ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD) in specialty 8D07108 – "Basic processes for the synthesis and production of new organic and polymeric materials"

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SYNTHESIS AND CHARACTERIZATION OF POLYAMPHOLYTE NANO- AND MICROGELS BASED ON ACRYLAMIDE DERIVATIVES

Relevance of the work. Polyampholytes are unique macromolecules containing acid/base or anionic/cationic groups in their main or side chains. They can be used to model the behavior of proteins, polypeptides or polynucleotides. Polyampholyte nano- and microgels are three-dimensional macromolecular polymer networks that swell when exposed to a dispersing solvent.

Stimulus-responsive polyampholyte nano- and microgels, which respond adequately to external factors such as temperature, pH, salt composition, solvent, electric or magnetic fields and light radiation, represent tremendous potential for designing "smart" materials in medicine, biotechnology, nanotechnology, catalysis, the oil industry and environmental protection, among others.

Analysis of literature data reveals that polyampholyte nano- and microgels are predominantly pH-sensitive. In contrast, highly charged polyampholyte nano- and microgels, which contain both hydrophilic and hydrophobic groups (thermo- and salt-responsive fragments), remain relatively understudied. This is especially true in the context of their applications in controlled drug release and as thickening agents in the production of oil.

The aim of the research work is to prepare and study thermo- and salt-responsive polyampholyte nanogels using a combination of hydrophobic monomer - N-isopropylacrylamide (NIPAM), anionic monomer - sodium salt of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), cationic monomer - (3-acrylamidopropyl) trimethylammonium chloride (APTAC) and polyampholyte microgels from hydrophilic monomer - acrylamide (AAm), anionic monomer - sodium salt of 2-acrylamido-2-methylpropanesulfonate (AMPS), cationic monomer - 3-acrylamidopropyltrimethylammonium chloride (APTAC) for potential applications in the controlled delivery of drugs and thickening agents for increasing oil production.

The tasks of the research work:

- synthesis, characterization and properties of polyampholyte nanogels based on NIPAM-APTAC-AMPS obtained via free-radical polymerization;
- analysis of nanogels using NMR and FTIR spectroscopy, SEM, dynamic laser light scattering, zeta potential, TGA and DTA;
- study of thermal and salt sensitivity of nanogels, selection of suitable nanogels for immobilization of model drugs – anionic (methyl orange) and cationic (methylene

blue) dyes; study of release kinetics of model drugs from the nanogel matrix in dependence of temperature and salt composition;
- synthesis, characterization and properties of polyampholyte microgels based on AAm-APTAC-AMPS obtained via inverse emulsion polymerization;
- analysis of microgels by FTIR spectroscopy, TEM, dynamic laser light scattering, TGA and DTA;
- use of thermo- and salt-responsive polyampholyte microgels in core flooding experiments as a physical reservoir model to assess the oil-displacing (oil-producing) capacity in reservoir conditions, with a solution salinity of up to 200 g/L.

The objects of study are samples of polyampholyte nanogels based on NIPAM-APTAC-AMPS and polyampholyte microgels based on AAm-APTAC-AMPS of various compositions.

The subject of the study is synthesis and characterization of polyampholyte nano- and microgels derived from a combination of anionic, cationic, hydrophilic and hydrophobic acrylamide-based monomers to understand and assess their thermal and salt-responsive properties.

Research methods. NMR, FTIR and UV-visible spectroscopy, scanning electron and transmission electron microscopies, dynamic light scattering, zeta potentials, differential scanning calorimetry, thermogravimetric and differential thermal analysis were used for research.

The scientific novelty is preparation and characterization of polyampholyte nanogels based on NIPAM-APTAC-AMPS and polyampholyte microgels based on AAm-APTAC-AMPS, which exhibit thermal and salt responsive properties. The study of the structure, macromolecular organization, swelling and collapse of amphoteric nano- and microgels as a function of copolymer composition, temperature, ionic strength of the solution and mixture of aqueous-organic solvents. This research enables the development of a novel class of cross-linked structures with stimulus-responsive behavior.

The scientific, practical and theoretical significance of the study lies in the expansion of our fundamental knowledge about cross-linked polyampholyte nano- and microgels, consisting of non-ionic and highly charged anionic/cationic and hydrophilic/hydrophobic monomers. The fundamental results obtained can be used in medicine, in particular, for the temperature-controlled release of drugs, and in oil production to increase oil recovery. The results of research can be recommended to domestic and foreign companies engaged in medicine, pharmacy and oil production. On a National scale, the results of research work is of interest in terms of maintaining Kazakhstan‘s leading position in the world in the field of synthesis and research of synthetic polyampholytes, raising the prestige of Kazakhstan science at the world level, developing public-private partnerships and attracting young scientists and specialists to science. On an international scale, the results of research are of interest to scientists and specialists involved in the theory of polyampholytes, the study of polyampholyte solutions and the development of thermo- and salt-responsive amphoteric nano- and microgels.

The main provisions for defense:

- results on the development of optimal synthesis conditions for obtaining linear polyelectrolytes and polyampholytes, samples of polyampholyte nano- and microgels with the required physical-chemical, physical-mechanical, rheological, thermal and salt-responsive properties;
- results on the identification and study of polyelectrolyte and polyampholyte nano- and microgels by NMR and FTIR spectroscopy, SEM, TEM, dynamic laser light scattering, zeta potential, TGA and DTA;
- results on the immobilization of model drugs – anionic and cationic dyes (methyl orange and methylene blue) into the matrix of amphoteric nanogels and the determination of the kinetics of the release of model drugs from the matrix of nanogels depending on temperature and salt composition;
- results on the study of the thermal and salt-responsive properties of polyampholyte nano- and microgels, which can be recommended as thickening agents for leveling the injectivity profile of oil reservoirs and increasing oil production;
- results on the use of microgels in core flooding experiments to assess the oil-displacing (oil-producing) capacity in reservoir conditions.

