

ABSTRACT

of the thesis for the degree of the doctor of philosophy (PhD)

on the specialty 6D060600 - Chemistry

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Synthesis and research of metal-polymer complexes based on copolymers of polyglycol maleates with acrylic acid

General characteristics of the thesis. This thesis is devoted to synthesis of new metal-polymer systems (MPS) based on copolymers Polyethylene Glycol Maleinate (p-EGM) /Polypropylene Glycol Maleinate (p-PGM) with acrylic acid (AA) and particles of silver, nickel and cobalt, and research of their physico-chemical characteristics, catalytic properties by the electrocatalytic hydrogenation of organic substances and hydrogenation, as well as the ecotoxicological assessment and research of antibacterial activity on some strains.

The relevance of the work. The first President of the Republic of Kazakhstan-Leader of Nation N. Nazarbayev in the message "Kazakhstan-2050" to the people of Kazakhstan in the ten global challenges of the XXI century have paid special attention to new scientific advances in the field of nanotechnology and the role of the Kazakh scientists.

The main direction of the modern stage of scientific and technological progress is research of cost-effective systems that can be used in various fields of production and science. These requirements are met by metal-polymer nanocomposites with immobilized metal nanoparticles that can purposefully change their character. These nanosystems are unique materials with high electrical conductivity and catalytic, ferromagnetic, antibacterial, etc. properties, therefore, there are in great demand in industry and science, including "green" chemistry, catalysis, oil and coal processing, electronics, medicine. Therefore, the synthesis and research of nanostructured systems such as "polymer-metal" is an important and urgent task for science and production.

Goals and objectives of the research. The main goal of this work is the synthesis of new mono-and bi - metal-polymer complexes based on copolymers of Polyethylene(propylene) Glycol Maleinate with acrylic acid (p-EGM:AA, p-PGM:AA), description of their physico-chemical properties and catalytic research, antimicrobial activity. In accordance with the purpose of the research, the following tasks were set:

- synthesis of new mono- and bi- MPS by chemical reduction of transition (Ni, Co) and precious metals (Ag) into polymer matrices based on copolymers p-EGM:AA, p-PGM:AA;

- determination of the structure of the composition and main characteristics of the synthesized mono - MPS(p-EGM(PGM):AA/Ni⁰, Co⁰, Ag⁰) and bi-MPS (p - EGM(PGM):AA/Ni⁰-Co⁰, p-EGM(PGM):AA/Ni⁰-Ag⁰) physical and chemical methods of research;

- study and comparison of the catalytic properties of mono-and bi-MPS in the process of electrocatalytic hydrogenation of pyridine;

- consideration of the effect of temperature and current on the electrocatalytic process carried out in the presence of MPS;

- study of catalytic properties of mono-and bi- MPS in the process of hydrogenation of model objects (anthracene).

- ecological and toxicological assessment of MPC impact on experimental animals and study of its antibacterial properties on bacteria *S. aureus* (ATCC 25923), *P. aeruginosa* (ATCC 27853), *E. coli* (ATCC 25922);

Objects of research: copolymers p-EGM:AA, p-PGM:AA and mono-, bi-metal-polymer systems based on them.

Subject of research. Physical and chemical properties of metal-polymer systems, features of formation processes, composite, structural characteristics and catalytic, medical and biological properties.

Method of research. The research was carried out using generally accepted scientific and experimental methods. We used modern devices, Institute of chemical problems of the University engineering laboratory "Physico-chemical methods of research", SIC of KSMU, Charles University: X-Act detector electron microscope MIRA 3TESCAN "Oxford Instruments" (UK, 2012), transmission-electron microscope (TEM) JEOL JEM-2100 200 kV (Japan), JEOL JSPM-5400 atomic force microscope, TGA/DTA/DSC analyzer LabSYSEvo (2014), laser-emission spectrometer Laes matrix (2012), 5975 C mass selective detector chromatograph Agilent 7890A, IR Fourier spectrometer (FSM 1202, 2011), device Malvern Zetasizer Nano ZS90, x-ray phase examination on PIXcel detector PanAlyticalx'pert PRO MPD device.

Scientific novelty.

- in nanoparticles of transition and precious metals (Ni, Co, Ag) on polymer matrices p-EGM:AA, p-PGM:AA were immobilized and a number of new mono- and bi- MPS were synthesized in the dissertation work.

- on the basis of physical and chemical research methods (microscopy, spectroscopy, thermogravimetry, chromatography), were determined the structure, composition and main characteristics of MPS.

- in the presence of synthesized MPS on the model objects. Determined the optimal conduct of the electrocatalytic hydrogenation process and the factors

affecting the process, including the influence of temperature and current considered; the activity and properties of nanocatalysts.

- studied catalytic properties of mono- and bi- MPS in the process of hydrogenation of model objects anthracene.

