Prague, August 23th, 2024

Review Report on the Ph.D. thesis of ***Sachin Gupta,***

entitled

**New Applications of copper-catalyzed reversible deactivation radical polymerization**

The research reported in the submitted Ph.D. thesis represents an original contribution to the emerging field of controlled radical polymerizations. The study focuses on the synthesis of complex polymer architectures by optimized protocols for Cu-mediated reversible deactivation radical polymerizations (RDRP), in particular, atom transfer radical polymerization (ATRP) and Cu(0)-mediated RDRP. The key discovery of the thesis lies in the development and optimization of a straightforward protocol for the synthesis of highly branched (star-shaped) polymers via trifunctional trichloroacetyl initiator, which can be easily and quantitatively introduced into various substrates via reaction with trichloroacetyl isocyanate. The Cu-RDRP from trichloroacetyl initiator has been optimized for several industrially relevant vynilic monomers, in particular, methyl acrylate, methyl methacrylate, and styrene. The optimized protocol has been then utilized for the successful growth of polymer brushes from a wide range of initiator-modified molecules and objects, e.g., cyclodextrin or cellulose. As a second topic, the candidate optimized conditions for Cu-RDRP of 2-hydroxyethyl methacrylate (HEMA) in a non-polar solvent (dioxane), providing straightforward access to copolymers of HEMA with lipophilic monomers.

The research presented in the thesis is very interesting and original. In particular, the part focusing on the introduction of trichloroacetyl initiator to various substrates with subsequent polymerization is very innovative.

The results included in this dissertation demonstrate the student's ability (i) to understand in detail the principles and mechanisms of Cu-RDRP, (ii) to optimize the polymerization conditions to achieve a controlled polymerization process, (iii) to synthesize advanced polymer architectures via Cu-RDRP (iv) to characterize the prepared polymer materials by methods such as NMR or SEC.

The scientific level of the thesis can be evaluated as very high, as the thesis covers an enormous amount of experimental work, both synthetic and characterizations. All polymers are well characterized; in particular, I appreciate the study of polymer branching by Mark-Houwink plots from SEC data. The results have been published as two articles in renowned journals, especially the recent publication of the

trichloroacetyl-based research in Chemical Science deserves appreciation and just underscores the research quality.

The thesis is well-structured and correctly presented. The graphics are visually appealing. It is written in good English with very rare mistakes and typos (e.g., sometimes not using italics in quantity symbols or missing page numbers in reference 17). The obtained results were well-discussed. All literature sources are well-cited. On the other hand, despite an enormous amount of experimental data in the polymerization optimization parts, these parts are mostly descriptive, describing the obtained data without explaining the effects of varied parameters (initiator, solvent, ligand temperature, etc.) on polymerizations from the mechanistic perspective. Such a discussion would be very interesting to read.

To summarize, the dissertation represents high-level scientific work on a very actual topic. All experiments have been well arranged; all measurements have been correctly applied. The scientific level of the thesis and its presentation can be rated as excellent.

**In my opinion, the reviewed thesis fulfills all the requirements posed on these aimed at obtaining a Ph.D. degree. Therefore, I can recommend this thesis to be defended in front of the respective committee.**

RNDr. Ondrej Sedlacek, Ph.D.

Questions for the defense:

1. The conditions for MTAC-initiated polymerizations differed based on the used monomer. Can you explain why Cu(0)-RDRP was a good technique for the polymerization of methyl acrylate, while ATRP was optimal for styrene (and not vice versa)?
2. On page 60, you write: "Notably, gel formation was observed on the copper wire when Me6TREN was used as a ligand which makes these conditions less usable." Can you explain the formation of the gel?

3. Can you explain how the α parameter has been derived from the Mark-Houwink plots, as some of the M-H plots are not very linear? In Figure 21E, can you explain the increased α at higher molar masses?
4. Some size-exclusion chromatograms of low molar mass polymers do not show the whole distribution (e.g., Figure 7), and the peak is cut due to the presence of low molar mass impurities (buffer peak). Were the molar masses calculated from these incomplete peaks, or have you used any data extrapolation to compensate for the missing short chains?