

**Review**  
**by the official reviewer on the doctoral dissertation of Aygerim E. Ayazbaeva**  
**on the topic “Synthesis and characterization of polyampholyte nano- and microgels based on acrylamide derivatives”,**  
**submitted for the degree of Doctor of Philosophy (PhD)**  
**in the speciality 8D07108 – “Basic processes of synthesis and production of new organic and polymeric materials”**

№ p/sp	Criteria	Compliance with criteria (one of the answer options must be selected)	Justification of the official reviewer’s position
1.	The dissertation topic (as of its approval date) corresponds to the directions of scientific development and/or state programs	Compliance with priority areas of scientific development or state programs: 1) The dissertation was carried out within the framework of a project or target program financed from the state budget (specify the name and number of the project or program). 2) The dissertation was carried out within the framework of another state program (specify the name of the program). 3) The dissertation corresponds to the priority direction of scientific development approved by the Higher Scientific and Technical Commission under the Government of the Republic of Kazakhstan (specify the direction).	This work was conducted in relation with scientific and research programmes is confirmed by its implementation in accordance with the research plans of the Institute of Polymer Materials and Technologies and Satbayev University as well as in the frame of projects “Synthesis and study of thermo- and salt-sensitive polyampholyte nano- and microgels” (AP0885552, 2020-2022) and “Development of new thermal and salt-resistant amphoteric terpolymers for enhanced oil recovery” (AP09260574, 2021-2023) funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan. This work was also partly funded by the Horizon-2020 Research and Innovation Programme of the European Union Maria Sklodowska-Curie (Grant Agreement 823883-MSCA-RISE-2018 NanoPol).
2.	Importance to science	The work contributes/does not make a substantial contribution to science, and its importance is well disclosed/not disclosed	In the past decades, a large amount of research from experimental and theoretical points of view has been devoted on developing interpolyelectrolyte complexes formed by electrostatic attractive forces and/or interpolymer complexes stabilized by hydrogen bonds. By contrast, relatively less attention has been given to polymer-polymer complex formation with synthetic polyampholytes (PA). Developing novel materials, in particular, with improved functional characteristics and properties, is one of the driving forces to progress fundamental knowledge and applied science as well as industrial applications. Therefore, in this context, the

			<p>dissertation work of PhD candidate Aygerim Ye. Ayazbaeva, is aimed at macromolecular design and fundamental study of novel synthetic quenched polyampholytes of linear and crosslinked structures (nano- and microgels), is very relevant and modern, is devoted to stimuli-responsive, i.e. thermo- and salt-sensitivity behaviour of the materials.</p>
3.	Principle of independence	<p>Level of independence:  1) High;  2) Moderate;  3) Low;  4) No autonomy</p>	<p>Based on the publications and work done by Aygerim Ye. Ayazbaeva demonstrates a remarkable level of autonomy in her PhD research. Aygerim managed the entire research process, from conceptualization to publication, demonstrating self-reliance in literature review, experimental design, data collection, analysis, and manuscript preparation. Additionally, as the first and corresponding author in all publications, Aygerim took full responsibility for communication with editors. Overall, A.Ye. Ayazbaeva demonstrates a commendable level of independence in her research endeavours.</p>
4.	The principle of internal unity	<p>4.1 Justification of the relevance of the dissertation:  1) <u>Justified</u>;  2) Partially justified;  3) Not justified.</p>	<p>The relevance of the dissertation is well justified based on the provided statement in the dissertation work. It highlights the unique properties of polyampholytes and their potential applications in various fields such as medicine, biotechnology, nanotechnology, catalysis, the oil industry, and environmental protection. The statement underscores the significance of stimuli-responsive polyampholyte nano- and microgels in designing “smart” or “intelligent” materials that can adapt to external stimuli, offering promising avenues for technological advancements. Additionally, it identifies a gap in the literature regarding the study of highly charged polyampholyte nano- and microgels with thermo- and salt-responsive properties, especially in the context of controlled drug release and oil recovery.</p>