- investigated the effect of MPS on the body of experimental animals and, its antibacterial properties on some strains;

Theoretical and practical value. The theoretical significance of the work is to obtain new data on the relationship of polymers in the formation of nanocomposites with ions of transition and precious metals. The practical significance of the **research** is to obtain and study new and effective metal-polymer systems. The synthesized MPs exhibit catalytic activity in the processes of electrocatalytic hydrogenation and hydrogenation, as well as antibacterial properties on some strains and has the ability to be used in medicine, catalysis and organic synthesis.

The reliability and validity of the data obtained are confirmed by the results of repeated experiments, the use of the most modern and reliable equipment. The interpretation of the research results is based on modern principles of the structure and physico-chemical properties of nanomaterials.

Basic provisions for protection:

- structure, composition and main characteristics of the synthesized mono- (p-EGM (PGM):AK/Ni⁰, p-EGM(PGM):AK/Co⁰, p-EGM (PGM):AK/Ag⁰) and bi- (p-EGM (PGM):AK/Ag⁰-Ni⁰, p-(EGM)PGM:AK/Ni⁰-Co⁰) MPs;

- results of electrocatalytic hydrogenation of pyridine in the presence of synthesized mono- and bi- MPs;

- influence of temperature and current on the activity and properties of catalysts;

- catalytic activity of MPs in the process of anthracene hydrogenation;

- toxicity results and activity to bacteria (*S. aureus* (ATCC 25923), *P. aeruginosa* (ATCC 27853), *E. coli* (ATCC 25922))

Discussion on this work. The main results of the thesis were presented and discussed at the following conferences: 11th International Saint-Petersburg conference of Young Scientists "Modern problems of polymer Science" (St. Petersburg, Russia, 2015), "Chemistry, physics, biology, mathematics: theoretical and applied research" III-IV international scientific and practical conference (Moscow, Russia, 2017), "Current issues of modern chemical and biochemistry of materials": V international scientific and practical conference (Moscow, Russia, 2017). The International scientific and practical conference "Science, Education and production in the Fourth industrial revolution: international scientific and practical conference (Karaganda, Kazakhstan, 2018), "Current chemical problems" International (XI Ukrainian) scientific conference for students and young scientists (Donetsk, Ukraine, 2018).

The degree of development of the problem. The first information about polymer nanocomposites is found in patent of 1950 year (Carter L. W., Hendrics J. G., Bolley D. S. United States Patent. - 1950. No. 2,531,396). Bloomstein described the properties of polymer nanocomposites in 1961 years (Blumstain A. Bull Chem Soc. – 1961. –P. 899-905). Obtaining the clusters associated with polymers in the 1970 years carried out by the authors: J. P. Collman, L. S. Hegedus, M. P. Cooke (1972). After the publication of G. Gleitor (1981) information in works on metal-polymer systems such terms as "nanostructured", "nanophase", "nanocomposite", etc. became widely used. One of the scientists in this field, having more than 300 works is Pomogailo A.D. ("Metal nanoparticles in polymers", Moscow, -2000; "Catalysis by Polymer-Immobilized Metal Complexes" Gordon & Breach Sci. Publ.: Amsterdam, 1998, 424 p.; Polymer-immobilized metal-complex catalysts. Moscow, Nauka, 1988, -303 p.).

The first significant work in the synthesis of metal-polymer complexes in the country was presented by academician E. A. Bekturov and the active work of his followers (Bekturov E. A., Kudaibergenov S. E. Catalysis by Polymers. Zug, Heidelberg, Oxford, 1996. – P. 153.; Bekturov E. A., Kudaibergenov S. E. and other Polymer-protected metal nanoparticles. Almaty, 2010. – 274 p.;) still have been continuing. Doctor of science, professor Kudaibergenov S.E. and his followers have made many innovations in the synthesis and application in the catalysis of metal-polymer complexes, to date, a number of studies based on this industry are implemented in the "Institute of fuel, catalysis and electrochemistry. D.V. Sokolsky". The founder electrocatalytic hydrogenation of organic compounds is doctor of chemical Sciences, Professor I.V. Kirilus (Kirilus I. V. Electrocatalytic hydrogenation of organic compounds. Alma-ATA: Nauka Of The Kazakh SSR, 1990. 128 p.).

The author's personal contribution consists in planning and direct implementation of the experimental part of the work, analysis, generalization and interpretation of the data, collection of literary data on the goals and objectives, discussion of the results and their design in the form of scientific publications and reports.

Connection with the main scientific works. Part of the thesis work was carried out within the framework of research work №0112RK02369 of the state budget program of the Ministry of Education and Science of the Republic of Kazakhstan for 2015-2017 years ("Development of technology for the production of nanoparticles of transition metals with controlled particle size»).

Publications. According to the results of the work published 22 publications, including 7 publications in publications approved by the Committee of Control of Education and Science MES, 2 publications in international scientific journals included in the database Thomson Reuters and Scopus, 11 publications in international and national conferences, 2 innovative patents of the Republic of Kazakhstan.

Structure and scope of work. The thesis is presented on 141 pages of computer layout and includes an introduction, 3 sections, conclusion, 58 figures, 20 tables and a list of sources from 334 titles and applications.