Experimental report

26/05/2022

Proposal:	**INTER-534**	**Council:**	10/2020
Title:	Hydrogels from polyethyleneimine and from hydrophobically-modified chitosan		
Research area:			

This proposal is a new proposal

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Samples: Hydrophobically modified chitosan
Polyethyleneimine in D2O with NaCl and DCl

Instrument	Requested days	Allocated days	From	To
D11	1	1	27/03/2021	28/03/2021

Abstract:

Hydrogels from Polyethyleneimine and from Hydrophobically-Modified Chitosan

Experiment Report for Experiment INTER-534 at D11 (March 27-28, 2021)
Berlin, February 14, 2022

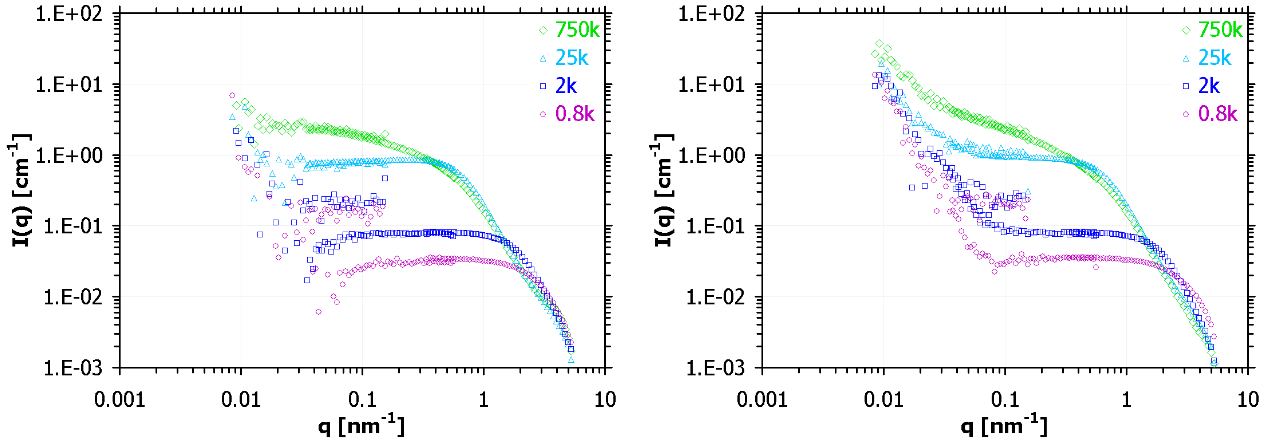
The main purpose of this study was to investigate the structures of unmodified and quaternized branched polyethyleneimine (PEI and qPEI) and quaternized hydrophobically modified linear chitosan (qhmCS) at acidic to slightly basic pH. Such systems are expected to have high potential for application in the field of water treatment, e.g. removal of natural organic matter (NOM). The research will also contribute to the fundamental understanding of the phase behavior of polyelectrolytes of special geometric and hydrophobic characteristics.

PEIs are expected to have pH-dependent potential to form hydrogel systems, while quaternized macromolecules are separated from each other by electrostatic repulsion. We expected from the SANS beamtime to determine how the structure of the hydrogel is controlled by MW and concentration, and to check the detailed effect of pH. In the qhmCS systems, we would like to see the electrostatic repulsion compromised on the hydrophobic effect from the aliphatic side-chain.

Data analysis

1. PEI

As the first step, the original molecular structures formed at pH~12 were measured as reference. SANS measurements of the samples without added salt successfully proved that the system was dominated by spherical aggregates, which coincides with the assumption that the polyelectrolyte branches capture some charges from water and expand under the repulsive electrostatic force, as shown in Fig 1a. The higher the molecular MW, the larger the size of aggregates.


a) 5wt% PEIs with various MW, pD ~12

b) 5wt% PEIs in 20 mM NaCl, pD ~12

Fig. 1: *SANS intensity functions of 5 wt% PEI mixture at pD~12. (Background subtracted.) a) Without salt; b) with 20 mM NaCl.*

With additional 20mM NaCl, sharp increases of intensity at low-q were observed, while the size of core PEI aggregates detected at mid- and high-q almost remained. This might indicate that much bigger secondary structures were formed by the aggregation of the original spheric PEIs due to reduced intermolecular electric repulsion.

