R E P O R T

by

Assoc. Prof., Ph.D. Natalia Toncheva-Moncheva

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 following the decision made by the Academic Jury in response to Order № РД 09-182 from 02.12.2025 issued by the Director of the Institute of Polymers, Bulgarian Academy of Sciences

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*.

PhD candidate: Ina Anastasova

Title of dissertation: Electrospun Hybrid Materials from Poly(L-lactide-*co*-D,L-lactide) and Chitosan Derivatives with Directedly Modeled Design for Potential Applications in Biomedicine and for Photocatalytic Water Purification

Scientific Supervisors: Prof. Dr. Olya Stoilova
Prof. Dr. Milena Ignatova

The doctoral dissertation of Ina Anastasova is devoted to the preparation and characterization of electrospun hybrid materials based on poly(L-lactide-*co*-D,L-lactide) (PLDLLA) and chitosan derivatives with a targeted design architecture, as well as to the investigation of their potential applications in biomedicine and in photocatalytic water purification. The work includes the synthesis and modification of chitosan derivatives, the fabrication of fibrous systems (mats) incorporating complexed metal ions (Cu^{2+} and Fe^{3+}) and ZnO and Fe_3O_4 nanoparticles, as well as detailed physicochemical, morphological, and functional characterization. The topic is highly relevant, as it is related to the development of biodegradable hybrid materials for biomedical and environmental applications—fields undergoing intensive development and possessing significant applied potential.

The literature review is thorough, up-to-date, and well structured, demonstrating the PhD candidate's excellent knowledge of the subject area and spanning 41 pages. A significant portion of the cited sources consist of recent publications. In the concluding part, an analytical overview of the literature is provided, clearly outlining existing research gaps. The scientific directions discussed logically lead to the choice of the investigated polymer systems and to the formulation of the dissertation's research objectives. The review presents chitosan and its derivatives, poly(L-lactide-*co*-D,L-lactide) (PLDLLA) as a biodegradable copolymer, and electrospinning as a method for producing fibrous materials as well as its combined use with electrospraying. Modern hybrid fibrous systems based on biodegradable polymers and metal oxide nanoparticles with potential biomedical and environmental applications are also discussed. The main experimental approaches and instrumental methods used for their characterization are described as well.

The experimental section of the dissertation spans 9 pages and is clearly structured and concisely presented. It contains the necessary information on the starting materials, synthesis conditions, fabrication of fibrous materials by electrospinning and electrospraying, as well as procedures for subsequent modification and complex formation. The characterization methods employed are described, providing a reliable experimental basis for interpreting the results.

The results obtained within the dissertation and their discussion are presented over 36 pages. Chapter 1 addresses hybrid fibrous materials based on poly(L-lactide-co-D,L-lactide) (PLDLLA) and a Schiff base of chitosan with 8-hydroxyquinoline-2-carboxaldehyde, as well as their complexes with Cu^{2+} and Fe^{3+} ions. Their morphology, structure, thermal properties, and biological activity (antibacterial and antitumor) are investigated. The presented results demonstrate a successful approach to designing functional hybrid systems and a complete study of the relationship between composition, structure, and biological behavior of the materials. Chapter 2 presents hybrid fibrous materials with a targeted-designed architecture based on PLDLLA, quaternized chitosan oligosaccharide, and ZnO and Fe_3O_4 nanoparticles, prepared by combining electrospinning and electrospraying. Their physicochemical characterization is carried out, and their antioxidant and photocatalytic activities evaluated. The obtained results demonstrate the successful application of a combined technological approach for creating multifunctional hybrid fibrous materials with potential for environmental applications.

In this regard, I would like to formulate the following recommendations and remarks:

1. Considering the substantial length of the literature review, a more concise presentation of part of the literature data would contribute to a better structural balance and clearer highlighting of the author's original scientific contributions. In discussing PLDLLA as a class of materials, the description remains rather general. It would be appropriate to discuss more specifically the ranges of molecular weights and L/DL ratios, which would strengthen the link between the literature background and the PLDLLA copolymer used in this work.
2. The synthesis of the chitosan Schiff base is described in detail and well characterized structurally. Given the treatment in acidic medium at elevated temperature, it would be appropriate to assess a possible change in the molecular weight of chitosan (e.g., by viscometry). A control experiment without 8QCHO would allow clearer differentiation between the effects of chemical modification and those caused by the reaction conditions.
3. In Fig. 12, the DSC thermograms include temperature intervals where thermal degradation processes occur. Since DSC is not an appropriate method for assessing thermal stability, including these regions does not contribute to the correct interpretation of the results. For better visualization, it would be more appropriate to limit the DSC analysis to the temperature range in which the materials are thermally stable. In systems containing chitosan and its derivatives, a broad endothermic effect is observed in the range 25–100 °C, associated with the release of adsorbed and bound water in Ch and Ch-8Q. Since the glass transition temperature of PLDLLA lies in the same interval, these processes overlap; therefore, conclusions regarding the absence of influence of the additives on the mobility of the polymer chains should be interpreted with caution.
4. In Chapter 1 (p. 51), the discussion of the formation of secondary thin fibers population due to jet splitting is correct and consistent with the literature. To this explanation may be added the effect of increased electrical conductivity of solutions containing Ch and Ch-8Q, which enhances the electrical forces in the jet and favors the formation of branched and finer fibrous structures.

I would like to address the following questions to the PhD candidate:

1. Was a quantitative determination of the metal content in the fibrous materials performed after complexation with Cu^{2+} and Fe^{3+}, allowing differentiation between coordination-bound metal ions and potentially physically retained salt residues?
2. How can the selectivity of the cytotoxic effect of materials containing Ch-8Q complexes with Cu^{2+} and Fe^{3+} be assessed, considering the observed reduction in viability of both tumor and normal cells, with regard to their potential applicability for local biomedical use?
3. Has the stability of the surface-deposited ZnO/QCOS layer upon contact with aqueous media been investigated before and after exposure, considering the water-soluble nature of QCOS and the intended environmental applications?

In conclusion, the dissertation represents an innovative and purposeful study aimed at developing hybrid materials with biological activity and environmental applications. The selected synthetic approaches are well justified and consistent with the stated objectives, and the obtained results are clearly presented and correctly interpreted. The work demonstrates the PhD candidate's ability to plan and independently carry out complex scientific research. A significant fundamental contribution is the first-time synthesis of a chitosan Schiff base with 8-hydroxyquinoline-2-carboxaldehyde and the establishment of relationships between composition, structure, and properties of the obtained hybrid fibrous materials. Contributions of applied significance include the developed electrospun hybrid systems with potential for local biomedical treatment and for photocatalytic water purification.

The dissertation fully meets the requirements of the Institute of Polymers – BAS, containing original scientific and applied research results presented in scope and structure consistent with contemporary scientific standards.

The results are published in two scientific papers in the international journal *Polymers* (Q1, MDPI), which have received a total of 14 citations to date, thereby meeting and exceeding the minimum point requirements under this indicator (Г) according to the Bulgarian Law on the Development of the Academic Staff (*DASRB*) and its implementing regulations.

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 Ina Anastasova.

Date: Sofia, 10.02.2026

Report prepared by: . . . . . .
Assoc. Prof., Ph.D. Natalia Toncheva-Moncheva
Member of the Academic Jury