R E V I E W

from Prof. Doctor of Science Mihail Nedyalkov

in connection with a competition for the academic position of "Associate Professor",

field of higher education 4. Natural sciences, mathematics and informatics,

professional field: 4.2. Chemical sciences / Biophysicochemistry /

for the needs of the Department of Physical Chemistry of the Faculty of Chemistry and Pharmacy to Sofia University "St. Cl. Ohridski "

The only candidate for announced in SG no. 63 of 30.07.2021 competition for the academic position "Associate Professor" is Ch. Assistant Professor Dr. Nikolay Alexandrov Grozev from the Department of Physical Chemistry at the Faculty of Chemistry and Pharmacy at Sofia University.

Nikolay Grozev graduated from secondary education school in 1993 at 123 Sofia school, and during the period 1993-1998 he graduated from Sofia University "St. Cl. Ohridski ", Faculty of Biology with a master's degree in" Molecular Biotechnology "and with the defense of a thesis.

From 1999 to 2003 Ch. Assistant Professor Grozev is a PhD student at Sofia University "St. Cl. Ohridski "in the Laboratory of Biophysicochemistry at the Department of Physical Chemistry, where he received the educational and scientific degree" Doctor "with a defense before the relevant Higher Attestation Commission. The topic of his doctoral dissertation covers research on "Mechanical, electrical and chemical properties of layers of linear polyester and cross-linked lignin-like polymers on the water-air interface".

Meanwhile, during the same period and in connection with some of the forthcoming tasks in the dissertation, Nikolai Grozev twice visited for a short or long time two distinguished laboratories of the Roger Douillard group in France, where he where he does an excellent job with the purpose of his visits.

From 2008 until now he has been a senior assistant. During this time, in addition to his doctoral engagements, Nikolai Grozev had as his main activities and responsibilities teaching in Physical Chemistry (lectures and exercises), as well as scientific work in the field of physical chemistry. In addition to leading diploma theses, he has participated in a number of national and international projects, and he himself has been the leader of such projects at the Research Fund of the University.

Chief Assistant Nikolay Grozev is a co-author of 32 publications, 28 of which are referenced and indexed in Scopus. He participated in the competition with a total of 18 publications. All of them are referenced and peer-reviewed. Of these, 15 have been published in journals, 2 in conference proceedings and 1 is a chapter in the ***Lectures Notes in Physics series***. The total number of citations to these articles is 88.

The habilitation thesis is based on 5 articles [1, 3, 4, 13, 14] and is supported by a total of 53 citations.

The articles outside the habilitation paper are 13 [2, 5-12, 15-18] and the citations are 35.

Scientific contributions are in the field of surface physicochemistry and colloid chemistry. It is necessary to emphasize the rich research technique used, which would be envied by many researchers - optical microscopy (OM), atomic force microscopy (AFM, AFM), microscopy at Brewster angle (BAM), ellipsometry, Sheludko-Exerova cell, Langmuir scale with Wilhelmley method, Langmuir-Blodget films (LB films), hanging drop method (sitting bubble), contact angles.

The results described in all articles concern phenomena occurring at phase boundaries and adsorption of surfactants, which, according to the author, with some reservations can be further divided into 2 sections:

I. Processes occurring at the water / air phase boundary such as adsorption of inorganic ions and monolayer approach in Langmuir bath for the study of pharmaceutical products, for the synthesis of Pt nanoparticles and for the characterization of twin surfactants;

II. Thin films:

1. Hard films on a hard surface
2. Liquid films on solid and liquid substrates

Section I: The structure of the water / air surface is an old problem (ie how water dipoles are directed, the presence of free charges due to the adsorption of protons or hydroxyl ions), which is not yet fully understood. Here, in [8], in addition to using an extended Schmutzer model for the surface of aqueous, electrolyte solutions, a model of the hydration interaction between an ion and an aqueous surface was presented for the first time, in which the surface structure was taken into account.

Nikolay Grozev has a significant contribution to this research through his personal participation with work and knowledge, as well as enviable experimental skill in using different methods for measuring surface tension, as well as applying a new sensor for measuring it and finding optimal conditions for working with him.

In the study of a chemical reaction occurring at the same phase boundary, [12] described the reaction of reduction of chloroplatinum ions from hexadecylaniline molecules organized in a pre-applied insoluble monolayer at the phase boundary in question. As a final product of the reaction, the resulting nanoparticles can be transferred from the phase boundary to suitable solid substrates in the form of multilayer Langmuir-Blodget films. Subsequently, the films were characterized by atomic force microscopy and X-ray photoemission spectroscopy.

The most important thing that can be noted is that as a result of the reaction, the area occupied by the monolayer increases in contrast to the case of obtaining gold nanoparticles under the same conditions.