Subsequently we lowered the pH and investigated the complex structure at pH 8, 6 and 4. The result of selected examples is shown in Fig 2.

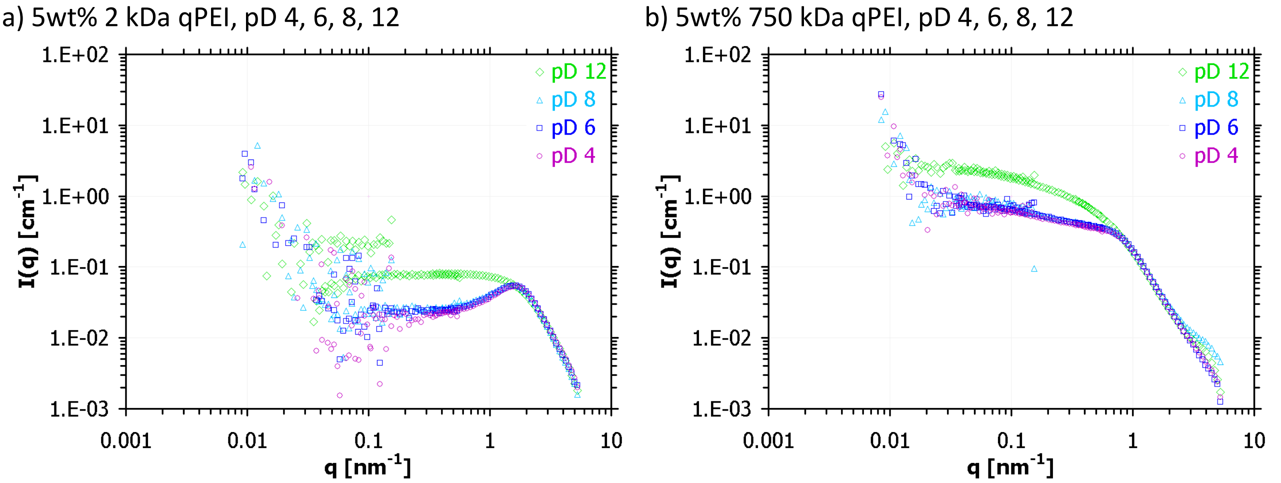


Fig. 2: *SANS intensity functions of 5wt% PEI mixture at pH 4 - 8 with pH 12 as reference. (Background subtracted.) a) MW = 2 kDa; b) MW = 750 kDa.*

At lower pH, more NH_2 groups become positively charged. For PEI with smaller MW, obviously the intensity decreases from high-q to mid-q, and a peak around q = 1.6 nm^{-1} is seen, which indicates strong intramolecular repulsion. This tendency gently increased in the pH range from 8 to 4, as shown in Fig 2a. This coincides with the fact that PEI aggregates below pKa of CH_2-NH_3^+ were well charged and became more and more difficult to compress by decreasing pH. For the case of PEI with higher MW, this intensity decrease did not lead to a peak formation, as shown in Fig 2b.

The influence of MW is shown in the Fig 3. Generally, MW of PEI at all pH demonstrated a positive effect to the size of formed aggregates.

