The thesis document includes the following changes in answer to the external review process.

Dear Jury Members,

First, I would like to thank all the reviewers for reading my manuscript and for all their helpful comments, corrections, and suggestions. As a result of your valuable feedback, I made several changes that have greatly improved my dissertation. I corrected spelling and grammatical errors, unified formatting style, and ensured consistency with the referencing style and bibliography. I have expanded the Introduction section to highlight the importance of the work and outline the research objectives that have been set. I will also consider all comments and suggestions in my future research.

Below you will find answers to questions and comments. Pages are listed here according to the final thesis version.

Sincerely,
Julia Bondareva

Reviewer: Professor Alexey Buchachenko

Comment #1: The Thesis does not set the overall goals of the work. Clear formulation of the goal normally sets the logic of the work and text and establishes its integrity by connecting different pieces in a coherent document. Otherwise, it is difficult to the reader (and reviewer) to apprehend the main targets to be achieved, main tasks to be solved, main messages to be taken. Moreover, the lack of goals undermines the value of the results and masks the novelty of conclusions of the work. I strongly suggest to rewrite introductory Chapter 1 adding clearly formulated research goals of the PhD project.

Answer: I rewrote and reorganized the Introductory Chapter (pages 14-25). The Introduction consists of the following sections:
1.1 Research Background and Motivation
1.1.1 Sulfonimide dendrimers as a substance of interest
1.1.2 Towards sulfonimide dendrimer films
1.1.3 Previous achievements in dendrimer film formation
1.2 Research objectives
Comment#2: Introductory Chapter strongly overlaps with the literature review (Chapter 2). Misleading is the placement of the potential applications of the sulfonimide-based dendrimers on the front cartoon (Fig.1) prior to exposure of a general landscape and essential relation between the physico-chemical properties and the particular field of application. The properties of dendrimers under study and other dendrimer families are compared to some extent in Chapter 2. The niches suggested for a new family can thus be rationalized only afterwards. Patent analysis also comes too early. Moreover, it hints that the Thesis will address particular applications and reveal commercialization prospects. Nothing fits these expectations. It is not clear why the works considered in Section 1.2 are “related” – this can only be substantiated by clear formulation of the goals. I suggest to make introductory Chapter more concise setting the goals and explaining them by indicating what specific features are expected from the sulfonimide-based dendrimers. Further details, including patent analysis, are more appropriate in the Section 2.1.7 - Application of dendrimers.

Answer: The introductory part contains information about my motivation and prerequisites for this project. Also, in the Introductory part, I added a separate section with established goals and objectives. Potential applications of sulfonimide-based dendrimers (Fig. 3, page 18) are located in the Introduction after information on the structure and physicochemical properties of sulfonimide dendrimers. The literature review (Chapter 2, pages 26 - 51) contains general information: historical background, approaches to synthesis, other classes of dendrimers. Patent search (section 2.1.8, pages 43 - 45), indicates the importance of investigating dendrimer structures in terms of commercialization, has been moved after section 2.1.7 Application of dendrimers.

Comment #3: Section 3.1 does not look instructive. Undoubtedly, synthetic protocols described therein to a degree allowing for reproduction are extremely valuable. However, being disconnected from the graphical schemes in Chapter 4, they only break the text flow. I suggest to present Section 3.1 as an Appendix and rearrange the rest and current Chapter 4 into two Chapters, one for essential synthetic information decorated with schemes, another for film preparation and characterization.

Answer: The experimental part is important for chemists not only by the opportunity to repeat the experiment but also by obtaining detailed information on the experimental conditions, reaction yields, and the purity of the products obtained. Therefore, the experimental part must necessarily be included in the text of the thesis. Still, taking into account the specificity of the information contained in it, I moved Chapter 3 to the Appendix, pages 90 - 104. Chapter 4 has been reorganized into two chapters: Chapters 3. Dendrimer synthesis. Result and Discussion, which contain essential synthetic information decorated with schemes, pages 52 - 64 and Chapter 4. Film preparation and characterization, pages 65 – 85.

