Review

By Prof.Dr. Stoiko Petrov

Of the PhD thesis of

Viktoria Trifonova Trifonova

Topic: **PREPARATION, CHARACTERIZATION AND APPLICATION OF POLYMER-METAL COMPLEXES**

For the scientific and eduational degree "Philosophy doctor"

In the scientific specialty 01.05.06. „Chemistry of high molecular weight compounds"

The review was written on the basis of Order UD-304/28.11.2019 of the Rector of University "Prof.Dr.Asen Zlatarov" – Burgas and Protocol № UD 320/ 17.12.2019 of the session of the Scientific jury.

1. Short biographical information

Viktoria Trifonova graduated with "master" degree the specialty (chemistry and chemistry teacher" at the Bourgas University in 2001. She has been an assistant in the Department of "Inorganic and analytic chemistry" of University "Prof.Dr.Asen Zlatarov" – Bourgas since 2007. She was put on the list for preparation of PhD thesis on 22.11.2018r. in specialty 01.05.06. „Chemistry of high molecular weight compounds for which the University has the necessary accreditation. Apart from the educational process, she took part in three scientific projects in the period 2015 – 2018. She also participated in the development of electronic educational textbook on "Analytic chemistry" in 2014. She has submitted twelve publications not related to her PhD thesis, she has taken part in many seminars and courses related to her teaching activities.

2. RELEVANCE OF THE SCIENTIFIC THESIS DEVELOPED

Because of their diversity, specifics and functionality, polymer materials are objects of numerous studies which characterize not only their structure but also the chemistry of the processes related to their modification and application. This is why the aim and the tasks formulated for the preparation of polymer complexes is a specific field in polymer chemistry in connection with the polymer matrix.

The conditions for the synthesis of polymer-metal complexes are stipulated by the type and functionality of the polymer chains providing the stability of the complexes and their reactivity. The accomplishment of such studies leads to the obtainment of new materials with highly developed well-arranged surface which facilitates the processes of complex formation under reduced influence of the steric factors. The studies were carried out at mictro level which determines also the specificity of the investigation. The results obtained and the application of the complexes indicates for the relevance of the problem.

3. DESCRIPTION OF THE Phd THESIS.

The PhD thesis is arranged according to the reauirements of the Rules for the conditions and procedure for acquisition of doctorate degree of University "Prof.Dr.Asen Zlatarov". It contains 136 pages arranged in the classic structure of a dissertation work. The author's summary fully reflects the studies carried out, as well as the results obtained and the analyses made.

The literary review contains 163 cited sources with 83 of them published after year 2000. It characterizes well the known results about the preparation of polymer complexes and tends to point out the specifics of the dendrite polymer structure the expected differences in the syntheses of these complexes. Simultaneously, the review defines the limits and the directions of the investigation planned. It would have been much better if special attention was paid to the conditions for the preparation of polymer complexes, e.g.: medium pH, molecular weight of the polymer, the ratio between the functional groups of the complex and the ions of the transition metals.

The conclusions, aims and tasks are properly designed. It would have been better if they were arranged in the sequence: synthesis, characterization and application. This would correspond better to the title of the doctorate and the sequence of the studies.

The Experimental section shows well the conditions for the preparation and modification of the complexes, the methods of their study, the methodology and background of the theoretical calculations, the juxtaposition of the results and the use of the complexes in technological processes. The combination of modern physicochemical experimental and theoretical methods of investigation is impressive.

4. RESULTS AND DISCUSSION

The dendramers are new kind of polymeric matrices characterized by high degree of arrangement which imparts them specific properties. Every process of physicochemical impact on them is determined by the properties of the dendrimer and the metal cation by the formation of the complex. The studies carried out confirmed the order of the complex forming ability of the metal cations and present substantial contribution to the studies of dendrimer properties. This is facilitated by the interesting approach to the work where the experimental activity is carried out in patallel with quantum-chemical calculations. The later are based on an elementary fragment of the dendrimer and are confirmed by the properties of the complexes obtained. Certain iterest arouses the study on the synthesis of complexes on the basis of glutathione, glycylglycine and several amino acids. It provides possibility to work at the boundary between the high molecular weight and low molecular weight components where the gradual change of the complex forming ability of the substances in this range is proved. The complexes obtained are characterized by modern instrumental methods. As a result, it is proved that:

- Coordination structures of the complexes

All possible structires were modelled and optimized. First, the structure of the five-coordinated complexes of molybdenum is studied. There are no data about these complexes in the literature. Using the theoretical approach suggested, the existence of five coordination centers is proved. Certain correlatin between the theoretic, crystallographic and spectral studies is used which describe both the five-coordinated structure and the possibility for the existence of six-coordinated structure which includes the medium characteritics in the system.

