

REVIEW

of the doctoral dissertation of Gaukhar Toleutay on the topic «Physico-chemical, complexation and catalytical properties of linear and cross-linked polyampholytes» submitted for the degree of Doctor of Philosophy (PhD) in speciality of 6D072100 – “Chemical Technology of Organic Substances”

1. The relevance of the research topic and its relationship with general scientific and national programmes.

At present, a large amount of research from experimental and theoretical points of view has been done on 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). The development of novel materials, in particular, combining environmentally friendliness and renewability along with improved functional characteristics, is one of the driving forces for the development of fundamental knowledge and applied science as well as industry. Therefore, in this context, the dissertation work of PhD candidate Gaukhar Toleutay, is aimed at macromolecular design and fundamental study of novel synthetic polyampholytes of linear and cross-linked structures, is very relevant and modern, is devoted to amphoteric behaviour of interpolyelectrolyte complexes. The realisation of the so-called “isoelectric effect” for interpolyelectrolyte complexes of water-soluble polyampholytes, amphoteric hydrogels and cryogels with respect to low-molecular-weight salts, surfactants, dye molecules is demonstrated. The relationship of the topic 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 in the framework of grant project No.AP05131003 “Fundamental problems of strongly charged polyampholytes at the isoelectric point” MES RK.

2. Scientific results in the framework of the requirements for PhD dissertations.

In this work, the following main scientific results were acquired:

1. For the first time, fully charged (or “quenched”) linear and cross-linked polyampholytes were synthesised based on the anionic monomer – 2-Acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) and the cationic monomer – (3-acrylamidopropyl)trimethylammonium chloride (APTAC) using free radical copolymerisation technique. These linear copolymers were characterised using cutting-edge instruments: FTIR and ^1H NMR spectroscopies were used to analyse the structure and composition of linear and cross-linked copolymers. It was revealed that the copolymer composition of linear polymers coincides with the feed composition, i.e. exhibited equal reactivity ratio in the course of polymerisation, for instance, AMPS:APTAC at molar ratio of 75:25 is equal to [AMPA]:[APTAC] – 74.4:25.6.

Using gel permeation chromatography (GPC), it was found that the quenched copolymers are characterised with sufficiently high molecular weights. The molecular weight distribution of AMPS-75 is a relatively narrow ($M_w/M_n = 1.01$) compared to AMPS-50 ($M_w/M_n = 1.65$). The thermal stability of linear polyampholytes is evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

2. Charge-balanced and charge-imbalanced quenched polyampholytes were exhibited core-shell structure and demonstrated antagonistic behaviour in aqueous – low-molecular-weight solution. Addition of low-molecular-weight salts tends to shrink the

shell (polyelectrolyte region) and swell the core (polyampholyte region). Such antagonism between polyelectrolyte and polyampholyte effects can take place at relatively high ionic strengths. Particularly, experiments conducted with dynamic light scattering (DLS) technique revealed that the positions of the isoelectric points (IEP) of fully charged polyampholytes were determined at a $\text{pH} \sim 6.3 \pm 0.2$. In the presence of potassium chloride (KCl) solution, the position of the IEP shifted to $\text{pH} 6.5\text{--}7.0$ due to the specific binding of chloride ions with quaternary ammonium groups of APTAC. These properties as well as polymers' behaviour at isoelectric point, change in hydrodynamic dimensions and zeta-potential were studied using viscometric and dynamic light scattering (DLS) techniques.

3. The mechanism of complex formation of fully charged polyampholytes with ionic dyes, surfactants and aqueous-organic solvents was studied. Particularly, the complexation of charge-imbalanced linear and cross-linked polyampholytes was studied in aqueous solution with respect to ionic dyes and surfactants.

