kPEG-PAA(10)

1.1 Cellulose DS276

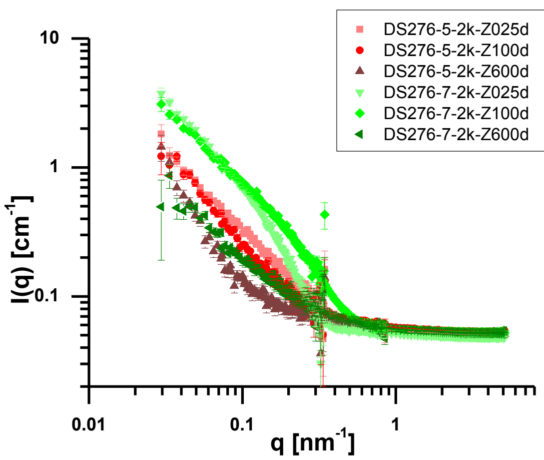

Figure 1 Z-variation: complexes of 2kPEG-PAA and Cellulose DS2.76; pH 5 and 7

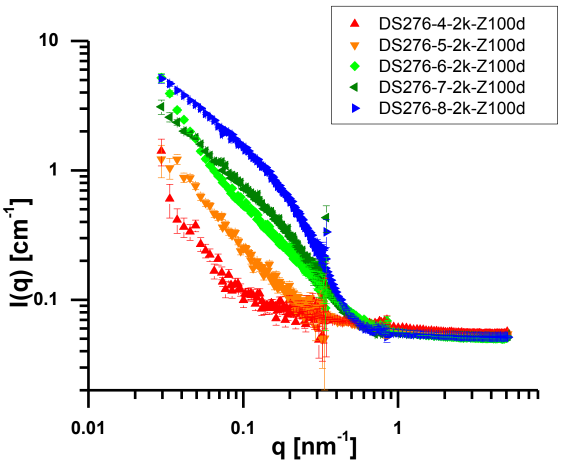

Figure 2 pH-variation: complexes of 2kPEG-PAA and Cellulose DS2.76; Z=1.00

From the first view the SANS curves give a hint that the size of the aggregates seems to increase with larger excess of 2kPEG-PAA.The strong effect of ionization due to the increasing pH is clearly visible here. In contrast the pure polymers of amino cellulose and 2kPEG-PAA(10) don't show a response in the pH range 5-7 (endosomal to isotonic pH).

2 5kPEG-PAA(10)

2.1 Cellulose DS099

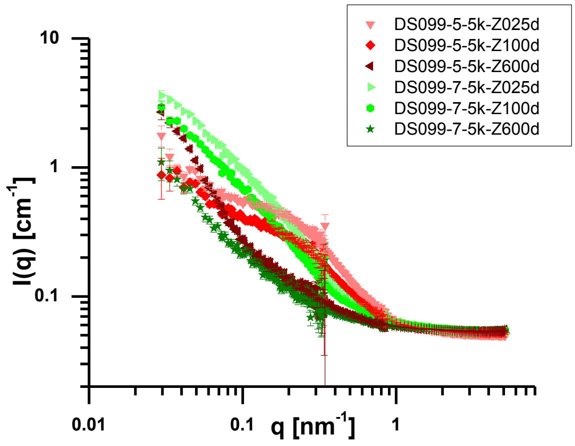

Figure 3 Z-variation: complexes of 5kPEG-PAA and CellDS0.99; pH 5 and 7

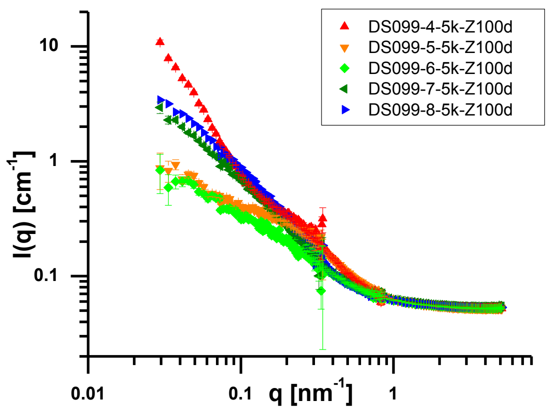

Figure 4 pH-variation: complexes of 5kPEG-PAA and CelluloseDS0.99; Z=1.0

The interpretation of complexes between 5kPEG-PAA and aminocellulose is becoming more difficult because there was also a strong pH dependency of 5kPEG-PAA. It seems that this is also dominating, when the block-copolymer is in excess (Fig. 3) and when the pH is below 6 at Z=1.0 (Fig. 4).

2.2 Cellulose DS276

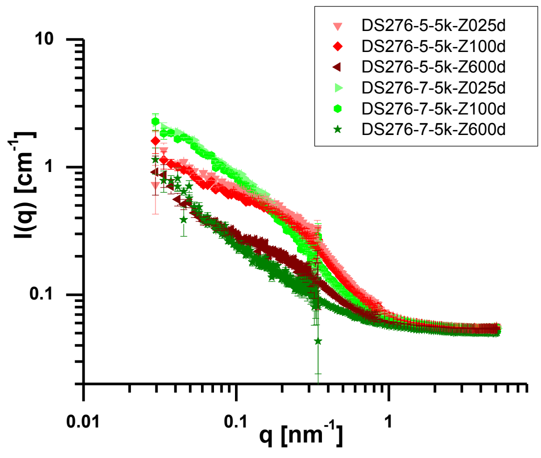

Figure 5 Z-variation: complexes 5kPEG-PAA and CellDS2.76; pH 5 and 7

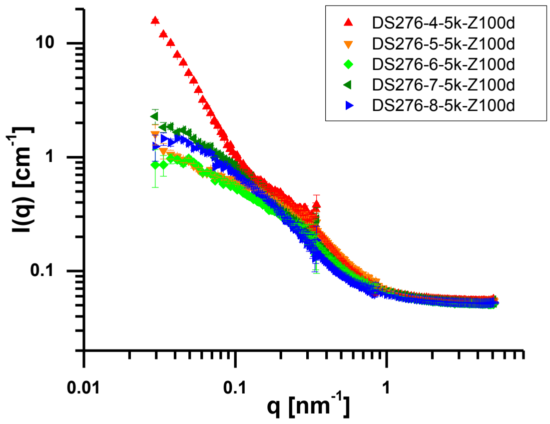

Figure 6 pH-variation: complexes 5kPEG-PAA and CelluloseDS2.76; Z=1.0

In agreement with previous measurements, also with PDADMAC for example, the pH affects the aggregates containing the shorter 2k PEG more than aggregates formed containing 5kPEG. This effect is especially visible by comparison of Fig. 2 and Fig. 6. If an excess of positively chargeable units is present (i.e. excess amino cellulose, Z=6.00) less compact structures are obtained – the curves resemble those of the unmixed components (Fig. 1 and Fig 5). Additionally it is again visible that the effect of pH on the size of the aggregates is most pronounced when there is an excess of AA-units in the solution (i.e. $Z \leq 1$) in case of 2kPEG, but becomes negligible with 5kPEG.

Further insight into the system will be gained by analyses of the complementary DLS and SLS measurement of the samples.