Comment #4: During the revision of the Thesis, I do recommend the author to keep in mind general goals and refer to them whenever appropriate.

Answer: The research goals are outlined in the Introduction Chapter and referred to in the text where set goals are achieved.

Reviewer: Dr. Sci. in Polymer Chemistry, corresponding member of Russian Academy of Sciences Sergey Ponomarenko

Thanks for your detailed feedback. I took into account the recommendation for measuring the angle of inclination (rolling angle) and added it to the Future Work Section, pages 88 – 89. I also tried to theoretically calculate the angle of rotation of the dendrimers from their 3D images Figure 13(2) page 67. Calculation results are presented in Figure 14 pages 67 – 68.
Comment #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 2nd, 3rd, 4th and 5th generations?

Answer: Based on the dendrimers' growth process, these can be classified according to their generation number G0, G1, G2, G3, G4, G5, etc. Typically, the dendrimer generation number is determined by the formula:

\[ N_{eg} = x^2^n \]

where \( N_{eg} \) – number of functional (end) group, \( x \) - is the number of branches off the core, and \( n \) is the number of generations. Following this formula, a sulfonimide dendrimer with four naphthyl groups belongs to G1, with eight naphthyl groups - G2, 16 naphthyl groups - G3, and with 32 naphthyl groups - G4. Dendrimers can also be systematized by the generation number, which corresponds to the number of repeated branches formed systematically during the synthesis. Thus, if two branching points are added to the target molecule during the synthesis, then the resulting dendrimer is considered G2 (in the case of sulfonimide dendrimer with four naphthyl groups) and so on. Moreover, other scientific groups working with sulfonimide dendrimers have already used this numbering style, and we decided to use it. In the dissertation's text, I added the traditional way of dendrimer generation's definition recommended by IUPAC along with what is generally admitted for sulfonimide dendrimers. You can see changes in Figure 2, page 17 and in Figure 13, page 67.

Comment #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).

Answer: As you can see, the melting regions are indicated for the high generations of dendrimers (Compounds 9a (172 - 188°C, 9b 155 - 178°C, and 11 (138 – 173°C)). The difference between the upper and lower melting points increases with increasing generation and is equal to 16, 23, and 35 degrees, respectively. The thermodynamic properties of a melt high generations dendrimers differ sharply from those of dendrimers with small generation number. Regions of low and high density are formed in the peripheral layer. The formation of these regions is associated with steric restrictions resulting from the growth of generations of dendrimers. Possibly areas of a high density lead to entanglements between dendrimers. Intermolecular cavities grow with increasing generation due to the increase of the dendrimer size and the decrease in macromolecules' penetration into each other. This factor may lead to the formation of a compact structure that minimizes free space in such systems. Therefore, the appearance of melting regions can be possible due to the physical entanglements in melts of high generation dendrimers.

Comment #3: Yields of the compounds synthesized should be discussed.

Answer: The reaction yields are indicated in the reaction schemes and discussed in the text Chapter 3 pages 52 - 64.

Comment #4: Scheme 7 is shown on page 79, but not discussed in the text.

Answer: Scheme 7 is discussed on page 57.

Comment #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 correlate to the molecular size of different dendrimers?
Answer: To answer this question, I decided to compare sulfonimide dendrimers G3 - G5, since they have similar structures. I plotted the mean molecular area at the first inflection point vs. the molecular weight of dendrimers and the mean molecular area at critical pressure vs. the molecular weight of dendrimers. The graphs are shown in Figure 17, page 72. As you can see from the graphs, the mean molecular area increases with increasing dendrimer generation and, accordingly, with an increased molecular weight in two cases (at different pressures). The nature of the dependences is different; for the case with critical pressure, there is a dense packing of dendrimer molecules into a layer on the water/air surface.

Reviewer: Postdoctoral researcher Xiaomin Zhu

Thank you for your detailed feedback. In accordance with your recommendations, I have added information about the research of the scientific group of Academician Aziz Muzafarov to the section Literary Review, page 48.