Relation of the dissertation with research and government programs. The work was conducted in the frame of projects "Synthesis and Study of Thermo- and Salt-Sensitive Polyampholyte Nano- and Microgels" for the period 2020-2022 (AP08855552) and "Development of New Thermal and Salt-Resistant Amphoteric Terpolymers for Enhanced Oil Recovery" for the period 2021-2023 (AP09260574) funded by the Ministry of Science and High Education of the Republic of Kazakhstan. It was partly funded by the Horizon 2020 research and innovation program of the European Union Maria Sklodowska-Curie (grant agreement 823883-MSCA-RISE-2018 NanoPol).

Approbation of work. The dissertation materials were reported and discussed at international scientific-practical conference "Modern aspects of chemical science and chemical education: Theory and Practice" (December 13-14, 2021, Almaty, Kazakhstan), XVI St. Petersburg conference of young scientists with international participation "Modern problems of polymer science" (October 24-27, 2022, St. Petersburg, Russia), XI International Conference on "Times of Polymers (TOP) & Composites" (June 11-15, 2023, Ischia, Naples, Italy).

Publications. The main results of the study are presented in 3 articles published in journals from the list approved by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry of Education and Science of the Republic of Kazakhstan, 2 articles indexed in the Scopus and Web of Science, 2 innovative patents of the Republic of Kazakhstan, 3 abstracts of reports were published in proceedings of international conferences.

Articles published in journals from the list approved by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry of Education and Science of the Republic of Kazakhstan:

1. Ayazbayeva A.Ye., Shakhvorostov A.V., Seilkhanov T.M., Aseyev V.O., Kudaibergenov S.E. Synthesis and characterization of novel thermo- and salt-

sensitive amphoteric terpolymers based on acrylamide derivatives // Bulletin of the University of Karaganda – Chemistry. - 2021. - Vol.104, №4. - P.12-20. doi. 10.31489/2021Ch4/9-20;

2. Ayazbayeva A.Ye., Shakhvorostov A.V., Kudaibergenov S.E. Temperature and Salt Responsivity of Anionic, Cationic and Amphoteric Nanogels Based on N-Isopropylacrylamide, 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid Sodium Salt and (3-Acrylamidopropyl) Trimethylammonium Chloride // Bulletin of the University of Karaganda – Chemistry. — 2022. - Vol.108, №4. - P. 14-24. doi.10.31489/2022Ch4/4-22-15;

3. Ayazbayeva A.Ye., Nauryzova S.Z., Aseyev V.O., Shakhvorostov A.V. Immobilization of Methyl Orange and Methylene Blue within the Matrix of Charge-Imbalanced Amphoteric Nanogels and Study of Dye Release Kinetics as a Function of Temperature and Ionic Strength // Bulletin of the University of Karaganda-Chemistry. - 2022. - Vol.107, №3. - P. 127-140. doi.10.31489/2022Ch3/3-22-4.

Articles indexed in the Scopus and Web of Science:

1. Ayazbayeva A.Y., Shakhvorostov A.V., Gussenov I.S., Seilkhanov T.M., Aseyev V.O., Kudaibergenov S.E. Temperature and Salt Responsive Amphoteric Nanogels Based on N-Isopropylacrylamide, 2-Acrylamido-2-methyl-1-propanesulfonic Acid Sodium Salt and (3-Acrylamidopropyl)Trimethylammonium Chloride // Nanomaterials — 2022. — Vol.12. — 2343. doi.10.3390/nano12142343;

2. Ayazbayeva A., Baddam V., Shakhvorostov A., Gussenov I., Aseyev V., Yermagambetov M., Kudaibergenov S. Amphoteric nano- and microgels with acrylamide backbone for potential application in oil recovery // Polymers for advanced technologies. - 2023. doi.10.1002/pat.6182.

Patents of the Republic of Kazakhstan:

1. Pat.№7008 Kazakhstan. C08F 8/00 B82B 1/00. Polyampholytic nanogel for thermo- and salt-sensitive materials (options) and method for production thereof / S. Kudaibergenov, A.V. Shakhvorostov, A.Ye.Ayazbayeva, G.M. Kudaibergenova; applicant and patentee Institute of Polymer Materials and Technology. 09.11.2021;

2. Pat.№8346 Kazakhstan. Polyampholite microgel for production of a thickening agent / S. Kudaibergenov, A.V. Shakhvorostov, A.Ye.Ayazbayeva; applicant and patentee Institute of Polymer Materials and Technology. 28.07.2023.

The personal contribution of the Ph.D. candidate to the preparation of each article.

The main materials of the dissertation work were published in scientific publications in the form of 5 scientific articles. When preparing each publication, Ayazbayeva A.Ye. carried out the following work: conceptualization, collection and verification of the necessary literature, methodology, conducting all experiments and studies, independent data collection, processing, analysis and interpretation of results, writing and preparing the initial version of the article, preparing responses to reviewers' comments, further refinement and editing until complete acceptance of the article for publication. In all 5 published articles, the doctoral student was the first author and corresponding author, responsible for communication with the editor regarding all publication issues.

The volume and structure of the dissertation. The dissertation work is presented on 109 pages of a computer text and consists of an introduction, 3sections, a conclusion, and a list of used literature from 146 titles, contains 70 drawings, 27 tables.