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Evaluation report for the PhD manuscript of Leonid Kaberov:
"2-Oxazoline triblock copolymers with hydrophilic, lipophilic and fluorophilic blocks: from synthesis to hierarchical self-assembly"

The manuscript submitted by Mr. Leonid Kaberov deals with the controlled synthesis of di- and triblock copoly(2-oxazoline)s with fluorinated blocks and their aqueous solution behavior. The self-assembly behavior of block copolymers is studied in detail using various scattering techniques (DLS, SAXS, and SANS) and cryo-transmission electron microscopy (cryo-TEM). Such fluorinated copolymers are not only interesting polymeric amphiphiles but are also potentially useful as ^{19}F magnetic resonance imaging (MRI) contrast agents.

The thesis is a cumulative dissertation based on three published manuscripts and one submitted manuscript: M1 *European Polymer Journal* **2017**, *88*, 645-655; M2 *European Polymer Journal* **2018**, *99*, 518-527; M3 *ACS Macro Letters* **2018**, *7*, 7-10; M4 *Macromolecules* **2018**, submitted. The thesis (64 pages) is written in English language and contains six chapters: (1) Theoretical part, (2) Aims of the thesis, (3) Experimental, (4) Overview of results, (5) Summary, and (6) References. The four manuscripts and related supporting informations (SI) are provided as Appendix.

Chapter 1 contains the theoretical part to cationic ring-opening polymerization of 2-oxazoline monomers, with a particular focus on fluorine-containing monomers, and to characterization methods, *i.e.*, DLS, SAXS, and SANS. Chapter 2 briefly states the aims of the thesis, which are the synthesis of amphiphilic, fluorine-containing (quasi-)triblock copoly(2-oxazoline)s and the study of their self-assembly behavior. Chapter 3 contains the experimental part in which all used characterization techniques are described. Chapter 4 is the main chapter of the thesis providing an overview of the results. Chapter 4.1, based on manuscripts M1 and M2, describes the synthesis of amphiphilic diblock copoly(2-oxazoline)s carrying a perfluoroalkyl chain at the ω-chain end (= "quasi-triblock"). Self-assemblies obtained by direct dissolution and solvent exchange method were analyzed in detail by scattering techniques and cryo-TEM. Spherical and cylindrical micelles and vesicles were observed depending on the chemical compositon of polymers and the method of sample preparation. Chapter 4.2, based on manuscript M3, contains kinetic studies on the polymerization of fluorinated 2-oxazoline monomers and the synthesis of triblock copolymers. Self-assembly behavior is studied in lesser detail by DLS and cryo-TEM. Chapter 4.3, based on manuscript M4, describes the synthesis and polymerization of highly fluorinated 2-oxazoline monomers. The synthesized triblock copolymers were found to self-assemble into spherical micelles; the formation of a small fraction of vesicles was only observed (cryo-TEM) when polymers were directly dissolved in water. Aggregates were also characterized by SANS. Chapters 5 and 6 contain a short summary of the thesis and list of references.

To my judgment, the manuscript fulfills rather high quality requirements in the fields of polymer synthesis and self-assembly and is recommended for acceptance. The dissertation is scientifically correct and truly significant and original, part of which has been published in peer-reviewed journals. Hypotheses and objectives of the research are clearly described and sound. References are correct and balanced. The dissertation is logically structured and the language is excellent.

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Minor remarks/comments

Title. The use of the term "hierarchical self-assembly" is rather questionable. Block copolymers were found to self-assemble into spherical and cylindrical micelles or vesicles with a core-shell structure, none of which exhibit any hierarchical structuring on different length scales. Maybe it is more appropriate to use the term "complex" instead of "hierarchical"?

Page 33, Table 2. The critical micelle concentration (CMC) of the quasi-triblock copolymers is slightly increasing with increasing amount of perfluoroalkyl fraction. Even though the hydrophobic self-assembly was dominated by the hydrophobic POctOx block, as claimed, one would neverthless expect that the quasi-triblock copolymers exhibit a lower CMC value as the parent diblock copolymer. The measured CMC values and the applicability of the used pyrene method could have been discussed in a bit more detail.

Page 42, Figure 25. The polymerization kinetics of the CF_3MeOx can hardly be explained by slow initiation. The polymerization seems to follow a decent pseudo first-order kinetics during the first stage ($t < 4000$ s) before the polymerization rate starts to increase continuously. The final rate (slope) is, however, very similar to that observed for the more nucleophilic CF_3EtOx or non-fluorinated 2-oxazoline. It might well be that the increasing polymerization rate (and the very broad molar mass distribution) is not due to slow initiation but due to chain transfer processes leading to an continuous increase in active chain ends?!

It is claimed that the polymerization of CF_3EtOx suffers from chain transfer/coupling reactions at longer reaction times. Does this coupling reaction also occur during the synthesis of the triblock copolymers by sequential monomer addition (CF_3EtOx being the third monomer)? Unfortunately, SEC chromatograms of the triblock copolymer samples are not provided. Maybe the coupling reaction is less evident or suppressed for longer polymer chains, but if not, this would result in the (partial) formation of pentablock copolymers.