Reviewer's report on dissertation thesis

Student: MSc. Yu-Min Wang

Doctoral Thesis topic:

Macromolecular avenues for the creation of bio-inspired hierarchically structured surfaces

The dissertation of Yu-Min Wang is divided into two parts. The first deals with the synthesis of new polymeric brushes and their very deep and detailed characterization. The second, much shorter part focuses on 3D printing incorporated with PET-RAFT polymerization.

In the modern fields of biomedicine and tissue engineering, there is an urgent need for versatile and multifunctional biomaterials in clinical applications. Consequently, the subject matter of this dissertation addresses the current needs of biomaterials, offering highly adaptable platforms to meet the specific requirements of individualized medicinal or diagnostic applications.

The work is packed with information, both mediated and new. The PhD student tackled a complex multidisciplinary topic, so she had to study several theoretical disciplines and master and understand several unconventional, experimental procedures and techniques. The candidate also needed a relatively deep knowledge of physical chemistry, significantly higher than that of classical polymer chemists.

The theoretical part is treated in an insightful manner, showing that the candidate understood the topic. It is sufficient in scope and balanced in content. In about 20 pages, it summarises the state-of-the-art in the field of polymer brushes and controlled polymerization.

The citations are carefully handled, and a random check revealed no errors.

The experimental part of the thesis, documenting the candidate's very extensive synthetic work, is handled relatively carefully. It summarizes a significant amount of synthetic work. I would be interested to know how much the candidate participated, especially in the wide range of methods used to characterize the prepared materials.

The core of the work is the results and discussion part, clearly a very rewarding and interesting part of the work, certainly with many new insights. The discussion has a logical structure, the organization cannot be faulted much. After the larger logical units, there is always a short

summary, which is not quite usual, but I admit, that I rate this innovative element very positively.

The candidate investigated the impact of grafting methods on the fouling properties of poly(HPMA) brushes prepared through both conventional and surface-initiated RAFT polymerization. These brushes comprised polymer chains of comparable chemical composition and molar mass, as confirmed by SEC-MALS and AFM-SMFS measurements.

This thesis has introduced several innovative and unique techniques for the characterization of polymer brushes synthesized via the grafting-from method, including atomic force microscopy-based single molecule force spectroscopy (AFM-SMFS), electrokinetic (EK), and neutron reflectometry (NR). The incorporation of AFM-SMFS has effectively surmounted the challenges associated with the retrieval of de-grafted polymer chains from surfaces, facilitating the determination of molar mass and dispersity.

The results of the dissertation fully correspond to the set objectives. The evaluation of the thesis was facilitated by the fact that most of the results have already been published or under review in highly reputable journals. This fact also documents the high scientific quality of the dissertation. It is evident from the thesis that the author has mastered not only the techniques of advanced polymer synthesis but also very advanced physicochemical characterization of polymeric materials.

Comments:

There are a few typing errors and mistakes. For example, in Scheme 3, the carbonyl is missing in the monomer structure. In Scheme 10, two n indexes are used for different repeating units.

Questions:

1) Can you compare the SI-RAFT and SI-ATRP for methacrylamide-based monomers, especially for HPMA?
2) During SI-RAFT, the CTA molecule was also present in the solution. Why? What is the role of the CTA molecule in the solution, and how does it affect the SI-RAFT polymerization?
3) How will stirring the reaction mixture affect the GF-SI-RAFT polymerization?
4) What is the optimal thickness of the coating layer to achieve sufficient antifouling capabilities and preserve sufficient sensor sensitivity?

5) How can you prove that the AFM tip is covalently bound to the polymer chain?
6) Why do you use AFM-SMFM instead of cleaving the coated layer from the chip and determining the molar mass directly via SEC?

Conclusion:

The candidate has clearly demonstrated the ability to creatively address a complex research task and critically evaluate the obtained results. The results are original and contribute to the further development of science and technology. In my opinion, the thesis definitely meets the requirements set for similar types of theses. It brings original scientific results, which have also already been published. **I thoroughly recommend that this dissertation be accepted for defense.**

In Prague, 18.4.2024

Ing. Libor Kostka, Ph.D.