**REVIEW**

by Prof. Petar Dimitrov Petrov, DSc.
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member of the academic jury set to render a decision on the competition for occupying the academic position "Associate Professor" in Professional Field 4.2. Chemical Sciences /Polymers and Polymeric Materials/, published in SG No.65 on August 12th, 2022, for the needs of Department Macromolecular Engineering at IP-BAS.

This review is prepared in response to Order № RD-09-148 from 11.10.2022 issued by the Director of the IP-BAS. The review is in compliance with the Act on Development of the Academic Staff in the Republic of Bulgaria (ADASRB), the Rules for applying ADASRB, and the Rules for development of academic staff set at the Bulgarian Academy of Sciences (BAS) and the Institute of Polymers - BAS.

**1. Information about the candidate(s)**

The only candidate in the competition is Assistant Professor Dr. Radostina Genova Kalinova from the IP-BAS. She is a team member of the Department Macromolecular Engineering" at IP-BAS and works under the supervision of Prof. Dr. Ivaylo Dimitrov.

Radostina Kalinova graduated in 1998 with MSs degree form Sofia University "St. Kliment Ohridski", with specialty "Applied Chemistry and Business Management". Since 1998 until 2008 she has worked as a chemist at the IP-BAS. During the period 2009 - 2012 she was a PhD student in the Laboratory for Polymer and Composite Materials at the University of Mons, Belgium. In October 2012, she defended her dissertation under the supervisor Prof. Philippe Dubois and obtained the educational and scientific degree "Doctor". In 2013, Dr. Radostina Kalinova was appointed to the academic position "Assistant" at the IP-BAS, and after a competition in 2014, she was promoted to the academic position "Assistant Professor" at the same institute.

The candidate's professional experience is in the field of controlled synthesis of functional copolymers and development of (nano)materials with different architectures and properties, which

fully corresponds to the needs of Department Macromolecular Engineering, regarding the current competition. According to SCOPUS, Dr. Kalinova (6508295182) is the co-author of 20 scientific publications in peer-reviewed international journals, which are cited more than 130 times by other authors (H-index = 6). It is evident form the materials submitted for the competition, that she is the co-author of additional 9 articles in Bulgarian issues and conference proceedings and is team member of 13 research projects.

**2. Assessment of the research accomplishments of the candidate/s**

In this competition Assoc. Prof. Kalinova participates with 18 scientific publications, which are different from the publications for obtaining the educational and scientific degree "Doctor". 17 of the papers are published in specialized journals with impact factor and 1 in a journal with SJR. Half of the works are in journals falling in the Q1 quartile for the corresponding year of publication. The candidate's scientific output significantly exceeds the minimum requirements for the academic position "Associate Professor" in the Professional Field 4.2. Chemical sciences /Polymers and polymeric materials/, defined in the above-mentioned Rules of the IP-BAS. Dr. Kalinova collects a total of 691 points in the mandatory groups of indicators (A, C, D and E), while the sum of minimum requirements is 430 points.

Regarding the indicator of group A, the requirement for holding "Doctoral" degree is fulfilled.

The candidate has presented 5 publications relevant to the indicators from group C (equivalent to habilitation thesis). All of them are published in high impact journals indexed in the world-known databases Web of Science and Scopus - *Molecules* **2022**, *27*, 2178 (Q1), *Nanomaterials* **2022**, *12*, 434 ((Q1)), *Reactive and Functional Polymers* **2020**, *157*, 104763 (Q1), *Chemistry Select* **2017**, *2*, 12006 (Q2) and *Journal of Physical Chemistry B* **2015**, *119*, 6813 (Q1). Here, the minimum required is100 points, while the candidate collects 120 points. Dr. Kalinova is the first author of 4 and second author of 1 of the publications, which is a direct proof for a significant contribution to the corresponding works. The studies are focused on the design and preparation of multifunctional copolymers and nanocarriers on their basis for controlled delivery of biologically active (macro)molecules.

13 publications, relevant to the indicators of group D, bring the candidate a total of 241 points, which exceeds the required minimum of 220 points. The distribution by quartiles is as follows: 5

publications in Q1 (125 points), 2 publications in Q2 (40 points), 2 publications in Q3 (30 points), 3 publications in Q4 (36 points) and 1 publication with JCR (10 points). The presented works describe the synthesis of polymers and assessment of their used in capacitors, polymer-photovoltaic cells, LEDs, etc.

According to the candidate's documents, the publications with co-author Dr. Kalinova (without self-citations) are cited 140 times, bringing 280 points. This exceeds several times the minimum requirements of 60 points (Group E).

The minimum required points and candidate outcomes are summarized in the table below:

| **Indicators by groups** | **Minimum points** | **Candidate's points** |
|---|---|---|
| A | 50 | 50 |
| C | 100 | 120 |
| D | 220 | 241 |
| E | 60 | 280 |
| Total | 430 | 691 |

I should point out that the candidate also fulfils two of the optional criteria of the IP-BAS rules, namely, she is the co-author of 7 publications in the last 5 years, and she has contributed for the implementation of 13 scientific projects.

