Appendix 12b

REPORT

of dissertation for the acquisition of:

educational and scientific degree " **doctor** "	X
scientific degree **"Doctor of Science"**	
	the true is indicated by the sign "X"

Author of the dissertation:

	Eng.	Nikoleta	Dragomirova	Philipova	UCTM
academic position	scientific degree	name	middle name	last name	workplace

Topic of the dissertation:

Antibacterial photoactive polymer coatings

Scientific area:

	4. Natural sciences, mathematics and computer science, professional field
code	name

Professional area:

	4.2 Chemistry
code	name

Scientific specialty:

Chemistry of high molecular comounds

The report was written by:

Prof.	Dr.	Elena	Dimitrova	Vassileva	Sofia University “St. Kl. Ohridski”
academic position	scientific degree	name	middle name	last name	workplace

1. Meeting the minimum requirements under the Regulations:

A) The candidate meets the minimum requirements	20 points	X
B) The candidate doesn’t meet the minimum requirements	0 points	
		one of the answers given is marked with the sign "X"

It is mandatory to fill in if answer B is marked. The publication activity of the candidate is analyzed. The response of the results achieved (quoted) is analyzed.

The dissertation fully meets the requirements of the Law for the Development of Academic Staff in the Republic of Bulgaria (ADSRB), the Regulations for the Implementation of the ADSRB and the requirements of the University of Chemical Technology and Metallurgy for dissertation work, namely:

- contains scientific and applied results that represent an original contribution to the field of polymer materials science
- has the features and volume corresponding to the requirements in the field of polymer science for dissertation
- based on results included in five scientific publications, two of which are in journals with quartile Q2 (Journal of Applied Polymer Science and in the Journal of Polymer Research), two of which are in a journal with quartile Q3 (Journal of Chemical Technology and Metallurgy) and one in a journal with SJR (Bulgarian Chemical Communication)
- the abstract corresponds to the content of the dissertation and correctly reflects its contributions.

2. The relevance of the topic of the dissertation:

A) The topic is relevant and new (there are no known results on the topic by other authors)	8 points	X
B) The topic is relevant and results from other authors are known	6 points	
C) The topic is not relevant, but results from other authors are known	2 points	
D) The topic is not relevant and no results from other authors are known	1 point	
E) The topic does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign "X"

The evaluation of the relevance of the dissertation must be substantiated
The presented dissertation of doctoral student Nikoleta Filipova is in the advanced field of polymer materials science as it aims to develop new smart photosensitive polymer materials for creating antibacterial coatings using layer-by-layer technology. The goal is well justified by the growing threat of bacterial resistance and the dissertation presents an appropriate way to overcome this challenge.

3. Type of research:

A) Theoretical	4 points	
B) Applied	4 points	X
C) Theoretical with application elements	4 points	
D) It does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign "X"

The level of research must be substantiated if answer D is marked.

4. Objectives of the research:

A) Realistic and of scientific and / or applied interest	8 points	X

B) Realistic, but not of scientific and / or applied interest	3 points	
C) Unattainable (unrealistic)	0 points	
		one of the answers given is marked with the sign "X"

