

REPORT

by

Assoc. Prof. Dr. Georgy Bogomilov Grancharov

Member of the Academic Jury set to render a decision
on a procedure 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”)

This Report is prepared in response to Order № ПД-09-178 of 19.12.2024 issued by the Director of the Institute of Polymers, Bulgarian Academy of Sciences (BAS), following the decision made by the Academic Jury that was held on 17.12.2024.

The Report 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 -

Eng. Simona Zahova graduated from the University of Chemical Technology and Metallurgy - Sofia with a master's degree in "Polymer Engineering" in 2014. She works in the industry, applying her knowledge of polymers and polymer additives, and was adopted as a doctoral student at the Institute of Polymers - BAS in 2019 in the laboratory "Phosphorus-containing Monomers and Polymers". The topic of her dissertation is "Obtaining phosphorus-containing products with added value based on waste PET" with scientific supervisors Assoc. Prof. Dr. Violeta Mitova and Prof. Dr. Kolyo Troev. In addition to work on the dissertation thesis, the candidate has also participated in 7 scientific forums.

In the present dissertation, the results of Simona Zahova are summarized in 2 scientific publications. The articles have been published in international journals, referenced and indexed in world-recognized databases with scientific information (Web of Science and Scopus) and fall into the Q1 quartile. One of the articles was awarded as the most significant scientific and applied achievement of the Institute of Polymers for 2023 and has been cited in the scientific literature. Extended abstract was also prepared based on the dissertation work. It is noteworthy that in both publications of Eng. Simona Zahova, she is in first place, which unequivocally shows her personal contribution to scientific works. The points awarded by this indicator for fulfilling the minimum requirements for the scientific degree "Doctor of Philosophy" are 50 with required 30 points. Taking into account that the articles submitted by the candidate have already been cited eight times in the

scientific literature, the minimum requirements are met unconditionally and exceed the requirements of the Rules.

2. Assessment of the candidate to meet the minimal criteria for Academic Degree “Doctor of Philosophy” (DSc)

The scientific works of PhD student Simona Zahova are the result of research dedicated to the degradation of polyethylene terephthalate (PET, flakes obtained from waste bottles) by glycolysis in the presence of a titanium (IV) phosphate (TiP) catalyst applying microwave (MW) heating to a degraded product containing mainly bis(2-hydroxyethyl) terephthalate (BHET). The possibilities for its potential application after the reaction with phosphorus-containing agents for flame retardant additives or thermal stabilizers in new polymers are also shown.

During the development of the dissertation work, Simona Zahova successfully learned and applied the synthesis of titanium (IV) phosphate, as well as the methods for its characterization with the aim of using it as an effective catalyst in the glycolysis of PET with ethylene glycol. Its structure was additionally proven by X-ray structural and X-ray fluorescence analyses. One of the most widely used polymers in our time for packaging or as a textile material – PET is subject to degradation. Its annual production worldwide is over 30 million tons, which in turn leads to the search for solutions for the utilization of PET waste and its transformation into new valuable raw materials.

The degradation of waste PET via the glycolysis process in the presence of a titanium (IV) phosphate catalyst was chosen in the dissertation thesis. The influence of the reaction conditions in the PET degradation process under conventional and microwave (MW) heating was well monitored and compared. In the latter was shown that the reaction proceeds in a shorter time and leads to a decrease in energy consumption. Subsequently, the products of glycolysis were analyzed - mainly the starting monomer BHET, dimers, trimers and residual ethylene glycol. Various methods for characterizing the resulting reaction products have been learned and applied, such as ^1H , ^{13}C and ^{31}P nuclear magnetic resonance spectroscopy, infrared spectroscopy, gel permeation chromatography, ultraviolet and visible spectroscopy, etc.

The second stage of the doctoral student's dissertation work includes the phosphorylation of the resulting products of the glycolysis of PET with phosphorus-containing agents in a polycondensation reaction with phenylphosphonic acid dichloride (PPHA) or transesterification with trimethylphosphate (TMP). Thus synthesized polyphosphonates and polyphosphates have been characterized by the above-listed analytical methods and their structure has been proven. Their thermal stability has been determined by thermogravimetry and it has been shown that the amount

of charred residue is over 13%. Therefore, the obtained phosphorus-containing products based on degraded PET may have potential application as additives, imparting flame retardant properties to new polymers.

All this, in combination with Simona Zahova's skills in the field of catalytic degradation of PET by glycolysis under different reaction conditions, the characterization of oligomeric degradation products and their successful phosphorylation with phosphorus-containing agents, leads to the preparation of attractive materials with valuable and desirable properties that can be used again.

The dissertation thesis is written on 118 pages which the literature review covers 38 pages, and the description of the results and discussion - 36 pages. The literature review provides the preparation of PET and the various methods for its recycling, the main ones being mechanical and chemical. Solvolysis degradation methods are considered, of which the most extensively included are the varieties of the most used method - glycolysis. Attention is paid to the way of conducting and the reaction conditions that affect the process and, accordingly, the obtained degradation products. Catalytic glycolysis is specially described, as well as further applications of the degradation products obtained through this method. The results of the dissertation work are divided into 3 chapters, and finally the main conclusions and contributions of the dissertation work are presented.

3. Opinions, notes and recommendations -

Simona Zahova is an extremely active and focused young researcher in her research work. In addition to the two publications presented, falling into the highest quartile of scientific journals, she has also participated in 7 scientific forums with oral and poster presentations, which were reported personally by the PhD student. As the author of the dissertation, she tried to present the scientific work in the most comprehensible way for the reviewer, in order to facilitate his work as much as possible. I have no objections on the dissertation work but only one question related to it:

- In the chapter "Results and Discussion" is shown that in the degradation product obtained during the glycolysis of PET consists residual ethylene glycol. In the following phosphorylation reactions, it also reacts with a phosphorus-containing agent and the resulting product is present in the final phosphorus-containing material. Does this product have the same flame retardant properties as the phosphorus-containing product obtained with BHET or should its amount be reduced by further reducing the ethylene glycol and intensifying the mixing in the system during glycolysis?

4. Conclusion-

The main contributions of the presented dissertation work clearly outline the current and perspective topic on which the doctoral student Simona Zahova works in depth and systematically. This characterizes her as a researcher who has acquired, in the process of work new knowledge, experimental skills and the ability to thoroughly interpret the results obtained, as well as skillfully apply modern analysis methods. The research conducted by the author will enrich and supplement scientific knowledge, and will introduce innovations in the field of polymers, polymer degradation, recycling, reuse of recycled materials and environmental protection. The most appropriate conditions for conducting catalytic glycolysis, selection and synthesis of a catalyst, methods for proving the structure of the degraded oligomeric materials, as well as their possibilities for application after their phosphorylation with phosphorus-containing agents, which I consider is the personal work of the doctoral student.

The dissertation work presented by Simona Miroslavova Zahova and the materials to it fully meet the requirements for awarding the educational and scientific degree "Doctor of Philosophy" according to the Act on the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for its Implementation, as well as the Regulations of the BAS and the Institute of polymers (BAS). All this, as well as my personal impressions, give me reason to confidently express my positive opinion and to recommend to the Academic Jury to render a positive decision for the acquisition of the Academic Degree "Doctor of Philosophy" to Simona Miroslavova Zahova in professional direction 4.2. Chemical Sciences: Specialty Polymers and Polymeric Materials.

Date: 07/02/2025

Sofia

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**Member of the Academic Jury
Assoc. Prof. Dr. G. Grancharov**