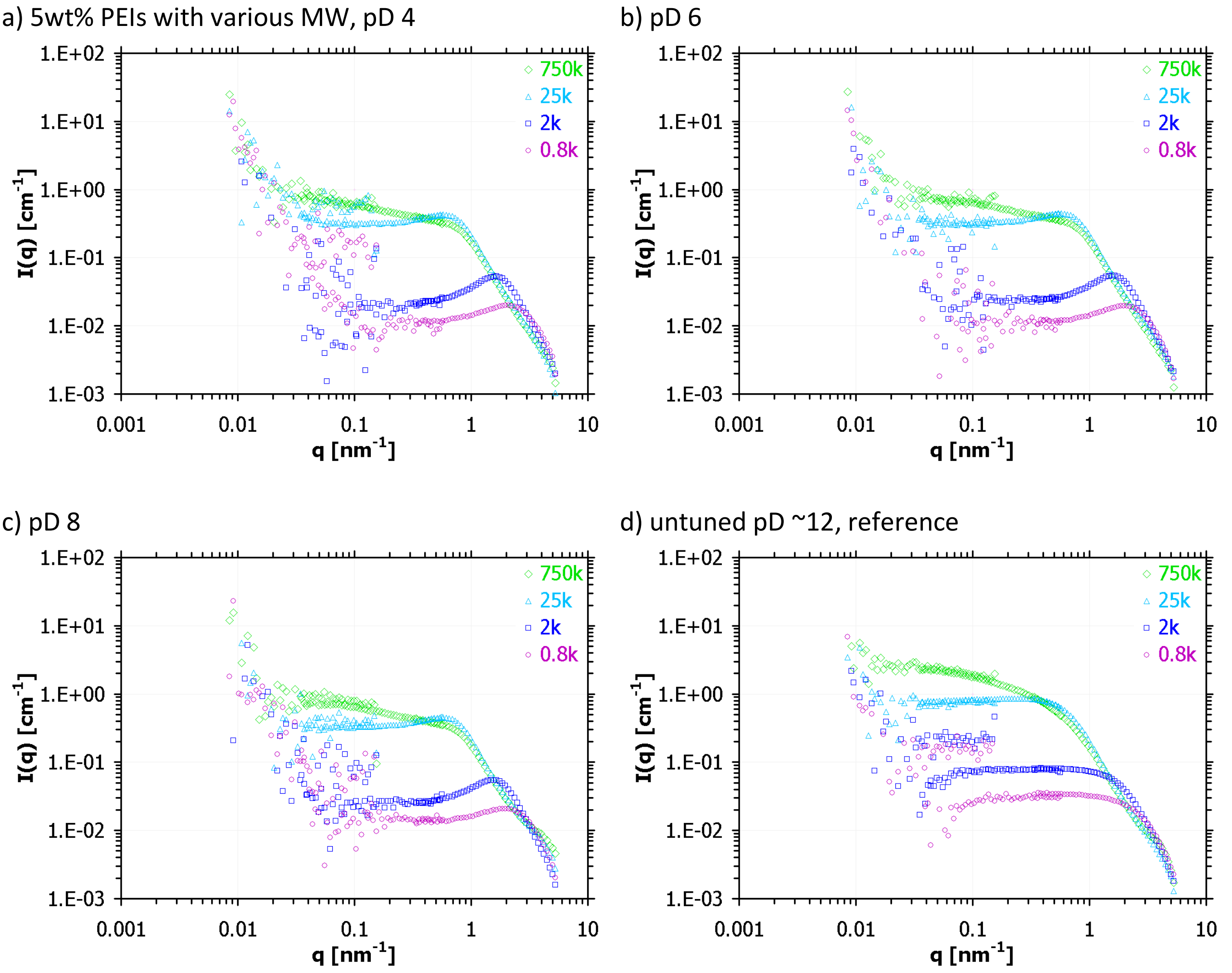
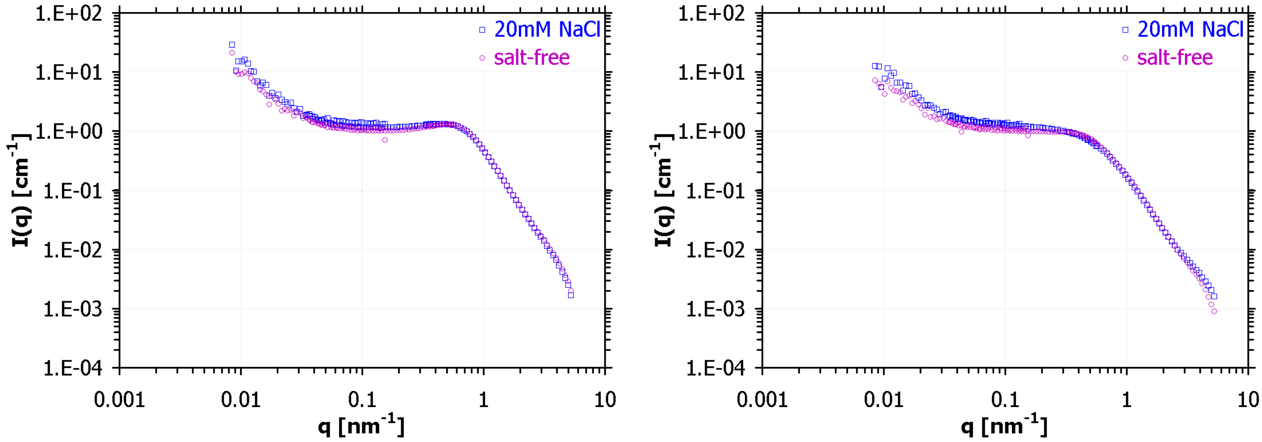


