

## REVIEW

**to the Ph.D. thesis of Toletay Gaukhar «Physico-chemical, complexation and catalytical properties of linear and cross-linked polyampholytes» submitted for a requirement of a Ph.D. degree in Chemical Technology of Organic Substances (the specialty of 6D072100).**

### **1. The relevance of the research topic and its relationship with general scientific and national programs**

Synthetic and natural polyampholytes as proteins and nucleic acids are a class of polymers possessing unique properties due to the both positively and negatively charged monomer subunits, interaction among themselves and with the surrounding low molecular weight counter-ions. This determines a great interest in the study of polyelectrolytes of all kinds since the regularities of synthetic polymers are also characteristic of biopolymers. Polyampholytes are widely used in various fields of science and technology. From this point of view, this type of polymers continues to be one of the relevant areas of fundamental and applied research.

Toletay's thesis is devoted to developing new linear, cross-linked and gel-type polyampholytes based on AMPS anionic monomer and APTAC cationic monomer, and their characteristics, behavior and catalytic properties. The purpose, tasks, and results of the dissertation confirm the relevance of the presented research.

The work was performed in the framework of grant project № AP05131003 of the Ministry of Education and Science of the Republic Kazakhstan: "Fundamental Problems of Strongly Charged Polyampholytes at the Isoelectric Point" (2017-2020).

### **2. Scientific results in the framework of the requirements for Ph.D. thesis**

The author of the thesis presented the following basic scientific results.

1. Highly charged linear and crosslinked polyampholytes and polyampholyte hydrogels based on the AMPS anionic monomer and APTAC cationic monomer have been synthesized and compositions of the prepared polymers identified by the set of modern physicochemical methods.

The obtained results show that the structure of the prepared linear copolymers coincided with the original monomer mixture formulation. The findings agree with theoretical assumptions and previous literature.

2. The behaviors of the developed polyampholytes have been studied in aqueous and aqueous-salt solutions. Quenched polyampholytes (QPAs) have been found to occur in core-shell state and demonstrate antagonism in aqueous-salt solution. Adding low-molecular-weight salts tends to shrink shell, polyelectrolyte, field, and swell core, polyampholyte, area.

3. The complexation of charge unbalanced linear and crosslinked polyampholytes was analyzed in aqueous solution with anionic sodium dodecylbenzene sulfonate (SDBS) and cationic cetyltrimethyl ammonium chloride (CTMAC) surfactants and organic dyes, namely methylene blue (MB) and methyl orange (MO). Polyampholytes with the highest concentration of the negative charged monomer AMPS interacts with the positively charged MB and CTMAC form an associate stabilized by ionic bonds, and opposite for polyampholytes with the highest concentration of the positive charged monomer APTAC.

4. Chemically and physically crosslinked polyampholytes, containing hydrophilic and hydrophobic monomers polyampholyte hydrogels were prepared from anionic AMPS and cationic APTAC monomers. They were characterized by swelling measurements, rheological and mechanical experiments.

Charge-balanced physically crosslinked polyampholyte hydrogels containing 60-90% water sustain a high tensile strength (up to 202 kPa) and exhibit a high stretchability (up to 1239%). Cut-and-heal tests reveal that as-prepared hydrogels exhibit a healing efficiency of  $90 \pm 10\%$  concerning their Young's modulus. The obtained results can be used in further testing as antibacterial, anti-fouling, and saline-resistant materials.

5. Gold nanoparticles have been immobilized within the cryogel matrix of poly(DMAEM-co-MAA) and poly (APTAC-co-AMPS) and studied by several methods including methods: SEM, DLS, H NMR, and Raman spectroscopy. The particles of less than 100 nm were detected after reduction with  $\text{NaBH}_4$ .

Catalytic properties of the gold complexes with amphoteric cryogel samples have been studied in the hydrogenation of nitroaromatic compounds. A new approach has been developed to carry out catalytic reactions as catalytic reactors. The developed catalyst showed rather high stability in the hydrogenation reaction.

### **3. The level of validity and reliability of each scientific results, provisions and the conclusions formulated by the applicant in the Ph.D. thesis**

The thesis tasks and methods of goal achievement are valid due to the use of many techniques for identification of composition, characterization of the developed polymers, their behavior in different surroundings and in catalytic hydrogenation. The study was carried out using certified equipment. Part of the investigation was conducted at Istanbul Technical University. The results of different methods consistent with each other, proving the reliability of the obtained research data.

Data validity is also confirmed by 18 publications, 3 articles among them are in journals included in the Scopus database with nonzero impact factor (0.6-1.6).

### **4. The level of novelty of each scientific results formulated in a PhD thesis**

The novelty of the research results is the following.

1. The charge-balanced and charge-imbalanced quenched polyampholytes of linear and crosslinked structure based on anionic monomer (AMPS) and cationic (APTAC) monomers have been synthesized and analyzed by a set of relevant

methods ( $H^1$  NMR, FTIR, GPC, DLS, DSC, viscometry, swelling-deswelling experiments, and mechanical tests). The developed polymers are characterized as a “core-shell” structure. The addition of low-molecular-weight salts tends to shrink the “shell”, (polyelectrolyte region) and to swell the “core”, (polyampholyte region) due to the relatively high ionic strengths.