The differences in the complex forming properties of the dendrites D-8 and D32 are proved. By the interaction between monometoxy polyethylene glycol and amber anhydride, the ring of the latter is opened to produce carboxyl group with good complex forming ability. Here, the studies involve also the changes taking place with the increase of glycol molecular weight. Naturally, the longer molecules affect the complex forming process while the coordination of molybdenum can take place predominantly with the amino groups or in coordination with the carboxyl groups. This coordination of the complexes increases its pseudo-crystallinity and thermal resistance.

The structure of the glycylglycine complex is proved using modern calculation methods based on the presumed geometry, the electron properties and the vibration spectra of the complexes obtained. In these compounds, again, the structure is oriented simultaneously towards the amine and carboxyl groups. It indicates for the similarity of the complex forming processes for both low and

high molecular weight matrices. The differences are purely steric and are due to the specific properties of the higher molecular weight chains.

The structures of a series of complexes of transition metal ions are optimized with respect to three different by chemical structure and functionality amino acids. By the use of DL-lysine and L-methionine, the higher efficiency the molybdenum and vanadium complexes is proved. The study shows that these complexes have axial symmetry.

Similar results are obtained from the study of the system transition metals and glutathione. Here, the systems with molybdenum, cobalt, copper and iron are optimized. The latter two complexes are active participants in the biologic oxidation processes. The knowledge about the structures of the complexes and their action could help for their use as biologic carriers of medications.

- The thermal stability of the complexes is proved

The differences in the efficiencies of the molybdenum and vanadium catalysts are proved. The stabilities of the catalysts are proved by IR investigation before and after the catalytic process on the basis of the stabilities of the bonds Mo=O Mo-N which provides possibility to assume epoxidation as the most probable mechanism of the process. In the glycine complexes with transition metals, a two stage decomposition process occurs while the molybdenum complexes remain stable up to 330 ^{0}C.

- Application of the complexes

One of the main contributions of the studies carried out is the real use of the catalytic complexes obtained in the technological processes. By the use of dendrimer complexes in the processes of oxidation of cyclohexene with tret-butyl hydroperoxide, the differences of the efficiencies of the catalysts based on D8 and D32 dendrites are proved. The dependence of the catalytic properties of the substances on PEG molecular weight is proved.

By the use of the complexes of MoO_2^{2+}, VO^{2+}, Cu^{2+}, Fe^{2+}, Co^{2+} with glycylglycine, the higher activity of the molybdenum and vanadium complexes is proved and, besides, their yield of side products does not exceed 2 %. Here, the efficiency of the complexes depends on the mechanisms of the processes taking place.

By the use of the complexes of amino acids with molybdenum and vanadium, the more effective ones are the molybdenum ones. Such results were

obtained by other authors, too, who reported that metals with low oxidation potential and high Lewis acidity are effective catalysts for oxidation of alkenes.

In conclusion, it can be accepted that great amount of studies has been carried out on the processes formation of complexes of different by properties polymeric and low molecular weight products and the choice of these materials was made purposefully. Modern theoretical and experimental methods have been used and the conciseness and precision of the analysis of the results makes a good impression.

5. CONCLUSIONS AND CONTRIBUTIONS

The conclusions and contributions characterize precisely the results obtained from the studies carried out. They are tangible and reflect every stage of the study. It is possible to formulate also several substantial contributions related to the coordination advantages of the dendrite complexes, the dels applied and the assumed coordination structures of the complexes or complexes' activities with respect to the molecular weight of the matrix. All these contributions determine the dissertation potential of the study and the possibility to develop new concrete ides in this scientific field.

6.PUBLICATIONS RELATED TO THE DISSERTATION WORK

Among the five publications presented, the PhD applicant is the first author and the second one in the others. They have been published in influential scientific journals and this indicates for the interest towards such studies. The participation in four scientific conferences which increases the publicity of both the scientific field and the results obtained. The publications obey the requirements of the Regulation of the University "Prof.Dr.Asen Zlatarov" Bourgas about the scientific degrees and positions.

CONCLUSION

The PhD thesis of Viktoria Trifonova Trifonova on the P***reparation, characterization and application of polymer-metal complexes*** is topical and suitable for doctorate study. The applicant has acquired both research and practical experience by carrying out different by nature theoretical, experimental and analytical methods for investigation of various complexes and their application in technology.

In my opinion based on the considerations made above, Viktoria Trifonova Trifonova fully complies with the requirements of ACDARB and the Regulation for its implementation and obeys the requirements of the Regulations od University "Prof.Dr.Asen Zlatarov" - Bourgas.

This is why I grant positive estimation of the PhD thesis and support the conference of the educational and scientific degree "doctor" to Viktoria Trifonova Trifonova in the scientific specialty: *01.05.06.* ***Chemistry of high molecular weight compounds.***

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/проф. д-р Стойко Петров/