

ABSTRACT

of the thesis for degree of Doctor of Philosophy (PhD)
on specialty 6D060600 - Chemistry

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Research of Radical Copolymerization of Polyethylene (Propylene) Glycole Fumarates with Unsaturated Carboxylic Acids

The general description of work. The thesis is devoted to the creation of “smart” materials based on co- and terpolymers of polyethylene (propylene) glycole fumarates with acrylic, methacrylic acids and dimethylaminoethyl methacrylate, the study of the regularities of radical co- and terpolymerization, the study of polymer sorption and the influence of external factors such as pH, addition of the low-molecular mass salts and organic solvents on swelling of polymers.

The main physical and chemical methods of research in the work are ^1H and ^{13}C -NMR, IR-spectroscopy, nephelometry, chromate-mass spectroscopy, potentiometry, scanning probe microscopy.

The relevance of the research topic (theme). Currently much attention is paid to the study and synthesis of properties of polymeric materials sensitive to changes in the external environment. Among compounds of this class a special place is occupied by “smart” polymers that respond to changes in environmental properties such as pH medium, ionic strength of solution, temperature, light, electromagnetic effects, etc., they and are characterized by a first order phase transition with a sharp change in the volume fraction of macromolecule. “Smart” polymers can deliver the drug to the human body in a target direction, they can also be used as biocatalysts for the isolation and purification of biomolecules, in the manufacture of microlenses, sensors and membranes. From this point of view they are of great interest in such areas as biology, medicine, bio- and nanotechnology.

Over the past decades work is carried on to apply new monomers for the synthesis of “smart” polymers. Unsaturated polyester resins containing unsaturated compounds, in particular polyglycol fumarates are promising in this direction. Unsaturated polyester resins based on fumaric acid are widely used in the preparation of biopolymers and are actively used in the field of biomedicine. It is known that such polymers decompose on fumaric acid and 1, 2 – diol. Fumaric acid is natural compound formed during Krebs cycle and 1, 2 – diol is commonly used as a diluent in drug formulations. These polymers have an advantage in contrast to other synthetic materials by virtue of their properties such as degradation rate and mechanical resistance. Therefore the synthesis of “smart” materials based on unsaturated polyester resins is relevant.

Many studies are devoted to the study of “smart” polymers, but before our research there is no information about the synthesis and study of copolymers, polyampholytic terpolymers based on unsaturated polyester resins. At the same time the study of co- and terpolymers based on unsaturated polyester resins is theoretically and practically interesting one because of their simplicity and economic efficiency as well. The presence of unsaturated double bonds allows one to obtain spatial cross-linked polymers by reacting with ionic monomers. Such materials can retain their properties against exposure to high temperatures, corrosive environments, moisture and other destructive factors.

The aim of the work is to obtain and develop new “smart” materials based on co- and terpolymers of polyethylene (propylene) glycole fumarates with acrylic, methacrylic acids and dimethylaminoethyl methacrylate.

In accordance with the aim the following objectives were set:

- study of the kinetics of radical copolymerization of systems based on polyethylene (propylene) glycole fumarates with acrylic and methacrylic acids;
- synthesis of new hydrogels based on copolymers of different composition: polyethylene (propylene) glycole fumarate with some unsaturated carboxylic acids - acrylic and methacrylic acids;
- synthesis of new terpolymers of different composition based on polyethylene (propylene) glycole fumarate with acrylic acid and dimethylaminoethyl methacrylate;
- determination of the composition of co- and terpolymers based on polyethylene (propylene) glycole fumarate with acrylic acid, methacrylic acid and dimethylaminoethyl methacrylate;
- study of the structure of polymers depending on the nature and composition of the starting materials;
- study of the swelling of copolymers as a result of changes in the medium pH, the addition of organic solvents and low molar mass salts, the determination of the isoelectric point of terpolymers as well;
- study of surface morphology of the synthesized co- and terpolymers;
- identification of promising aspects of the practical application of new “smart” copolymers.

Objects of the study: p-EGF with AA and MAA, new copolymers of p-PGF with AA and MAA, terpolymers of p-EGF:AA:DMAEM and p-PGF:AA:DMAEM, their physical and chemical properties.

Subjects of study: p-EGF with AA and MAA, p-PGF with AA and MAA, radical co- and terpolymerization of p-EGF:AA:DMAEM and p-PGF:AA:DMAEM, basic principles of the interaction of polymers as well as the swelling properties of the new polymers synthesized.

Scientific novelty of the study

The kinetics was studied and the radical copolymerization constants of the synthesized macroporous co- and terpolymers were determined for p-EGF with AA and MAC, p-PGF with AA and MAA, p-EGF:AA:DMAEM and p-PGF:AA:DMAEM. The composition of the synthesized polymers was confirmed by chromate-mass spectroscopy, NMR-, IR-spectroscopy.

