Reviewer’s report on dissertation thesis

Student: MSc. Sachin Gupta

Doctoral Thesis topic:

NEW APPLICATIONS OF COPPER-CATALYZED REVERSIBLE-DEACTIVATION RADICAL POLYMERIZATION

Satchin Gupta's thesis has a classical structure. The aim of this thesis was to identify new applications of Cu-RDRP, focusing on the synthesis of complex polymer architectures and the optimisation of polymerisation conditions for important functional monomers. The theoretical part of the thesis is quite condensed, summarising in 18 pages the current state of the art in the field of controlled polymerisation technique. All important aspects of radical polymerisation, mainly from the ATRP family, are briefly introduced. The theoretical part is treated in an insightful manner, showing that the candidate has understood the subject. It is sufficient in length and balanced in content. Citations are handled carefully and a random check did not reveal any errors.

The experimental part of the thesis, which documents the candidate's very extensive synthetic work, is treated relatively carefully and logically. It summarises a considerable amount of synthetic work, which is divided into two parts. In the first part, it has been shown how Cu-RDRP in conjunction with the TAI strategy can be advantageous in the synthesis of different types of complex polymeric architectures, combining the speed and cleanliness of TAI reactions with the well-controlled character of TAG-initiated Cu-RDRP. Based on an extensive optimisation study, Cu-RDRP conditions were provided that could be readily applied to the polymerisation of a variety of monomers to different MWs in both polar and non-polar solvents. It was shown that the multifunctionality of the initiator allows access to complex polymer architectures with novel features, e.g. ultra-dense bottle brushes, multi-armed stars or branched (co)polymers with novel topologies. Furthermore, the high reactivity of TAI opens avenues for innovative synthetic methods and also greatly facilitates the modification of problematic substrates such as polysaccharides.

In the second part, the novel Cu(0)-RDRP method of HEMA polymerisation, discovered during the development of the TAI strategy, was tested with commercially available monofunctional initiators. Using purified HEMA, the newly developed method provided rapid access to well-defined poly(HEMA) in an unprecedented range of MWs without the risk of solvent transesterification side reactions. In addition, the developed conditions were shown to be particularly useful for HEMA copolymerisation with non-polar/lipophilic monomers.

The core of the work is the results and discussion part, which is clearly a very rewarding and interesting part of the work, certainly with many new insights. The discussion has a logical structure, the organisation is not much to criticise. The work is full of information, both conveyed and new.

The PhD student tackled a deep knowledge of radical polymerisation, so he had to study several theoretical disciplines and master and understand several experimental procedures and techniques. The candidate also needed a relatively deep knowledge of physical chemistry to characterise all the synthesised products.

The results of the thesis are fully consistent with the theoretical part of the thesis. The evaluation of the thesis was facilitated by the fact that most of the results have already been published in peer-reviewed journals of high reputation. This fact also documents the high scientific quality of the thesis. It is clear from the thesis that the author has not only mastered the techniques of advanced polymer synthesis, but also very advanced physicochemical characterisation of polymeric materials.

Comments:

There are a few typographical errors and mistakes. For example, the legend in Figure 21 is incorrect. Instead of “RI traces (b,c) and M-H plots (d,e)” should be RI traces (b,d) and M-H plots (c,e) and instead of poly(MMA) (b,d) and PS (c,e) should be poly(MMA) (b,c) and PS (d,e).

Questions:

1) In Tables 2-7, many values of theoretical Mn are significantly lower than the measured values. For example: Table 2, entry 42; Table 5, entry 8; Table 7, entry 3. Can you explain or comment on this?

2) Why did you not try to synthesise linear polymers with molar mass above 50 000 g/mol?

3) In Figure 21 C and D at least two different slopes for 12-arm stars and hydrolysis product can be determined for certain molar mass ranges. Can you comment on this phenomenon?

4) Did you also try to use methacrylamide-based monomers in your study? And are they compatible with the TAI strategy?

Conclusion:

The candidate has clearly demonstrated the ability to creatively approach a complex research task and to critically evaluate the results obtained. The results are original and contribute to the advancement of science and technology. In my opinion, the dissertation definitely meets the requirements set for similar types of dissertations. It provides original scientific results that have already been published. **I fully recommend that this thesis be accepted for defence.**

In Prague, 23.8.2024

Ing. Libor Kostka, Ph.D.