		<p>4.2 The content of the dissertation reflects the dissertation topic:</p> <ol style="list-style-type: none"> <li>1) <u>Reflects</u>;</li> <li>2) <u>Partially reflects</u>;</li> <li>3) <u>Does not reflect</u>.</li> </ol> <p>4.3 The objectives and tasks correspond to the dissertation topic:</p> <ol style="list-style-type: none"> <li>1) <u>correspond</u>;</li> <li>2) <u>partially correspond</u>;</li> <li>3) <u>do not correspond</u>.</li> </ol> <p>4.4 All sections and provisions of the dissertation are interrelated.</p> <ol style="list-style-type: none"> <li>1) <u>completely interrelated</u>;</li> <li>2) <u>partial interrelation</u>;</li> <li>3) <u>no interrelation</u>.</li> </ol> <p>4.5 The author's proposed new solutions (principles, methods) are justified and evaluated compared to known solutions:</p> <ol style="list-style-type: none"> <li>1) <u>critical analysis provided</u>;</li> <li>2) <u>partial analysis</u>;</li> <li>3) <u>the analysis consists of opinions of other authors rather than the author's own views</u></li> </ol>	<p>The content of the dissertation fully reflects the dissertation topic.</p> <p>The aim and objectives/tasks fully correspond to the dissertation topic.</p> <p>All sections and provisions of the dissertation are completely interconnected.</p> <p>Determining the isoelectric point for novel polyampholyte systems based on fully charged (quenched) linear and/or nanoparticles is a key criterion among the main physicochemical parameters. The methods used may include classical viscometry and/or electrophoretic mobility.</p>
5.	Principle of scientific novelty	<p>5.1 Scientific results and positions are new?</p> <ol style="list-style-type: none"> <li>1) <u>completely new</u>;</li> <li>2) <u>partially new (25-75% are new)</u>;</li> <li>3) <u>not new (less than 25% are new)</u>.</li> </ol>	<p>The scientific results and findings are partially novel. According to the literature similar work in the context of the quenched linear NIPAM-APTAC-AMPS terpolymer with different copolymer compositions has already been synthesised and characterised (Braun O., Selb J., Candau F. Synthesis in microemulsion and characterization of stimuli-responsive polyelectrolytes and polyampholytes based on <i>N</i>-isopropylacrylamide // Polymer. – 2001. – Vol.42. – P.8499-8510. <a href="https://doi.org/10.1016/S0032-3861(01)00445-1">https://doi.org/10.1016/S0032-3861(01)00445-1</a>. However, other studies, such as the synthesis of nano and microgels, their characterisation, drug loading, release, oil recovery studies, etc. have not been conducted yet, which have been reported in this</p>

		<p>5.2 Conclusions of the dissertation new?  1) completely new;  2) <u>partially new</u> (25-75% are new);  3) not new (less than 25% are new).</p> <p>5.3 Technical, technological, economic, or managerial decisions are new and justified:  1) completely new;  2) <u>partially new</u> (25-75% are new);  3) not new (less than 25% are new).</p>	<p>dissertation work.  Based on the provided information, the conclusions of the dissertation seem to be new as they present findings derived from the research conducted on polyampholyte nanogels and microgels. These findings include the synthesis and characterization of polyampholyte nanogels and microgels, their behavior under various conditions such as temperature and ionic strength, their interactions with model dyes, and their potential application in oil recovery. Therefore, it can be inferred that the conclusions of the dissertation are new.</p> <p>The polyampholyte nano- and microgels obtained <i>via</i> free-radical and emulsion polymerization serve as stimuli-responsive systems with controlled physico-chemical and physico-mechanical properties. The incorporation of hydrophobic monomer (<i>N</i>-isopropylacrylamide) into highly charged polyampholyte nanogels promotes the self-organization of macromolecular chains through the formation of micellar-like structures, facilitating the immobilization of poorly water-soluble (lipophilic) drugs with controlled release upon changes in the external environment parameters. On the contrary, the inclusion of hydrophilic monomer (acrylamide) into highly charged polyampholyte microgels may enhance the thermal stability of the microgels and their resistance to salts in conditions of an oil reservoir with high temperature and salinity.</p>
6.	Justification of the main conclusions	All main conclusions are based/not based on substantial scientific evidence or are sufficiently well justified (for qualitative research and fields of study in arts and humanities).	Based on the provided information, the conclusions of the dissertation seem to be new as they present findings derived from the research conducted on polyampholyte nanogels and microgels. These findings include the synthesis and characterization of polyampholyte nanogels and microgels, their behaviour under various conditions such as temperature and ionic strength, their