Here, too, the conduct of the experiments with the Langmuir scale, the training of the graduate in the various monolayer techniques, the proposing of an appropriate kinetic model, as

well as the interpretation of the results obtained are entirely inspired and directed by Ch. Assistant Professor Grozev.

The further use of the monolayer technique for studying the behavior of pharmaceutical products [7] is related to the following: the natural lung surfactant that covers the inner walls of the alveoli is a complex mixture of phospholipids and proteins. Clinically used artificial surfactant, in order to overcome the respiratory distress syndrome, is usually only a mixture of phospholipids or an extract of surfactant from animals.The present study compares the surface properties of commercial water / air boundary products as a model system of alveolar surface, in the presence of bovine serum albumin and hydrophilic polymers polyvinyl pyrrolidone, polyethylene glycol and dextrin. As a result of this study, the effectiveness of the spread of products on the surface and the order in which it occurs have been established, and the generally accepted ideas about the mechanisms of serum protein inactivation and the restorative effect of hydrophilic polymers have been confirmed.

The scientific interests of the associates of the Laboratory of Biophysicochemistry, including those of Dr. Grozev find a place in the field of transport of various dosage forms, as well as the processes that take place when reaching these carriers at the water / air phase limit. The next [9] of the research papers submitted for the competition show the results of research on some model systems of visicules, nanocapsules and biodegradable polyester matrices.

Briefly, following the monolayer approach, these particles or substances are deposited on the phase boundary where reorganization processes or interesting chemical interactions, including enzymatic or alkaline hydrolysis, begin. The developed models represent an important first step for assessing the behavior of drug carriers.

In [2] the sol-gel technique is applied for making films on solid pads containing Ru (II) - oxygen sensor complexes. It was found that an important factor for the quality of the film, respectively the full functioning of the sensor, is its thickness and porosity.

The articles [5, 6, 10, 11] describe the leakage of foam films of a suspension of silver nano-clusters stabilized by poly-methacrylic acid by the interference method. For comparison, the leakage of foam films containing aqueous solutions of the same acid with and without silver nitrate was observed. It is a well-known fact that the presence of polymeric acid chains will lead to steric repulsion between the two surfaces of the film. However, in nano-cluster suspensions, reduced steric repulsion is observed, leading to stable but thinner films.

In [6] we consider the kinetics of retreat of the three-phase contact line of evaporating small water droplets on glass surfaces. The experiment showed significantly smaller angles of deviation than theoretical predictions. For this reason, a new theory has been developed that takes into account the periodicity of the surface and the contribution of the three-phase contact line to the contact angle.

Among the more interesting studies we can further mention those described in the works [10, 15-17] related to the friction of the three-phase contact line, and the study of the free energy of the latter. This is how the value of the surface tension of the solid / air surface was calculated.

Last but not least, a new method for determining the critical concentration of coalescence of foamers has been proposed in [17]. The values of a number of known foaming agents were measured and the concentration dependences of the surface tension of their aqueous solutions were established. Their adsorption parameters have also been determined by applying one of the last adsorption models known in the literature.

As in all the studies described so far, so in the following, except for conducting some of the experiments and participating in the experimental setup, the author shared his experience with graduates and PhD students and also participated in discussions and various theoretical discussions.

As mentioned above, the documentation required for the purposes of the competition is accompanied by a habilitation thesis based on 5 articles [1, 3, 4, 13, 14] with a total citation index of 53.

Before proceeding to the evaluation of the works included in the habilitation work, I would like to present a few clarifications made by me and by Dr. Grozev himself, with whom I, as a reviewer, fully agree.

The main contribution of the author in all works (including those submitted for the competition, but outside the habilitation thesis) is experimental, although at some points, and due to the complexity of the experiment, he was not the only experimenter. And the manipulations generally include: applying the films, determining their thickness with an ellipsometer, experiments with optical and atomic force microscopy in the case of polymer crystals and structures, experiments with monolayers, etc.

In connection with the elaboration and writing of the habilitation thesis, Dr. Grozev correctly indicated the names and the specific participation of the other authors, for which he expresses his gratitude. Naturally, during all this interaction the author took an active part in the discussion of the obtained results, the preparation of the manuscripts, etc.

The next 3 works out of the 5 included in the habilitation work, namely (1, 3, 4) according to the conditional division made by the author fall into the Section II of the research.

The works [1,3,4] in Section II of Nikolay Grozev's research on hard films on solid substrates, as well as on liquid films on solid and liquid substrates were conducted during his post-dock internship in the Gunter Reiter group at the Institute in surface chemistry to SNRS in France and are studies of the structure formation in thin polymer films of diblock copolymers consisting of a crystallizing and an amorphous part. In one case, the driving force is the change in crystallization temperature, and in the other case - the change in the concentration of the polymer in the thin film.

