

ANNOTATION

To the Ph.D. Thesis submitted for a requirement of a PhD degree in Chemical technology of organic substances (specialty 6D072100).

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PHYSICO-CHEMICAL, COMPLEXATION AND CATALYTIC PROPERTIES OF LINEAR AND CROSSLINKED POLYAMPHOLYTES

The Ph.D. Thesis is devoted to synthesis and characterization of strongly charged linear and crosslinked polyampholytes derived from anionic and cationic monomers, behavior of polyampholytes in solution and gel state, complexation of polyampholytes with ionic surfactants and dyes, and evaluation of the catalytic properties of amphoteric cryogel-immobilized gold nanoparticles hydrogenation reaction.

The relevance of the research topic. Synthetic polyampholytes constantly attract the attention of theorists and researchers because the hierarchy of amphoteric macromolecules can repeat, more or less, the structural organization of proteins. That is why the study of polyampholytes falls within several disciplines, including polymer chemistry and physics, molecular biology, colloid chemistry, and catalysis.

The “quenched” or strongly charged polyampholytes represent amphoteric macromolecules consisting of static positive and negative charges that slightly depend on pH. The electrostatic interactions between the charged monomeric units of polyampholytes are of primary interest because the conformational and volume-phase properties of linear and crosslinked QPA depend on charge density, charge balance, charge spacing and distribution, as well as ionic strength of the solution adjusted by low-molecular-weight salts.

Understanding of the fundamental relationships between the microstructure and property of linear and crosslinked amphoteric macromolecules accompanied by systematic evaluation of literature sources will open renewed interest to polyampholytes in whole and QPA in particular. Evaluation of the structure, swelling and collapsing of hydrogels based on QPA as a function of copolymer composition, microstructure, temperature, ionic strength and mixture of water-organic solvent will provide the development of a novel class of networks that possess the stimuli-responsive character, self-healing ability, strong adhesion, and mechanical flexibility.

Macromolecular complexes of polyampholytes (MCP) represent the products of complexation of linear and crosslinked synthetic polyampholytes with proteins, polyelectrolytes, metal ions, surfactants, dyes, drugs, and nanoparticles. To the best of our knowledge the complexation of QPA with respect to high- and low-molecular weight substances is less considered subject. From theoretical point of view, both polyampholytes and their MCP are interesting for understanding the protein folding mechanism, molecular simulation study of polyampholyte-protein

complexes, enzymatic properties of protein-metal complexes, function of biological tissues, membranes etc. From practical point of view, the fundamental findings of MCP can be utilized in the field of bio- and nanotechnology, medicine, catalysis, hydrometallurgy, oil industry and environment protection.

Reduction and stabilization of metal nanoparticles by functional groups of polyampholytes followed by immobilization within hydrogel and cryogel matrix is perspective for construction of active, stable, selective, and reusable nanocatalysts for hydrogenation, oxidation and isomerization processes at mild conditions.

The purpose and tasks of the research. The aim of the research work is to synthesize and characterize the strongly charged linear polyampholytes, hydrogels and cryogels, followed by the study of their physico-chemical, physico-mechanical, complexation and catalytic properties.

Main tasks of the research:

- Synthesis and characterization of strongly charged linear and crosslinked polyampholytes based on sodium 2-acrylamido-2-methyl propane sulfonate (AMPS) and 3-acrylamidopropyltrimethylammonium chloride (APTAC);
- Study of the hydrodynamic, conformational, and volume-phase properties of AMPS-APTAC polyampholytes as a function copolymer composition, ionic strength and in mixtures of water-organic solvents;
- Study of the complexation properties of AMPS-APTAC polyampholytes with respect to ionic dyes and surfactants;
- Study of the physico-mechanical and self-healing properties of soft, flexible and highly stretchable AMPS-APTAC polyampholyte hydrogels prepared in the presence of hydrophilic – N,N-dimethylacrylamide (DMA) and hydrophobic – N-octadecyl acrylate (ODA) monomers;
- Immobilization of gold nanoparticles within amphoteric cryogel matrix and study of the catalytic properties of cryogel-immobilized gold nanoparticles in hydrogenation of *p*-nitrobenzoic acid (*p*-NBA).

Objects of the research. Linear and crosslinked polyampholytes derived from anionic (AMPS, MAA), cationic (APTAC, DMAEMA), nonionic (DMA), and hydrophobic (ODA) monomers.

The novelty of the dissertation topic. For the first time the charge-balanced and charge-imbalanced quenched polyampholytes of linear and crosslinked structure based on anionic monomer – sodium 2-acrylamido-2-methyl propane sulfonate (AMPS) and cationic monomer – (3-acrylamidopropyl) trimethylammonium chloride (APTAC) were synthesized. They were analyzed using H^1 NMR, FTIR, GPC, DLS, DSC, viscometry, swelling-deswelling experiments, and mechanical tests.

Charge-balanced and charge-imbalanced quenched polyampholytes (QPAs) were found to exist in “core-shell” state and exhibit antagonism in aqueous-salt solution. Addition of low-molecular-weight salts tends to shrink the “shell”, (polyelectrolyte region) and to swell the “core”, (polyampholyte region). Such antagonism between polyelectrolyte and polyampholyte effects can take place at relatively high ionic strengths.