**Contributions relevant to the indicators from group C**

Regarding the works relevant to the indicators from group C, Kalinova's contributions are focused on the synthesis of original functional copolymers, their aggregation in aqueous environment, and loading of the obtained nano-sized aggregates (micelles) with low molar mass drugs and biological molecules.

Polyionic complex micelles have been obtained by electrostatic interactions between oppositely charged poly(2-hydroxyethyl methacrylate)-*block*-poly(L-lysine) and poly(ethylene oxide)-*block*-poly(L-aspartic acid) block copolymers in an aqueous medium. For the first time, these carriers are loaded with the hydrophobic active substance curcumin, while preserving its

antioxidant activity. An original nanocarrier of curcumin is also obtained by another approach involving a three-step synthetic procedure of a triblock copolymer composed of biodegradable poly(D,L-lactide) and hydrophilic segments of poly((2-dimethylamino)ethyl methacrylate) and poly(oligo(ethylene glycol) methyl ether methacrylate).

A new synthetic strategy for the preparation of multifunctional amphiphilic copolymers based on poly(ethylene oxide)-*block*-poly(lactide-*co*-carbonate) has been developed, which enables the incorporation and control of the number of cinnamyl side groups along the chain of the hydrophobic block. It has been found that by varying the number of cinnamyl groups, the loading and release profile of the natural bioactive substance caffeic acid phenethyl ester can be controlled.

Copolymers with a grafted hybrid block architecture have been obtained by an original synthetic procedure in which for the first time an N-Boc-protected ATRP initiator is used for the controlled polymerization of poly(ethylene glycol) methacrylate. The copolymers possess a block of densely grafted oligomeric PEO side chains and a poly(L-lysine) block. Next, these copolymers are used to form nanosized polyplexes with DNA molecules. Polyplexes are characterized with good colloidal stability, low cytotoxicity, and relatively high transfection efficiency, which is a prerequisite for successful gene therapy. To increase the therapeutic potential of insulin, nanosized complexes have also been developed by electrostatic interactions between the positively charged segments of a poly(ethylene glycol)-*block*-poly(L-lysine) copolymer and the negatively charged protein molecules.

**Contributions relevant to the indicators from group D**

One part of the works relevant to the indicators from group D are thematically identical to those from group C, namely the development of novel systems for delivery of bioactive substances and biomacromolecules. Another group of publications presents fundamental studies on newly synthesized linear (co)polymers and their behaviour in different solvents. The effect of the concentration, polymer composition, type of solvent, and temperature on the size and shape of the formed aggregates is studied. The potential of a transition metal complex to catalyse a carbonyl-olefin metathesis reaction of two different molecules, having two functional groups which are not conjugated, is investigated. A new approach for surface modification of polydimethylsiloxane has been developed. It involves attachment of amphiphilic block copolymers during the crosslinking

process. Dr. Kalinova has contributed to the preparation of new polymers and polymer films with potential applications in capacitors, flexible polymer-photovoltaic cells, and LEDs. The use of polyionic liquids based on new pyrrolidinium based polymers ensured high stability of the investigated symmetric supercapacitor and a high charge-discharge efficiency. Polydiphenylacetylenes with Schiff bases as terminal groups have been successfully synthesized by carbonyl–olefin exchange reaction. The materials possess photoluminescent properties and potentially can be used in electronics as LEDs. Polymer–organic solar cells based on a bulk heterojunction poly(3-hexylthiophene) (P3HT) / fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) active layer blend have been successfully constructed on a flexible poly(ethylene terephthalate) substrates under environmental conditions. The cells exhibited photovoltaic parameters similar to those made on conventional glassy substrates.

**3. Opinion, recommendations, and notes**

The materials submitted by the candidate are in accordance with the requirements of the ADASRB and its regulations. The "habilitation thesis" summary is comprehensive and clearly depicts Kalinova's personal contributions. From my direct impressions, I can confirm that Radostina has been involved in all activities related to the preparation and implementation of experiments, collection of data, interpretation and dissemination of the results. The candidate's scientific papers are of high quality; they are published in high impact journals and received an impressive number of citations from other authors. Regarding Kalinova's works, I have no remarks and recommendations. I have a question:

It is known that double-hydrophilic block copolymers can aggregate in aqueous media. Do you have any evidence for such phenomenon regarding your POEGMA-*b*-poly(L-lysine) copolymers and how this process would affect the complexation with DNA molecules?

**4. Conclusion**

The submitted by Dr. Radostina Kalinova materials are legitimate, and her research outcome exceeds the minimum requirements for the abovementioned academic position, in the corresponding research field. The candidate has undoubtedly made a significant contribution to the presented research papers (equivalent to habilitation thesis), which describe original synthetic approaches and advanced nanomaterials with potential application in medicine and pharmacy.

Therefore, I give my positive assessment and I would like to recommend to the esteemed members of the Scientific Council of IP-BAS to elect Dr. Radostina Kalinova for the academic position of "Associate Professor" in Professional Field 4.2 Chemical Sciences /Polymers and Polymer Materials/ for the needs of Department “Macromolecular Engineering” at the IP-BAS.

30.11.2022, Sofia REVIEWER:

/ Petar Petrov/