The examples presented in the present paper on the morphology of lamellar polymer crystals strongly support the possibility that the mechanism of diffusion-constrained aggregation is the most appropriate for the description of crystal formation. In these studies, the possibility of delayed nucleation was used to study in detail the growth regime of polymer crystals. It is concluded that slow growth rates, together with the ability to form simple plane structures, make polymer crystals ideal model systems for fundamental studies of crystal growth. This, including some computer simulations, provides a promising approach to improving our understanding of polymer crystallization and may shed light on key issues for crystal growth in general. These publications are one of the few works on crystallization in thin films in general.

While in [1] and [4] the driving force is supercooling, ie the change in crystallization temperature, in [3] is the change in the concentration of the polymer in the bubbling thin films. The

films applied on a silicon substrate were observed in real time under an optical microscope, and the formed structures were further characterized by atomic force microscopy.

Further in the habilitation work, studies on the surface activity of newly synthesized L-Asp-based twin surfactants are presented. It has been found that the molecules of these substances tend to self-organize into 1D supramolecular complexes. Finally, it was found that the presence of supramolecular complexes makes it possible to determine the so-called critical concentrations of aggregation. It is stated that the observed phenomena have not yet been well studied.

At the end of the habilitation work, the author draws our attention to the fact that in the areas affected there is a huge volume of articles that are constantly expanding and it is impossible to cover. He therefore directs readers to the specialized literature added below without claiming to be exhaustive.

1. Xu, J., Ma, Y., Hu, B., Rehahn, M. and Reiter, G. (2009) – Cloning polymer single crystals through self-seeding, *Nature Materials*, **8**, pp. 348–353. 205 citations.

2. Reiter, G. (2014) – Some unique features of polymer crystallization, *Chemical Society Reviews*, **43**, pp. 2055-2065. 92 citations.

3. Majumder, S., Poudel, P., Zhang, H., Xu, J., Reiter, G. (2020) – A nucleation mechanism leading to stacking of lamellar crystals in polymer thin films, *Polym. Int*, **69**, pp. 1058–1065.

The results of the works on the basis of the habilitation work are presented at national and international scientific events by the author alone, as well as together with John Botiz, with Ch. Assistant Professor Kristina Mircheva and independently by the doctoral student Borislav Anchev.

Finally, I would like to emphasize that the candidate's research has been conducted at a high professional level and is described in an understandable, detailed and correct manner. As it was said in several places in this exhibition, the personal contribution of Nikolay Grozev in the conducted research is indisputable. I find Dr. Grozev an established specialist with very rich experimental and theoretical experience in the field of physicochemistry and colloid chemistry.

My personal impressions are that he is honest and dedicated to his work not only in terms of his research activities, but especially in terms of his work with students and practical activities with them. Metaphorically, it can be said that for many years Nikolai Grozev has been carrying almost entirely the Colloid Chemistry workshop on his shoulders.

After a thorough review of the submitted scientific papers, list of citations, participation in scientific forums (Results reported in more than 15 international and national scientific forums, such as oral presentations or poster sessions), as well as project activities and reference for teaching the candidate I express my firm opinion that Ch. Assistant Professor Nikolay Alexandrov Grozev fully deserves to hold the academic position of "Associate Professor".

Conclusion:

From the documentation submitted to me for participation in the competition and the review of the information related to the candidate's educational activity, as well as the one related to the research activity, I conclude that the candidate has fulfilled all the necessary indicators for this purpose. In support of my opinion below, I present a brief comparison between the recommended criteria for the implementation of the minimum national requirements under Art. 26 of the Law on Scientific Research and Development and the indicators fulfilled by the candidate for this scientific field:

I. For indicator group **G**: Scientific publications in publications that are referenced and indexed in world-famous databases (Web of Science and Scopus)

Recommended - at least 220 points

Completed – 242

II. For group of indicators **D**: Citation in scientific journals.

Recommended - at least 70 points

Implemented - 230

III. For group of indicators **G**: new courses defended graduates, scientific projects

Recommended - at least 70 points

Implemented - 190

The coverage of the others and these indicators evident from the reference convinces me that the scientific production of Ch. Assistant Professor Dr. Nikolay Grozev has gained fame and international recognition. He is an established specialist in the field of physicochemistry and in particular biophysicochemistry, and this gives me reason to recommend to the esteemed Scientific Council to award Ch. Assistant Professor Dr. Nikolay Alexandrov Grozev the academic position of "Associate Professor".

Sofia, December 6, 2021. Reviewer: ..... .

/ prof. Doctor of Science Mihail Nedyalkov /