The swelling degree of charge-imbalanced quenched polyampholytes decreases, whereas the swelling degree of charge-balanced quenched polyampholytes increases with a rise in ionic strength. The value n that characterizes the relative contribution of penetrant diffusion and relaxation of crosslinked polymer chains, irrespective of the composition of QPAs, crosslinking degree and ionic strength of the solution, is close to Fickian diffusion ($n = 0.5 \pm 0.1$). Shrinking of linear and crosslinked QPAs in water-ethanol and water-acetone mixtures was also observed.

The complexation of charge unbalanced linear and crosslinked polyampholytes was studied in aqueous solution with respect to ionic dyes and surfactants. Complexation of QPAs with anionic surfactant – sodium dodecylbenzenesulfonate (SDBS) and cationic surfactant – cetyltrimethyl ammonium chloride (CTMAC) is accompanied by changing in turbidity, zeta-potential and average hydrodynamic diameter of colloid particles, while complexation of AMPS-APTAC hydrogels with SDBS and CTMAC is accompanied by gradual shrinking of samples due to binding of anionic and cationic surfactants with excessive anionic and cationic groups of hydrogels.

Gradual decrease in the optical intensity of organic dyes, namely methylene blue (MB) and methyl orange (MO), in the presence of quenched polyampholyte hydrogels confirms the penetration of dye molecules into the hydrogel matrix *via* the race-relay or ion-hopping transport mechanism resulting in gel contraction. Release of dye molecules (up to 70-75%) from the hydrogel matrix was performed in a medium of 0.5M KCl.

For the first time, hydrophobically modified quenched polyampholyte hydrogels were prepared *via* micellar polymerization of cationic and anionic monomers in the presence of hydrophobic monomer ODA. Hydrogels containing 60-90% water sustain a high tensile strength (up to 202 kPa) and exhibit a high stretchability (up to 1239%), demonstrating much better mechanical properties in comparison with corresponding non-swollen ones. Cut-and-heal tests revealed that non-swollen hydrogels exhibit a healing efficiency of $90 \pm 10\%$ of their original Young's modulus.

Macroporous amphoteric cryogels of annealed and quenched types were initially prepared, then gold nanoparticles were immobilized inside of the porous structure. Afterwards, the system was used as an effective flow-through catalytic reactor for hydrogenation of nitroaromatic compounds into corresponding aminoaromatic derivatives, with high conversion and low activation energy.

Practical significance. The fundamental findings found for strongly charged polyampholytes may be used for solving of the following practical tasks:

1) QPA due to salt- and temperature resistance can widely be applied in enhanced oil recovery (EOR) as viscosifying agents where thickeners are required in brine solution;

2) The ability of QPA hydrogels to absorb saline water can be used for production of drinking water;

3) Purification of wastewater from metal ions, organic dyes, surfactants is due to micro- and macroporous structure, high sorption capacity, easy and fast desorption, durability, and good mechanical stability;

4) QPA hydrogels due to high toughness, excellent bio- and hemocompatibility, anti-biofouling, self-healing ability, cytotoxic and adhesive properties in physiological conditions are advanced to the forefront of perspective structural biomaterials, such as cartilage, antithrombogenic implants, wound dressing and blood-contacting materials, drug delivery systems.

5) The flow-through catalytic reactors based on macroporous amphoteric gel-immobilized metal nanoparticles will provide a new platform for production of fine chemicals and treatment of wastewater from organic pollutants.

As a result of the research conducted, the following theses are put forth to be defended:

1) Quenched linear polyampholytes, chemically and physically crosslinked quenched polyampholyte hydrogels and cryogels based on anionic, cationic, nonionic and hydrophobic monomers were synthesized.

2) The composition, structure, molecular weights, polydispersity, conformation, swelling, shrinking, volume-phase behavior, rheology, morphology, mechanical properties and thermostability of quenched polyampholytes of linear and crosslinked structure were evaluated by various physico-chemical and physico-mechanical methods.

3) The complexation of linear and crosslinked quenched polyampholytes with respect to ionic surfactants and dyes was studied;

4) Tough and highly stretchable, chemically and physically crosslinked polyampholytes, containing hydrophilic and hydrophobic monomers and possessing self-healing properties were obtained;

5) Flow-through catalytic reactor based on macroporous amphoteric cryogels with immobilized gold nanoparticles was developed.

Relationship of the present research with other work. The research was carried out 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” (2018-2020).

The Thesis consists of synthetic, physico-chemical, and catalytic parts. The used methods are: free radical polymerization, UV-polymerization, cryopolymerization, gravimetry, volumetry, potentiometric and conductometric titration UV-visible spectroscopy, FTIR spectroscopy, SEM, DSC, TG, GPC, DLS electrophoresis, compression, tensile and rheological tests.

Approbation of work and publications. The results of the work were published in 18 publications: 3 publications in journals included into the Scopus database, 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.