

Reviewer's comment on the Bachelor thesis by Paulína Šimková

The thesis *Polyelectrolyte behavior in solution as seen by scattering techniques* compares the structural characteristics of three different block polyelectrolyte (polyzwitterionic) systems with three different molecular weights.

The thesis has all the requirements of a scientific work in the field. The author first introduces basic concepts for the description of polyelectrolyte structures and for the used scattering techniques. Here I have to mention that the text sometimes does not flow as smoothly as expected- for example, p. 4 is clearly only about weak polyelectrolytes, although not stated before, and the reader might have a false impression that the described concepts are valid for both strong and weak polyelectrolytes. Results and Discussion are treated consistently and with care. All measured data and obtained results are described in detail. The included figures are clear and illustrative. I really appreciate the colour code for individual studied systems; it really helped the reader for easy orientation in the figures. However, I feel that the conclusions derived from the obtained results might be stronger and a little more extensive. I appreciate the author's spirit for writing the thesis in English.

I would like to ask the author to address the following concerns:

- p. 2: *"However, so far the influence of molar mass and pH on the behavior of the polyelectrolyte block itself has not been studied."*
Have been some samples with similar/analogical monomers already studied? If yes, can the author relate and compare the relevant (published) results with her data for the structures in this thesis?
- p. 4: *"Polyacidic chains are expanded, when pH of the solvent is greater than the pKA value and oppositely, while pH of solvent is lower than the pKA value, the chain length is decreased."*
Maybe you mean rather the chain size, in terms of end-to-end distance?
- p. 23: *"Although, PEs are 50% ionized at the maximum under these conditions."*
Can you support this statement by a reference?
- p. 24: *"Importantly, studied PEs contain 20% of unmodified monomeric units of the starting polymer PIS, which influences solubility (in terms of poorer solubility), because those parts are hydrophobic. Generally, PEs are water soluble. Moreover, hydrophobic domains influence ionization of PEs."*
Why did you need to lower the solubility?
Why did you introduce just 20% of PIS? (not more, not less)
- p. 24: *"Since, the studied aggregates are not homogeneous spheres"*
How could you support this statement?
- The Guinier plots in figures 4.2, 4.3, 4.4, 4.6, 4.7 E are missing description.
- p. 24: *"Only PISC 7k N shows monomodal distribution with not completely separated peaks with mean peak size 15 nm. "*

There are clearly visible two (partly blended) peaks. How much would the peaks need to be separated to call the distribution bimodal (polymodal)?

- p. 24: *"In span of couple of days, it formed gel-like structure, which indicates the instability of the solution."* p. 25: *"This solution precipitated in span of one day."*

How much in advance before the measurements were the samples prepared? Did you try to measure the same sample several times in span of hours or days? Maybe, some of the data in figures 4.2, 4.3, 4.5, 4.6 containing the 'monomodal' distributions (formed by partly blended peaks) could become either bimodal, or on the contrary, purely monomodal, if the solutions were let stay for some time.

- p. 24: *"PISC 7k A distribution shows small particles with size 0.58 nm and bigger particles with size 21 nm."*

What could belong the 0.58 nm peak to? (the typical monomer size is around 0.3 nm)

- p. 35: *"The explanation for that may be in more complex electrostatic behaviour and also some role plays presence of unmodified starting polymer PIS."*

Is there a (reference) study of systems without the PIS block?

- p. 36: *"Input parameter for this model is also the fractal dimension D , which was fixed parameter as $D = 2.5$. It is a limit for dilute solutions..."*

Did you estimate the overlap concentration of your samples? (how else would you know your solutions were dilute)

- p. 37: Why does figure 4.9 contains only a subset of samples? Other ones were not measured? (e.g. qPACIS NR A)

- p. 38: *"The differences between pH conditions can very much affect the contrast and also the counterion condensation is probably the reason of different behaviour."*

How does the pH value affect the contrast?

- p. 38: *"From Figure 4.9 A can be concluded that PISC NR A was not in the same state in case of measuring SAXS and SLS."*

Again, did you attempt to measure the samples at various times after preparation and thus exclude kinetic effects? Moreover, the samples differ in concentration: p. 21: *"The concentration of samples for LS was 1 mg/ml and for SAXS was 5 mg/ml."*

- p. 39, Figure 4.10: What could be attributed to the negative peak around pH=3 pro PACIS samples?

- p. 41: *"Our hypothesis was that PE with bigger molecular weight form bigger aggregates."*

Why should they do so?

In conclusion, it must be said that despite the number of concerns that I present here, I liked the work. I assume that the results presented here will be part of a publication in a scientific journal. I consider the work to be *excellent* and recommend it for the defense.

in Prague, 3rd September 2024

Ing. Lucie Nová, PhD