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# Jury Member Report – Doctor of Philosophy thesis.

**Name of Candidate:** Julia Bondareva

**PhD Program:** Materials Science and Engineering

**Title of Thesis:** Sulfonimide-based dendrimers: synthesis and application for surface functionalization

**Supervisor:** Associate Professor Igor Shishkovsky

**Name of the Reviewer:**

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|---|---|
| I confirm the absence of any conflict of interest | **Signature:**  **Date: 25-08-2020** |

*The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.*

*If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.*

**Reviewer's Report**

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The thesis of Ms. Bondareva deals with the synthesis of sulfonimide-based dendrimers of different generations and their formation of monolayers on a Langmuir-Blodgett trough. The thesis consists of 5 chapters including introduction, review of the literature, review of the literature, experimental section, result and discussion, and conclusions, i.e. it contains all necessary components of a PhD dissertation. My overall impression is positive. However, the literature review is not complete to my opinion. A world-famous Russian group under the leadership of Academician Aziz Muzafarov has worked since long with silicon-based dendrimers. It has been ignored in this thesis. Furthermore, the English language should be improved. There are plenty of errors and typos, and the quality of the layout may not be optimal.

Dendrimers comprise a very important research field due to their unique molecular architecture; therefore, development of dendrimers of new chemical structures is of high scientific importance. The subject of this thesis is sulfonimide-based dendrimers, which are interesting owing to their simple synthesis and certain attractive properties. Both divergent and convergent approaches were employed. A systematical study, however, was performed only for the divergent route. The biggest achievement of this work is the synthesis of such dendrimers of higher generations via a two-step method.

The compounds were characterized mainly by NMR spectroscopy. For certain products elemental analysis and mass spectrometry were used. Thin films of naphthyl-substituted dendrimers were obtained on a Langmuir-Blodgett trough, and ellipsometry, optical microscopy, AFM, SEM and TEM were employed for their characterization. Mechanical, hydrophobic and nonlinear optical properties of monolayers were measured. It is well known that the Langmuir-Blodgett technique can never lead to the formation of defect-free thin films, and this fact has been confirmed in this work (Figure 18). This is why this technique has not found any real applications. Why did the author not use industry-relevant deposition methods, e.g. spin-coating, dip-coating, etc. to cast thin films for e.g. hydrophobization?

In comparison with the state of the art, the author of this work managed to synthesize sulfonimide-based dendrimers of higher generations. It is a fair progress in this field. Moreover, the formation of freestanding thin films by these compounds at the water/air interface was studied on a Langmuir-Blodgett trough, and the properties of these films were investigated. All these results have certain scientific importance for understanding the self-assembly behavior of this kind of dendritic macromolecules, which forms the basis for their further applications.

The results of this thesis have certain scientific importance. I do not see any potential applications, which are, however, not important for a thesis work, to my opinion.

The author has 4 accepted publications in peer-reviewed journals. I would qualify them as routine publications, which have certain scientific value in the related research field.

Here is the summary of further issues to be addressed:

(1) According to the IUPAC recommendation (Pure Appl. Chem. 2019; 91, 523), the number of generation of a dendron is the number of constitutional repeating units on the path from the free valence to any end-group. It is correctly designated in Figure 7 and 8. However, for the dendrimers synthesized in this work, the designation is wrong. The highest generation (compound 11) synthesized by the author is actually G-4.

(2) For hydrophobization long alkyls, siloxane and perfluoroalkyl groups are normally used. Why did the author use naphthyl groups to achieve hydrophobicity? The highest contact angle reached in this work is ca. 90°, which cannot be considered as hydrophobization.

(3) Regarding the surface pressure – area isotherms shown in Figure 17, why does it differ from the one published in “Applied Surface Science”? From these curves, one should extract more information, for example molecular area vs. molecular weight.

(4) The discussion concerning the influence of surface roughness on wetting properties on Page 98-99 is not correct. The roughness of the films in this work is less than 1 nm, so it is a rather smooth surface.

(5) On Page 86-87, the author wrote that Dendrimers 7 and 9a exhibited LCST in dichloromethane and chloroform. This is an interesting phenomenon, since it is normally typical for polymer-water systems, where intermolecular hydrogen bonding is destroyed at higher temperature. Can the author provide an explanation for their system?

(6) On Page 82, the author wrote that “all sulfonamide dendrimers were isolated as crystalline solids with rather high melting points (>130°C)”. I doubt whether these dendrimers of higher generations can crystallize, since they exhibit a high glass transition temperature, which lies in the same range as the melting points. Maybe the author should show evidence of crystallization.

(7) For future, I would propose to find a way to use the unique properties of dendrimers, e.g. high functionality and defined molecular size, to create functional surfaces with precisely defined thickness.

**Provisional Recommendation**

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate’s thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*