Fig. 3: *SANS intensity functions of 5wt% PEI mixture at various pH. (Background subtracted.)*

2. qPEI

The quaternised PEIs, which should have no pH-response, were measured only at original pH near 6. The sample of 25 kDa PEI showed similar intensity curves as the unmodified PEI at pH 6 with relatively higher intensity at the same concentration. When 20 mM NaCl was added to the system, the electrostatic repulsion was slightly reduced, as shown in Fig 4a. MW of polyelectrolyte also had a similar positive effect to the size of aggregate, as shown in Fig 4b.


a) 5wt% 25 kDa qPEI, pD 6.6

b) 2wt% 750 kDa qPEI, pD 6

Fig. 4: *SANS intensity functions of 5wt% PEI mixture at untuned pD. (Background subtracted.) MW: a) 25kDa; b) 750 kDa.*

3. qhmCS

qhmCS is quaternized linear chitosan with hydrophobic C12 side chains. We expected that the dodecyl groups would act as intra- and intermolecular anchor leading to network formation of the well-charged macromolecules. The sample chitosans had MW about 200 kDa. The SANS experiments successfully proved that all samples formed networks at 1 wt%. The size of the formed structures was very large and out of the range of measurement, as shown in Fig 5. The C12 modification had a similar effect as the $C_6H_5(CH_2)_3$ group. This network structure was different to the one at lower concentration, which was measured before.

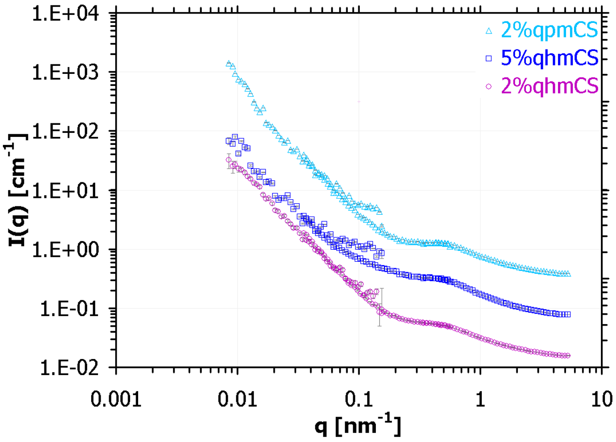


Fig. 5: *SANS intensity functions of 1wt% qhmCS mixture at untuned pH near 6.*

Conclusion

As conclusion, with this SANS beamtime we successfully investigate the hydrogel structure of our polyelectrolyte systems, and evaluated different factors to fine-tune these structures. The results are coincided with our assumption. More deep-in detailed information will be gained with further analysis. Further experiments of such polyelectrolyte mixing with counter-charged substances, such as humic acids, can be done in an efficient way.

Acknowledgement

We would like to thank ILL (D11) for this beam time and all the participants for the fruitful discussions.