

REVIEW

of the doctoral thesis for the acquisition of Academic Degree “Doctor of Philosophy” (PhD) in the Professional Field 4.2. Chemical Sciences according to the Classifier of the Areas of Higher Education and the Professional Fields (Scientific Specialty “Polymers and Polymer Materials”).

Author: **Eng. Simona Miroslavova Zakhova**

Topic: **Preparation of phosphorus-containing products with added value based on recycled PET**

Research supervisor: **Assoc. Prof. Violeta Mitova, PhD**

Scientific consultant: **Prof. Kolyo Troev**

Reviewer: **Prof. Nikolay Vassilev, PhD**, Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences

This Peer Review is prepared in response to Order № ПД-09-178 from 19.12.2024 issued by the Director of the Institute of Polymers, Bulgarian Academy of Sciences. The Review is in compliance with *Development of Academic Staff in the Republic of Bulgaria Act (DASRB)*, the *Rules for the Application of the Development of Academic Staff in the Republic of Bulgaria Act*, the *Rules of BAS* and with the *Rules set at the Institute of Polymers, Bulgarian Academy of Sciences, for applying the Act aforementioned*.

1. Biographical information about the candidate

Simona Miroslavova Zahova graduated from the University of Chemical Technology and Metallurgy in Sofia, where in 2012 she obtained a Bachelor's degree in Organic Chemical Technology and in 2015 a Master's degree in Polymer Engineering. In the period from 07.2011 to 02.2017, she worked at C.R.V. Global Ltd. as a trader of polymers, masterbatches and additives. Since 02.2017, she has been holding the position of Sales Manager in Impekstim Ltd. In 2019 Simona Miroslava Zahova was enrolled for a full-time PhD student in the Laboratory of Phosphorus Monomers and Polymers at IP-BAS. The dissertation was discussed and directed for defense by the Colloquium of IP-BAS held on 13.12.2024.

2. Assessment of the scientific and research accomplishments of the candidate

The submitted reference of the candidate shows that the minimum criteria of the Specific Rules for the Acquisition of Scientific Degrees, defined in IP-BAS, Appendix 1, are fully met and

even exceeded. Two publications have been published on the PhD thesis in Q1 and one of these publications has already collected 8 citations. My citation check showed one two more citation of this publication have already appeared in the journal ACS Applied Polymer Materials (<https://doi.org/10.1021/acsapm.4c03337>). Therefore, there is a significant exceed in the required scores for indicator groups D and E.

Overview of the doctoral thesis and analysis of results

The doctoral thesis presented by Simona Zahova is in a topical and promising area of modern science - development of methods for recycling of polymeric materials and in particular chemical degradation of PET and re-polymerization into high added value products. The thesis is written in 118 pages and includes the traditional sections: introduction, literature review (47 pages), aim of the thesis, experimental part (10 pages), results and discussion (36 pages), conclusions, contributions and references used. It is illustrated with 10 diagrams, 37 figures and 8 tables.

The doctoral thesis contains 306 references, the vast majority of which have been published since 2000. The literature review, like the doctoral thesis as a whole, is well structured and presents a thorough analysis of the problem under study. The synthesis methods of PET, their properties and applications are thoroughly discussed focusing on the recycling of PET and different solvolysis degradation methods. Efficient use of PET glycolysis products and phosphorus-containing polymer flame retardants are discussed in separate chapters. Extensive conclusions are then drawn from the literature review and the main objective of the thesis is defined: to obtain value-added phosphorus-containing products based on recycled PET. To achieve it, the following tasks are set:

- 1) Synthesis and characterization of an efficient catalyst for conducting glycolysis of PET.
- 2) Chemical degradation of waste bottles by glycolysis process and determination of optimum conditions for the process.
- 3) Preparation and characterization of phosphorus-containing products based on the resulting PET glycolysis product.
- 4) Determination of the field of application of the resulting materials.

From the literature review it can be concluded that the PhD student has a very good knowledge of the current state and development trends in the field under study. The aim of the dissertation is clearly defined and the four tasks identified are logical and well justify and guide the research to achieve the set goal. The experimental part of the dissertation contains comprehensive information on the solvents, reagents, materials and apparatus used, as well as on

the methodology for the preparation of titanium(IV)phosphate catalyst, the glycolysis of waste PET in the presence of this catalyst, and their further conversion to phosphorus-containing oligomeric products.

The results obtained are systematized and discussed in four chapters in the Results and Discussion section, the first of which deals with the synthesis and characterization of the catalyst. The second deals with the glycolysis of waste PET under conventional and MW heating. The third discusses the preparation of value-added phosphorus-containing products based on waste PET, and the fourth is devoted to the determination of the thermal stability of the resulting phosphorylated products.

The resulting products were studied by ^1H , $^{31}\text{P}\{\text{H}\}$, ^{31}P and ^{13}C NMR spectra, thermogravimetric analysis (TGA), gel permeation chromatography (GPC), infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), ultraviolet-visible spectroscopy (UV-vis), X-ray diffraction (XRD) and X-ray fluorescence analysis. The detailed characterization of the products at each stage of the synthesis is very impressive. Spectral methods were also used to quantify the structure and ratio of the products obtained by comparing the results of different spectral methods: (Tables 6 and 7) NMR, GPC and UV. The results clearly show that the errors in the measurements are negligible and within the expected range.

The conclusions in the concluding section of the thesis are precisely formulated, reflect thoroughly and fully derived from the investigations carried out and are well supported by the experimental results.

The contribution of the thesis can be summarized as follows:

1. For the first time, TiP catalyst was used for the degradation of PET, by a glycolysis process under MW heating.
2. For the first time, value-added products were obtained in the glycolysis of PET without the need for its further treatment, isolation or purification.
3. For the first time, a method is described for increasing the value of products obtained from the glycolysis of waste PET by phosphorylation with PPD and TMP to produce new materials with potential applications as flame retardant additives for polymers.

Some of the results described in the thesis have been formalized in 2 articles published in the prestigious international journals with high impact factor: *Polymer degradation and stability* (2023, IF=5.9, Q1) and *Molecules* (2024, IF=4.2, Q1). The relevance of the developed thesis can be judged from the fact that the first article has already been cited 9 times by foreign scientists. Four papers and three poster presentations have been presented on the dissertation topic at

national and international conferences. The scientific research "Glycolysis of waste PET under conventional and microwave heating" was also awarded as the most significant scientific and applied achievement of IP-BAS for 2023.

3. The abstract of 40 pages meets the requirements and presents well the essence of the PhD thesis. It includes all the significant results of the translated research, the conclusions based on them and the formulated contributions.

4. Opinions, comments and recommendations

I have found no errors, inaccuracies or omissions in the submitted dissertation and its abstract. The only possibly technical error is the use of the term 'phospholation' instead of 'phosphorylation'. I have no personal impressions of the doctoral student and my impressions are only from the materials presented. Eng. Simona Zahova has carried out a considerable amount of experimental work, has correctly presented the results obtained and has discussed them competently. She has applied modern methods for synthesis and analysis of complex polymer structures. The work on her thesis characterizes her as a very well prepared young specialist and researcher. Hence, the educational objective of the Ph.D. degree has undoubtedly been successfully fulfilled.

5. Conclusion

According on the grounds of the documentation presented by the candidate, on her publications reviewed and the above assessment, I recommend on the Academic Jury to render a positive decision for the acquisition of the Academic Degree PhD on Eng. Simona Miroslavova Zakhova.

Date: 11.02.2025

Reviewer:

Member of the Academic Jury