Comment #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. Answer: Based on the dendrimers' growth process, these can be classified according to their generation number $G_0$, $G_1$, $G_2$, $G_3$, $G_4$, $G_5$, etc. Typically, the dendrimer generation number is determined by the formula:

$$N_{eq} = x^{2n},$$

where $N_{eq}$ – number of functional (end) group, $x$ - is the number of branches off the core, and $n$ is the number of generations. Following this formula, a sulfonimide dendrimer with four naphthyl groups belongs to G1, with eight naphthyl groups - G2, 16 naphthyl groups - G3, and with 32 naphthyl groups - G4. Dendrimers can also be systematized by the generation number, which corresponds to the number of repeated branches formed systematically during the synthesis. Thus, if two branching points are added to the target molecule during the synthesis, then the resulting dendrimer is considered G2 (in the case of sulfonimide dendrimer with four naphthyl groups) and so on. Moreover, other scientific groups working with sulfonimide dendrimers have already used this numbering style, and we decided to use it. In the dissertation's text, I added the traditional way of dendrimer generation's definition recommended by IUPAC along with what is generally admitted for sulfonimide dendrimers. You can see changes in Figure 2, page 17 and in Figure 13, page 67.

Comment #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 hydrophobic.

Answer: Typically, the literature describes the use of the most prevalent chemical groups for hydrophobic functionalization, among them relatively short regular or branched alkyl groups (up to 6 carbons), long alkyl chains (more than eight carbons), long perfluoroalkyl chains, siloxanes, aryl alkyl, and aryl groups. Also, various phenyl-based aromatic groups (naphthalene, anthracene) can exhibit hydrophobic properties, but they are practically not used for hydrophobization. In this work, it was decided to decorate the target sulfonimide dendrimers with naphthyl groups, which on one side can give hydrophobic properties, but are also undergoing dimerization under the influence of UV radiation that provides an additional opportunity for film formation and stabilization. Ca 90° is the limit value. Typically, if the contact angle with water is less than 90°, the solid surface is considered hydrophilic. If the angle of contact with water is greater than 90°, the solid surface is considered hydrophobic. In our case, we did not achieve high or super hydrophobicity but showed a correlation between the number of attached functional groups and the contact angle with water. As a result, we observed that with the increasing generation, the
contact angle is also increased reaching 92°.

**Comment #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.

**Answer:** Regarding the surface pressure – area isotherms, one of the opponents pointed out an error in the isotherms published in “Applied Surface Science” journal. We conducted an additional experiment and obtained consistent data for all generations. The error was related to inattentive unloading of data for plotting isotherms from the KSV NIMA software v 11.1.3. I also added a Figure 16 (c) page 71 with a graph mean molecular area vs. molecular weight. As one can see from the graph, with an increase in generation and, therefore, with an increase in molecular weight, the mean molecular area increases. Mma of G4, for instance, was near 600 Å² and shot up to 1500 Å² for G5.

**Comment #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.

**Answer:** Surface roughness (as the name itself suggests) is the degree of unevenness of the film surface and provides a measure of how smooth (or rough) the surface of a film is. In my case, the average roughness is about 1 nm (0.67-0.74 nm), while the thickness of the film itself does not exceed 5 nm. Comparing film thicknesses and roughness values, I prefer to keep this discussion in thesis. Moreover, if the arrangement of organic patterns (naphthyl groups) can have an effect on the hydrophobicity of the surface, such small roughness values should be considered.

**Comment #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?

**Answer:** Some dendrimers can show upper critical solution temperature (UCST) or lower critical solution temperature (LCST)-type’s thermosensitivity. Many properties of dendrimers, as well as thermal sensitivity, depend on the nature of their functional end groups. In addition to the nature of functional groups, molecular architecture and the degree of branching can also influence temperature-sensitive behavior. Dendrimers 7 and 9a have a similar structure and have certain degree of substitution of m-nitrophenyl groups. The density of the terminal m-nitrophenyl groups at the periphery of the dendrimer progressively increases with increasing dendrimer generation. The behavior of mixtures with LCST is associated with unfavorable mixing entropy. Entropy is responsible for mixing due to the increased volume available to each component when mixed. In the general case, the unfavorable entropy of mixing responsible for the LCST has one of two physical reasons.