Objectives must be specified. The type of the set objectives must be justified.
The literature review includes 128 literature sources and is written on 36 pages. It presents the main techniques and methods for creating antibacterial coatings, as well as the main antibacterial agents (low molecular substances and polymer materials) currently used. Systems for delivering antibacterial agents in medicine are also presented, which are described together with their advantages and disadvantages. The literature review thus presentes a sufficiently clear picture of the field of the dissertation and well justifies its relevance, timeliness and the contributions that it is expected to make. The review, however, does not present sufficient details about the achievements so far and is not focused enough, but rather outlines the main trends and modern approaches. This is probably due in part to the fact that the development of antibacterial coatings has been worked on extremely intensively in recent years and the volume of existing research is very large. The main technology used in the dissertation, namely the layer-by-layer technique, is, however, presented critically enough in view of its application for creating antibacterial smart polymer systems. The experimental part is presented on 10 pages, with the description of the methods used, focusing mainly on the apparatus used. The measurement methodology itself, as well as the synthetic procedures, are briefly described, while the corresponding chemical equations are presented in the Results and Discussion section. The part of the dissertation, in which the scientific results are presented and discussed, is presented on 50 pages, and contains many results described accurately and clearly. Several approaches used to obtain antibacterial polymer coatings within the dissertation are presented, namely: *Polymer coatings based on Pox(mDOPA)/PAH nanogels*: The synthesis of polymer nanogels based on P(mDOPA)/PAH is briefly presented, using a synthetic procedure described in the literature. It would be useful to determine the conversion degree of the functional groups, i.e. to demonstrate the efficiency of the reactions used, although a methodology described in the literature was used. The variety of methods by which the obtained nanogels were characterized, as well as their coating on steel, achieved using the layer-by-layer technique, is impressive. The *preparation of a photoactive polymer coating based on 9-aminoacridine* is described in detail, supported by two methods confirming the successful modification of the photosensitizer. The photophysical behavior of the resulting amino modified 9-aminoacridine was also studied. The way in which the scientific results are presented is very good – without unnecessary verbosity, with critical consideration and discussion, described at the same time in sufficient detail. The combination of photosensitizer and Pox(mDOPA)/PAH nanogels to create an antibacterial coating is described in detail, and the resulting coatings are appropriately characterized. The presence of each of the components in this complex system is clearly justified and appropriately selected. The obtained new functional coatings are characterized not only in terms of their chemical composition, but are also thoroughly studied in terms of their mechanical and antibacterial properties, and it is shown that illumination with light affects the time profile of their antibacterial action. All these results confirm the initial design of the antibacterial coating, i.e. the correctness of the chosen approach. *Preparation of a photoactive polymer coating based on protoporphyrin IX*: The preparation of an ethylene diamine derivative of protoporphyrin IX has been demonstrated by three methods, aiming, as well as the modification of 9-aminoacridine presented above, at covalent attachment of the photoactive molecules to the polymer coating of Pox(mDOPA)/PAH nanogels. It has been shown that the chemical modification of protoporphyrin IX does not affect its antibacterial activity. Again, the obtained multilayer coatings are well characterized and demonstrate good antibacterial activity. *Preparation of polymer coatings based on Pox(mDOPA)-Ag0/PAH nanogels*: The incorporation of silver nanoparticles into polymer coatings is well known as a method for imparting antibacterial activity. In the dissertation, this approach was used to create even more active antibacterial coatings, as they were further used to create “dual” functionalized coatings, i.e. with both silver nanoparticles and antibacterial organic molecules. The synthesis and characterization of these coatings are described and discussed accurately and clearly. *Preparation of polymer coatings based on Pox(mDOPA)/PAH nanogels with incorporated silver nanoparticles and PPIX-ED photosensitizer*: The obtained coatings were appropriately characterized, and it was found that

they exhibit a synergistic effect of the silver nanoparticles and the photoactive PPIX-ED layer, which effect can provide longer-lasting bactericidal activity.
Preparation of polymer coatings based on Pox(mDOPA)/PAH nanogels and PPIX-ED/AgNps complex: The possibility of a previously prepared complex based on amino modified protoporphyrin IX with incorporated silver nanoparticles (PPIX-ED/AgNPs) to affect the antibacterial activity of the polymer coating was investigated. The obtained results confirm the initial hypothesis of this study.

I have the following questions for the PhD student:
1. How do you explain the slower formation of the second layer of Pox(mDOPA)/PAH nanogels (~17 min) compared to the first layer of P(mDOPA)-co-P(DMAEMA+) copolymer, which takes ~14 min?
2. How do you explain the different friction coefficients found within the characterization of the different polymer coatings – do they depend on the type of antibacterial agent or on the thickness of the resulting polymer layer?

5. Contributions of the dissertation:

A) With lasting scientific and / or applied response, they form the basis for new research and applications	20 points	
B) They are of significant scientific and / or applied interest, complete and / or summarize previous research	16 points	X
C) They are of scientific and / or applied interest	12 points	
D) Lack of significant contributions	8 points	
E) Lack of contributions	0 points	
		one of the answers given is marked with the sign "X"

Contributions must be specified. The type of results achieved must be justified.

The outlined contributions of the dissertation (formulated as conclusions) correspond well to the obtained results. The contribution to the development of polymer coatings with antibacterial activity, which are capable of changing this activity under the influence of light, is correctly outlined and is the most significant one in relation to the set goal of the dissertation. The approach used can be applied to many other antibacterial agents and photosensitizers, which expands the significance of the research and shows their universality. The presented scientific research is well planned, each step is justified and follows logically from the set goal. The fulfillment of the goal was achieved with by using appropriate methods for synthesis and characterization. All this shows in-depth thinking and precise work towards solving the problem set by the doctoral student and her supervisor.

6. Conclusion

A) The evaluation of the dissertation is **POSITIVE**	This evaluation is assigned to a total number of at least 40 points	X
B) The evaluation of the dissertation is **NEGATIVE**	This evaluation is assigned to a total number below 40 points	
		one of the answers given is marked with the sign "X"

To be filled in at the request of the member of the scientific jury

The presented dissertation of Eng. Nikoleta Filipova is interesting, significant from a practical point of view as it reveals the development of new photosensitive antibacterial polymer coatings, which gives me reason to confidently recommend to the scientific jury and to vote "for" awarding Eng. Nikoleta Filipova the educational and scientific degree "Doctor" in the field of higher education: 4. Natural Sciences, Mathematics and Informatics, professional field 4.2. Chemical Sciences, scientific specialty "Chemistry of High Molecular Compounds".

22.12.2024	The report was written by:	
date		signature