Complexation of quenched polyampholytes was found to occur with an anionic surfactant – sodium dodecylbenzenesulfonate (SDBS) and a cationic surfactant – cetyltrimethyl ammonium chloride (CTMAC), and was accompanied by changes in turbidity, zeta-potential and average hydrodynamic diameter of colloidal particles, while complexation of AMPS-APTAC hydrogels with SDBS and CTMAC was accompanied by gradual shrinking of samples due to binding of anionic and cationic surfactants with excessive anionic and cationic groups in hydrogels.

Similarly, in this context, the uptake and releasing ability of quenched polyampholytes were evaluated using dyes as model compounds. Hydrogels containing an excess of negative (AMPS-75H) and positive (AMPS-25H) charges effectively absorbed up to 80% of methylene blue (MB) and methyl orange (MO) respectively, due to electrostatic binding. Approximately 75% of dye molecules were released from the hydrogel matrix into the medium of 0.5M KCl over a period of 24 hours. The driving force of dye release is the replacement of electrostatically bound dye molecules by low-molecular-weight salt. The amount of released dye molecules was determined using UV/Vis-spectrophotometry.

4. For the first time, the mechanical (flexibility, elasticity, toughness) properties and self-healing ability of polyampholyte hydrogels was improved by modifying quenched polyampholytes with a hydrophilic monomer – N,N-dimethylacrylamide (DMA), and a hydrophobic monomer – N-octadecyl acrylate (ODA), respectively, using micellar polymerization technique. These hydrogels were characterised using swelling and rheological measurements, morphological analysis using scanning electron microscope (SEM) and mechanical tests.

Hydrogels containing 60-90% water sustained high tensile strength (up to 202 kPa) and exhibit higher stretching ability (up to 1200%), demonstrating good mechanical properties in comparison with corresponding non-swollen counterparts. Experiments conducted with cut-and-heal test revealed that hydrogels exhibit a healing efficiency up to $90 \pm 10\%$ with respect to tensile strength.

5. A methodology were developed to immobilise gold nanoparticles into a macroporous amphoteric cryogels matrixes of annealed and quenched types as well as technology for the hydrogenation of nitroaromatic compounds using flow-through nanocatalytic system with high conversion yield and low activation energy. The results acquired could offer a new strategy for the synthesis of amino compounds, azo dyes, or

benzamides from aromatic nitro-compounds using gold nanoparticles immobilised in the cryogel matrix as reduction system.

3. The level of validity and reliability of each scientific result (scientific positions) and conclusions formulated in the PhD dissertation.

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 series of repeated experiments. All objects of study, as well as synthesised copolymers are thoroughly characterised, and the research outputs are interpreted comprehensively.

4. The level of novelty of each scientific results (positions) formulated in the PhD dissertation.

All results acquired in this work are new, i.e. for the first time, fully-charged polyampholytes of linear and cross-linked structure (hydrogels and cryogels) based on the anionic monomer AMPS and the cationic monomer APTAC were prepared and studied comprehensively; hydrogels were hydrophobically modified and their mechanical properties of were improved possessing robust elasticity and self-healing ability; the effect of low-molecular-weight salt on the behaviour of polymers at isoelectronic points, determination of “anti-polyelectrolyte effect”; study of “isoelectric effect” for complexes of polyampholyte-dye, polyampholyte-surfactant; immobilisation of gold nanoparticles into cryogel matrix and study of their catalytic properties.

5. Assessment of the internal unity of the results.

The dissertation is characterised by internal unity due to the choice of commercially available monomers (AMPS, APTAC, DMAEMA, MAA) used in the synthesis of novel fully-charged polyampholytes of linear and cross-linked structure as well as systematic investigation of physicochemical behaviours of these polymers.

6. The focus of the results obtained by the applicant to the solution of the relevant actual problem, theoretical and applied tasks.

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.

7. Specific recommendations on the use of the results and conclusions of the PhD dissertation.

For practical applications, the following could be proposed: the use of fully-charged 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, development of selective flow-through catalytic systems functioning on the basis of enzymes action; in the design of pharmaceutical excipients for controlled drug delivery.

8. Confirmation of sufficient completeness of publication of the main provisions, results, conclusions of the PhD dissertation.

