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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<br><br>(Alternatively, Reviewer can formulate a possible conflict) | **Signature:**<br>  <br>**Date: 05-09-2020** |

*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**

The thesis evaluated has overall very good quality both from scientific and writing points of view. The dissertation has a standard structure, including Introduction, Review of the Literature, Experimental section, Results and Discussion, Conclusion and Future work. In addition, it has all necessary formal parts, such as Abstract, List of Publications, Author's contribution, Conferences, Acknowledgements, Lists of Symbols, Abbreviations, Figures, Table and Schemes as well as Bibliography. The thesis is written on 122 pages, which includes 25 Figures, 4 Tables, 10 Schemes and 153 cited items published from 1934 to 2020.

The Introduction describes research background and motivation of this work, illustrate possible application of sulfonimide dendrimers, growing interest to the dendrimers in general and in materials science in particular. Active patent families related to dendrimers are described and analyzed with a help of Cipher patent database service. Particular attention is devoted to sulfonimide dendrimers as substances of interest for this dissertation, and their advantages are highlighted. The methods for preparation of thin films of dendrimers, with a focus on Langmuir-Blodget films, are discussed. Some related works on dendrimer coatings are considered.

Chapter 2 of the thesis, Review of the Literature, gives a brief historical overview of dendrimers as a new class of synthetic macromolecules. Basic concepts and main synthesis approaches to the synthesis of dendrimers, such as divergent, convergent and double-stage convergent methods are smoothly presented. Also, hypermonomer and click-chemistry methods, which are particular cases of the methods mentioned above, are highlighted. Then some different types of dendrimers, their peculiar properties and applications are discussed. Particular attention is devoted to the application of dendrimers in medicine, sensing technology and materials science - as additives, inks and paints, catalyst and coatings. Finally, Langmuir-Blodgett (LB) technique is considered in details, starting from historical overview and LB films of dendrimers to the principles of the LB method, film formation procedure, analysis and characterization techniques of LB films and their quality assessment.

Chapter 3 of the thesis describes the Experimental techniques used in the dissertation. Synthetic procedures are described in details for 31 compounds shown in Schemes 1 – 10. Some of them were obtained by different methods. Their characterization, including reaction yield, melting points, description of $^{1}H$ and $^{13}C$ NMR spectra, data of MS and elemental analysis are given, which unambiguously prove the structure and purity of the compounds obtained. Then film formation experiments and their analysis are described, including film transfer on different substrates and their selection.

Chapter 4 is the main part of the thesis devoted to Results and Discussion. It starts from the synthesis of sulfonimide-based dendrimers, including selection of the core molecule, which happened to be very important. That was missing for me as a referee is the yield of all the compounds on the reaction schemes and their discussion in the text. For synthetic chemists the yield is one the one most important parameters of the reaction and it is a good practice to discuss it not only in the text of thesis but also in the main part of the synthetic papers. An interesting effect was found that dendrimers 7 and 9a, respectively, exhibited good solubility in cold dichloromethane and chloroform, but precipitate completely from the solution upon heating to 40 °C and dissolve again upon cooling to the room temperature. Unfortunately, it was only mentioned in the text, but not explained. Some polymers possess similar properties, which is called as the upper critical temperature of dissolution, but I have never heard that dendrimers show something similar.

The second part of this chapter is devoted to LB film formation from the dendrimers synthesized, with or without UV treatment, which leads to cross-linking of the dendrimers via dimerization of their terminal naphthyl groups. To visualization of the Langmuir layer at the air-water interface the author used Brewster angle microscope (BAM). The isotherms of surface pressure versus area per molecule were obtained for dendrimers of different generations investigated and main parameters, such as first inflection and critical pressure before the layer collapse, were extracted and discussed. What is missing for me is discussion how the mean molecular areas at these surface pressures corelates to the molecular size of different dendrimers, i.e. their gyration radii, which could be estimated either experimentally or theoretically from the models shown in Figure 15 (2).

The LB films obtained were analyzed by optical microscopy, SEM, TEM and AFM, which showed that the films are homogeneous at nm scale with some kind of cylindrical nanostructuring, but non-uniform at hundreds of μm scale (they contain some flakes of the film – see Fig. 18a). All of them has different thickness and roughness depending of the generation number, which was used to explain dependence of contact angles measured of these films of the chemical structure of the materials used. It was found also that the cross-linked by UV treatment LB films are denser than those without such treatment. However, the contact angles were higher for untreated films, which was explained by partial decomposition (oxidation) of the UV-treated films.

Finally, an attempt was made to characterize the LB films obtained by UV optical spectroscopy and measurements of non-linear optical properties. Albeit the signals were rather weak due to very thin films investigated (3 – 6 nm, while normally about 100 nm is required to get good response), it was found again that non-treated dendrimers show better response than the UV-treated dendrimers.

In the Conclusion section the results obtained are summarized. The multigram availability of the fourth-generation hexadecanitro-dendrimer is highlighted. The conclusion is made that the LB films obtained belongs to soft materials, which is definitely true. However, it is stated that the hydrophobicity of the films made from the 2nd generation to the 5th generation increased by 23%. For me it is not clear how it was calculated? This number was not discussed in the previous sections. Also it is concluded that the thin-film formation and contact angle measurements show the potential use of fourth- and fifth-generation species for surface engineering applications. It would be nice to compare it with the other known materials used for the same purpose.

Future work section is meanly devoted to discussion of possible application of synthesized dendrimers for surface modifications, in particular its wettability. The author discusses Wenzel and Cassie – Baxter models for wetting of rough surfaces. To define the suitable model, further investigations are needed to evaluate the experimentally measured parameters such as the spreading coefficient and the work of adhesion. It is advisable for these purposes to measure not only the contact angle, but also a rolling angle – incline at which the wetted drop of liquid is rolled out from the surface. If the dendrimer films will significantly decrease the rolling angle – it will not only favor of Cassie – Baxter model, but also allow unlocking the potential of such complicated and rather expensive materials as dendrimers for real applications, i.e. for self-cleaning surfaces, etc.

The is no doubt that the actual content of the thesis discussed above is relevant to the topic of dissertation. All the methods used correspond well to the state of the ark in this field and relevant to the materials synthesized and investigated in this work. The results obtained are published in high impact journals from the first quartile Q1 of the Web of Science/Scopus Databases, which prove their significance and compliance with the international level.

The summary of issues to be addressed during the thesis defense is below:

1) In Figure 6 the author nicely defined what it the generation number (G) of the dendrimer and how to define it. It is clear from this figure that if the branching core has a functionality of 3 and all further monomers attached to it doubles the number of terminal groups, G1 dendrimer will have 6 terminal groups, G2 – 9, G3 – 18, G4 – 36, etc. This is a common scheme and it is follows from it that in the case of functionality of 2 of the branching core, G1 will have 4 terminal groups, G2 – 8, G3 – 16 and G4 – 32. Why on Figure 15 the author calls compounds with 4, 8, 16 and 32 terminal naphthalene groups as dendrimers of the $2^{nd}$, $3^{rd}$, $4^{th}$ and $5^{th}$ generations?
2) In the Experimental section sometimes the melting region are given instead of the melting point. What is the reason for that? Usually wide melting point means that the compound has either some impurity or liquid crystal mesophase(s).
3) Yields of the compounds synthesized should be discussed.
4) Scheme 7 is shown on page 79, but not discussed in the text.
5) How the mean molecular areas at the surface pressures as first inflection and critical pressure before the layer collapse in Figure 17 and Table 2 corelate to the molecular size of different dendrimers?

| **Provisional Recommendation** |
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| ☒ *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* |