The first is the interactions of the two components, such as strong polar interactions or hydrogen bonds, which prevent accidental mixing. The second is the effects of compressibility in dendrimer-solvent systems. For nonpolar systems, phase separation has been observed at elevated temperatures approaching the liquid-vapor critical point for the solvent. At these temperatures, the solvent expands much faster than a highly branched dendrimer whose segments are covalently linked. Therefore, mixing requires a reduction in the solvent for dendrimer compatibility, resulting in a loss of entropy. Also, the surface tension for solvents such as chloroform and dichloromethane decreases with increasing temperature, which can affect this behavior of the dendrimer-solvent system.

**Comment #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.

**Answer:** Crystalline solids in our definition mean isolated air-stable solids of the corresponding dendritic sulfonimides purified by recrystallization or column chromatography.

**Comment #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.

**Answer:** Thank you for your useful advice for continuing this research in the future.

**Additional question:** 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 addition to the Langmuir-Blodgett, we also have a spin-coating unit in the laboratory. We tried to use this method for the deposition of sulfonimide dendrimers on solid substrates, but the homogeneity of the films obtained by this method was much worse than that of the Langmuir layers. In the case of dip-coating, a large amount of dendrimer is required, which, in my opinion, is irrational, taking into account the multistep synthesis. Drop casting, like dip coating, does not allow you to control the film formation process. Also, this information is indicated in the Introduction on pages 20-24.

**Reviewer:** Associate Professor Tanja Kallio

**Comment:** As a minor remake, checking that the captions are located in the same page as the illustrations and tables would facilitate reading of the thesis.

**Answer:** Thank you for your positive feedback on my research work and thesis text. I adjusted the format, and now pictures, tables, and captions are on the same page.

**Reviewer:** Professor Albert Nasibulin

**Comment #1:** The list of figures, schemes and tables (p.14-17) is not necessary, and can be easily cut off without harming the quality of the thesis. This is old style writing of theses, I would call this atavism.

**Answer:** I have removed the relevant pages from the text and table of content.

**Comment #2:** Section 3.1.1 (53-67 pp.) contains too specific information. I would think of shortening it either by giving only the most efficient schemes and/or creating an appendix with NMR library for each compound.

**Answer:** For chemists, the experimental part is essential, as it allows us to provide readers with detailed information about the experimental conditions, the difficulties in isolating or processing the final products, and their purity, which can also be useful for repeating the results obtained. Considering the above, I would not consider the option of shortening this section, but given its specificity, I decided to move it to the Appendix located on pages 90 – 104.

**Comment #3:** Table of Contents should be carefully checked, since it does not correspond to the thesis structure.

**Answer:** Table of Content has been checked and corrected in accordance with the text of the thesis.

**Comment #4:** I would unify the way how to give a reference on certain research group or paper in the thesis: Surname et al. [reference]: as an example, p. 50 exhibits three different ways to refer to papers.
Answer: The same reference style was selected and applied, pages 105 – 122.

Comment #5: Tables 4: please check the precision of all numbers: how many digits after dots are reliable? The precision should be the same for all numbers.
Answer: Table 4 (page 80) has been corrected accordingly.

Comment #6: Bibliography: please carefully check all the references, some of them lacks important information and should be unified.
Answer: The same reference style was selected and applied, pages 105 – 122.

Comment #7: Why to underline the first letters in abstract for very known terms?
Answer: The underscores have been removed.

Comment #8: P.32 and 43: the name of a German scientist Vögtle should be spelled similarly.
Answer: The German scientist Vögtle is now spelled the same, proper way throughout all document.