2. Micellar polymerization of cationic and anionic monomers in the presence of hydrophobic monomer ODA has been used to synthesize hydrophobically modified quenched polyampholyte hydrogels. Swelled hydrogels (60-90% water) demonstrated good mechanical properties characterized by a high tensile strength (up to 202 kPa) and a stretchability (up to 1239%). Cut-and-heal tests revealed that non-swollen hydrogels exhibit a healing efficiency of  $90\pm 10\%$  of their original Young's modulus (tested at Istanbul Technical University, Certificate is attached).

3. Macroporous amphoteric cryogels of annealed and quenched types have been prepared and gold nanoparticles immobilized inside of the porous matrix. The prepared complexes were used as an effective flow-through catalytic reactor for hydrogenation of nitroaromatic compounds into corresponding aminoaromatic derivatives. The high conversion and low activation energy have been detected (RK Patent for Invention #33596, 2017).

### **5. Assessment of the internal unity of results**

The internal unity of the results is based on the interconnection of the thesis aim, tasks, applied methods, presentation of the basic material of the research and interpretation of the findings. All sections of the thesis are logically interrelated and conclusions completely sum up the main results of the study.

### **6. The focus of the results obtained by the applicant on the solution of the relevant actual problem**

The work is mainly aimed at solving fundamental problems. At the same time, taking into account a very detailed review of the recent year literature presented in the dissertation, as well as the research results obtained by the author, it seems very promising to test the developed polyampholytes as viscosifying agents in the oil industry, agents for wastewater purification, and structural biomaterials in medicine.

I would like to note the part of the work devoted to testing cryogels as catalysts. The author designed an original reactor in which a cryogel with immobilized gold nanoparticles plays the role of both a reactor and a catalyst. It seems necessary to pay special attention to this direction in the future.

### **7. Confirmation of sufficient completeness of publication of the main provisions, results, conclusions**

There are 18 publications on the topic of the dissertation: 3 publications in journals included in the Scopus database (IF 0.6-1.6), 2 publications approved by

the Committee for Control in the Field of Education and Science of the Republic of Kazakhstan, 12 abstracts at International and National Symposia and Conferences, and 1 innovation patent of the Republic of Kazakhstan. The main provisions and results of the dissertation were reported and discussed at international scientific and practical conferences, both in Kazakhstan and abroad

#### **8. Correspondence of the abstract to the content of the Ph.D. thesis**

The abstract is completely corresponds to the content of the thesis, its results, provisions, and conclusions

#### **9. Deficiencies in the contest and design of the Ph.D. thesis:**

1. The choice of initial monomers for further synthesis of polyampholytes, in my opinion, is not clearly substantiated

2. Quenched polyampholytes can be obtained by free-radical polymerization (FRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization. What is the difference between FRP and RAFT? The microstructure of copolymers depends on the used polymerization methods. What is the microstructure of copolymers in your case (random, regular, block, etc.)?

3. The microstructure of quenched polyampholytes also depends on the activity of monomers. What are the activity of anionic (AMPS) and cationic (APTAC) monomers? How the activity influence on microstructure and composition of amphoteric copolymers?

4. The developed flow-through catalytic reactor for hydrogenation based on the swelled cryogel. It means that the substrate diffuses through the cryogel. What was the rate of passage of the substrate through the polymer matrix? Did the composition of the reaction products depend on this parameter? Does the degree of polymer swelling affect the rate of passage of the substrate through the polymer reactor?

5. Why didn't you use chromatographic analysis to identify the reaction products? It is a usually used method for testing products of catalytic reactions.

However, the above-referred comments and suggestions do not affect the overall positive impression of the thesis.

#### **10. Compliance with the Ph.D. thesis for passport**

The Ph.D. thesis of Toletay Gaukhar «Physico-chemical, complexation and catalytical properties of linear and cross-linked polyampholytes» complies with the passport of the specialty of 6D072100 "Chemical technology of organic substances".

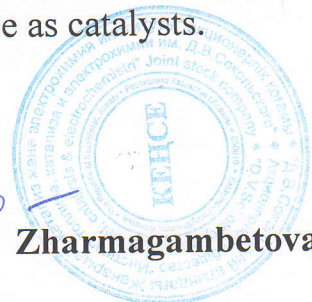
#### **12. The conformity of the dissertation to the requirements "Regulation of the attribution scientific degree"**

Dissertation of Toletay Gaukhar on scientific novelty, the results, their discussion and conclusions complies with the requirements of the Regulation for the thesis submitted for the degree in the 6D072100 "Chemical technology of

organic substances” and its author is deserved the required degree of Doctor of Philosophy in Chemical technology of organic substances (specialty of 6D072100) on the development of new polyampholytes and their use as catalysts.

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