Master thesis review report

The master thesis of Pavlína Marková, entitled "Post-polymerization modification of block copolymers as a tool for preparation of new drug delivery nanosystems" describes synthesis and subsequent characterization of PEO-b-PCL copolymers, which were then functionalized by propargyl groups. The candidate successfully completed the synthetic task using two alternative routes to functionalization: grafting-to and grafting-through. Each of these routes yielded copolymers with slightly different properties. These differences resulted in different self-assembled nanostructures, as revealed by detailed physico-chemical characterization. The thesis is written in very good English and presents novel scientifically valuable results.

I am impressed by the number of synthesized and characterized samples studied in this thesis, indicating that it entails a vast amount of experimental work. I highly appreciate the detailed description of experimental protocols, which is often neglected in similar theses or in the scientific literature. I also appreciate the discussion of possible artifacts, such as the drifting baseline in dn/dc measurements, and various attempts to avoid these artifacts.

On the other hand, the big amount of studied samples makes it sometimes difficult to follow the main line of thought, making it unclear why specific samples have been chosen for particular characterization experiments. Experimentally measured properties of these samples are summarized in tables 1-12. Unfortunately, a unified overview of samples and their characteristics is missing, making it difficult to keep track of the difference between specific samples, referenced by cryptic codes, such as 2"a or 3'b-11. Throughout the text, samples are referenced only through these codes, whereas the meaning of this notation is neither intuitive nor explained. References to these codes first appear already in Section 3.2.2 (page 23), without an explicit reference to Table 1 which appears only much later, in Section 4.1 (page 31). Sample codes mentioned in the Results and discussion also do not refer to the tables where their properties can be found, forcing the reader to permanently search the thesis back and forth in order to follow the line of thought.

On a similar note, figures appear only after the respective section where they are discussed whereas it is customary to place the figures close to the place where they are mentioned for the first time. The discussion seems to be mostly correct and rather detailed, however, it remains rather descriptive. A better connection between various results could have been established if the measurements and their discussion had been more clearly linked to properties of specific samples.

Notwithstanding the criticism mentioned above, I think that this thesis represents a very solid piece of scientific work, exceeding the requirements for a master thesis. My comments are mostly addressing the style of presentation, rather than scientific issues. Therefore, I propose that it should be awarded grade "A" (excellent).

Furthermore, I would like to ask the candidate to address the following points during the defense of the thesis:

- 1. Could the author present an overview of the samples, highlighting the key differences between them and explaining the notation used to describe them?
- 2. Could the author clarify based on what evidence she concluded that some structures are micelles while others are polymerosomes, fluffy aggregates or vesicles? Cf. Section 4.3.2, Fig.12 and Section 4.3.3, Fig.13.
- 3. Could the author comment on the scaling analysis in Fig.12d? What is the theoretical value of the scaling exponent mentioned on page 56 and how does the experimental value compare with this prediction? How reliable is the experimentally determined scaling exponent, given that it is based on 3 data points which do not exactly match the line in Fig.12d? Actually, it seems that the line presented in the log-log plot is not a straight line, suggesting that the data was fitted by some other function, not a power law.

In Prague, 12th September 2022

Peter Košovan