The processes of sorption of water and aqueous-organic solutions of polymers synthesized were studied by the gravimetric method. The effect of the pH of the medium and the ionic strengths of the salts on the swelling properties of polymers was studied. The isoelectric point of polyampholytic terpolymers was determined. The surface morphology of the synthesized polymers was studied using SEM. The antimicrobial activity of the synthesized polyampholytic terpolymers was studied.

The relationship of the thesis with the plan of scientific-research work and State programs. The results presented in the thesis were developed during the implementation of projects for grant financing of the Ministry of Education and Science of the Republic of Kazakhstan in the direction of “Rational use of natural resources, including water resources, geology, processing, new materials and technologies, safe products and structures” on “Development of technology for manufacturing new super humidifiers, ion exchangers and construction materials based on polypropylene glycol maleate, polypropylene glycol maleate phthalate with polymers” (#0713/GF4) for 2015-2017 and for 2018-2020 “Creation of theoretical and practical bases of new “intelligent” polymers based on polyethylene-(propylene) glycol fumarate” (#0118RK00024).

The theoretical significance of the study. Synthesis of new polymers based on unsaturated polyester resins obtained by radical co- and terpolymerization, research on the kinetics and determination of copolymerization constants, determination of the polymers composition on the residual content of the initial monomers, research on the sorption of polymers to the ratio of salts, solvents and pH make a big contribution to the theoretical understanding of ionogenic and polyampholytic polymers of macroporous structure.

The practical significance of the study. For the first time synthesized copolymers based on p-EGF with AA and MAA, p-PGF with AA and MAA, also terpolymers p-EGF:AA:DMAEM and p-PGF:AA:DMAEM can be used as hydrogels with a wide range of applications (in agriculture, tissue engineering, electronic systems, etc.), drug carriers, thickeners, special ion exchangers, and more others as other “smart” materials.

New “smart” materials derived from polyethylene glycole fumarate and polypropylene glycole fumarate can be offered as water sorbents, membranes for proteins in biological material separation systems, dyes, etc., also like biodegradable polymers in tissue engineering (scaffold engineering).

The antibacterial properties of new terpolymers of different composition based on polyethylene (propylene glycol) fumarate with acrylic acid and dimethylaminoethyl methacrylate were studied and the scope of their further application was determined.

The main provisions for the thesis defense:

- obtaining of unsaturated polyester resins based on polyethylene (propylene glycol) fumarates;
- methods of obtaining co- and terpolymers of p-EGF with AA and MAA, p-PGF with AA and MAA, p-EGF:AA:DMAEM and p-PGF:AA:DMAEM;
- physical and chemical properties of the synthesized polymers;

- results of the swelling properties of polymers from changes in the external environment (pH of the medium, solutions of organic solvents and salts);
- determination of surface morphology, thermal stability, antibacterial activity in synthesized co- and terpolymers.

The personal contribution of the author is the collection and processing of literary data, the implementation of experimental work, analysis and interpretation of the results.

Discussion and publication of the work. The main indicators of the dissertation have been published at International and regional conferences: the VIth International scientific conference “Theoretical and experimental chemistry” (Karaganda, 2017); The XI All-Russian School - a conference of young scientists “Theoretical and experimental chemistry of liquid-phase systems” (Ivanovo, 2017); VII International workshop "Specialty polymers for environment protection, oil industry, bio-, nanotechnology and medicine" (Almaty, 2017); XXVIII Russian Youth Scientific Conference with international participation (Ekaterinburg, 2018); V International Youth Scientific and Practical Conference "Actual issues of modern chemical and biochemical materials science" (Ufa, 2018); The III International Scientific Conference of Students, Postgraduates and Young Scientists “Chemical Problems of the Present” (Donetsk, 2018); The 5th International youth conference (New York, 2019); XXII All-Russian Conference of Young Chemical Scientists (Nizhny Novgorod, 2019).

Validity of the scientific results and conclusions presented in the thesis is based on the wide use of modern methods for the study of polymers such as ¹H and ¹³C NMR-, IR - spectroscopy, nephelometry, chromate-mass spectroscopy, scanning probe microscopy and mathematical-statistical methods of results data processing.

Publications. The main results of the research are presented in 17 scientific publications jointly with coauthors, including 5 articles in national special editions recommended by Committee for Control of Education and Science of Ministry of Education and Science of the Republic of Kazakhstan, 1 article in an international scientific journal included in the Thomson database Reuters and Scopus (Russian Journal of Applied Chemistry) as well as 11 reports and materials at Republican and International conferences and 1 innovative patent received.

Structure of the thesis. The thesis is presented in the extent of 123 pages, consisting of the introduction, literature review, experimental part, results and their discussion. The thesis includes 10 tables, 61 figures, 286 references and an appendix.