7	The main provisions for defence	<p>It is necessary to answer the following questions for each provision separately:</p> <p>7.1 Is the provision proven?  1) <u>proven</u>;  2) <u>mostly proven</u>;  3) <u>not proven</u>.</p> <p>7.2 Is it trivial?  1) <u>yes</u>;  2) <u>no</u>.</p> <p>7.3 Is it new?  1) <u>yes</u>;  2) <u>no</u>.</p> <p>7.4 Applicability level:  1) <u>narrow</u>;  2) <u>moderate</u>;  3) <u>broad</u>.</p> <p>7.5 Is it proven in the article?  1) <u>yes</u>;  2) <u>no</u>.</p>	<p>interactions with model dyes, and their potential application in oil recovery. Therefore, it can be inferred that the conclusions of the dissertation are new.</p> <p>The main provisions put forward for defence are formulated unclearly and require factual data.</p>
8.	The principle of reliability. Reliability of sources and provided information.	<p>8.1 The choice of methodology – justified or methodology sufficiently described:  1) <u>yes</u>;  2) <u>no</u>.</p>	<p>However, I would suggest adding more details in the experimental section. For instance, regarding the FTIR-spectroscopy technique used to characterise the structure of copolymers, it would be better to specify the recording parameters in more detail, examples include spectral resolution and data process based on average scan number. In TEM experimental condition: how specimens were prepared, do particles need a staining agent to give good quality of images (as these nano- and microgels are soft materials) or was it a cryo-TEM used. This applies to SEM specimen preparations.</p>

		<p>8.2 The results of the dissertation work were obtained using modern methods of scientific research and techniques for data processing and interpretation, utilizing computer technologies: 1) <u>yes</u>; 2) no.</p> <p>8.3 Theoretical conclusions, models, identified relations/links, and regularities are proven and confirmed by experimental research (for educational science directions, the results are proven based on pedagogical experiments): 1) <u>yes</u>; 2) no.</p> <p>8.4 Important statements are confirmed/partially confirmed/not confirmed by references to current and reliable scientific literature</p> <p>8.5 The literature sources used are sufficient/insufficient for the literature review</p>	<p>A high level of reliability and validity of the research results is ensured by the use of state-of-the-art physicochemical techniques and methodologies, good correlation of data acquired in a series of repeated experiments. All objects of study as well as synthesised co/terpolymers are thoroughly characterised, and the research outputs are interpreted comprehensively.</p> <p>Important statements are confirmed by providing references to current and reliable scientific literature, including the citations to the applicant's publications.</p> <p>The literature sources used are sufficient for the literature review.</p>
9.	The principle of practical value	<p>9.1 The dissertation has theoretical significance: 1) <u>yes</u>; 2) no.</p> <p>9.2 The dissertation has practical significance, and there is a high probability of applying the obtained results in practice: 1) <u>yes</u>; 2) no</p> <p>9.3 Are the proposed solutions new for practical</p>	<p>The results achieved in this research are aimed at solving the actual scientific issues/tasks on the development and studying, based on commercially available raw materials, novel quenched polyampholytes with enhanced physicochemical properties.</p> <p>For practical applications, the following could be proposed: the use of fully-charged (quenched) polyampholytes as thickeners in technologies for increasing oil recovery; wastewater treatment from metal ions, organic dyes and surfactants as well as desalination; separation and purification of proteins, developing pharmaceutical excipients for controlled drug delivery, etc.</p> <p>The proposed solutions could potentially be applied as</p>

		<p>application?</p> <p>1) completely new;  2) <u>partially new</u> (25-75% are new);  3) not new (less than 25% are new).</p>	<p>controlled drug delivery systems if all the required experiments met according to regulations in medicine/biomedicine, pharmaceuticals, assessment of toxicological properties; microgel systems could also be proposed as oil recovery agents, however this could be done through thorough comparative experiments to known systems/materials available on the market.</p>
10	<p>The quality of writing and presentation</p>	<p>Academic writing quality:</p> <p>1) <u>high</u>;  2) average;  3) below average;  4) low</p>	<p>However, the dissertation work contains stylistic and orthographic mistakes that can be corrected in a time manner. Also, the work contains some comments/notes regarding editing and revising English improvement of the text in which the applicant was advised to do so.</p>

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