The main provisions, results and conclusions of the dissertation were found in 18 publications, including 2 publications in journals recommended by the Committee for the

Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 3 publications in the international scientific journals included in the Scopus database, 1 innovation patent of the Republic of Kazakhstan, as well as materials and abstracts of 12 reports at international and national conferences/symposia.

9. Deficiencies in the content and design of the PhD dissertation

Nevertheless, there are some points deserve clarification:

1. Some mismatch between the synthesis protocol of linear polyampholytes (PA) presented in the protocol and Table 2.2.1, i.e. the variation of monomer feed composition, and modification of PA hydrogels, i.e. between protocols and Table 2.2.3 and 2.2.4 exist that one could expect a confusion during reproducing the synthesis. I suggested the applicant revise these issues.

2. Regarding the FTIR-spectroscopy technique used to characterise the structure of copolymers, it would be better to specify the recording parameters in more details, for instance, spectral resolution and data process based on average scan number.

3. Applicant used differential scanning calorimetry (DSC) results to confirm the thermogravimetric analysis (TGA) data in the context of only decomposition points of copolymers. However, it is believed that DSC instrument is commonly used to determine glass transition temperature (T_g) values of amorphous polymers, melting points, degree of crystallinity. Did the applicant consider characterise these values during the experiments conducted on thermal stability analysis of copolymers? I suggest the applicant on a few points: 1) to avoid the effect of moisture upon data retrieval on thermogrammes, hold a pre-weighted sample at 80 °C for at least 20-30 min to eliminate water from the sample during first heating and cool down to room temperature and heat again up to desired temperature while using TGA instrument. 2) upon determination of T_g values use the data of second heating scan and means of triplicate measurements + standard deviation as well as compare with T_g of homopolymers upon using DSC instrument.

4. In this work the copolymerisation kinetics have not been considered. The copolymer composition is a function of molecular weight, in most cases reactivity ratio depends on experimental conditions (temperature, pH, a type of method used in the synthesis, etc.). These also been demonstrated/manifested in many studies. However, the applicant stated that according to some studies on determination of the monomer reactivity ratio and composition, the monomers have $r_{AMPS} = 0.62-0.43$, $r_{APTAC} = 0.36$. Literature links to these values are not relevant as from my personal observations. Moreover, in the discussion section the applicant stated and characterised that prepared PA copolymer compositions have almost equalled to the feed compositions. Therefore, it would be better to determine the reactivity ratio of each monomer during polymerisation.

5. In the context of sorption and release kinetics of dyes methylene blue (MB) and methyl orange (MO), i.e. for potential use of PA hydrogels in biomedicine or drug delivery applications, it is advisable to demonstrate the cumulative drug release at different time points in order to obtain the release kinetic of a model drug compound from these polymers. Calculate the fitting release kinetics profiles or correlation coefficient.

6. In the technological part of the dissertation there is no economic justification of the proposed technological scheme. Some improvements needed in technological scheme, for instance, does this system require monomer purification/filtration units?

7. Is there any statistical analysis of data processing needed to compare the means in this work?

8. The dissertation work contains some comments/notes regarding editing and revising/English improvement of the text in which the applicant was advised to do so in a personal conversation.

However, the comments made on the work do not affect its main provisions, conclusions, and findings/scientific results, which are complete and solve an important scientific problem in the development and study of synthetic polyampholytes, since the outputs of fundamental research could potentially be implemented in the oil industry, solutions for environmental issues, in catalysis, biotechnology, medicine. Therefore, based on the foregoing, the dissertation entitled “Physico-chemical, complexation and catalytic properties of linear and cross-linked polyampholytes” fully comply with the requirements in Section 2 “Rules for awarding scientific degrees” of the Committee for Control and Certification in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, that is compulsory for dissertations to pursue the degree of Doctor of Philosophy (PhD) in speciality of 6D072100 – “Chemical Technology of Organic Substances”, and its author, the applicant Gaukhar Toletay deserves the award of the required scientific degree.

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