

ANNOTATION

of the dissertation for the degree of Doctor of Philosophy (PhD)
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Synthesis and study of new copolymers polypropylene glycol maleate phthalate with some vinyl monomers

The dissertation is devoted to the synthesis and study of the properties of new «smart»-polymers based on polypropylene glycol maleate phthalate with a number of vinyl monomers, in particular, with acrylic, methacrylic acids, acrylamide, as well as their joint terpolymerization. For this purpose, studies were carried out to establish the regularities of radical co- and terpolymerization, the equilibrium swelling of the obtained co- and terpolymers was determined, the influence of various factors was studied, including variation in temperature, the level of acidity and alkalinity of the medium, the presence of organic solvents and low molecular weight electrolytes in an external solution, on their behavior. Scanning electron microscopy of the surface of copolymers of polypropylene glycol maleate phthalate with acrylic and methacrylic acids and acrylamide made it possible to study the porosity of the structure in detail.

Gel permeation chromatography, ^1H NMR spectroscopy, high performance liquid chromatography, IR spectroscopy with a Fourier transducer, turbidimetry, and scanning electron microscopy were used as instrumental research methods.

Relevance of the research topic. The development of the country's industrial complex takes place in two directions: the introduction of the latest developments of scientists, including the use of new technologies and materials with unique properties, and giving them other properties through their modification.

The urgent need of the modern world for high-quality and inexpensive materials with high performance properties in any field of human activity provokes an active search for alternative sources of raw materials for their manufacture. From this point of view, the synthesis of unsaturated polyesters and the production of polymeric materials with specified practical-valuable properties on their basis are becoming promising. Various grades of unsaturated polyesters, produced in cured and uncured states on an industrial scale since the middle of the last century, have proven themselves well as structural materials, fiberglass plastics. Other unsaturated polyesters have found application as impregnating agents and polymer anticorrosive and flame retardant coatings on wood. Currently, copolymers based on unsaturated polyesters are used everywhere: they are used to make bumpers of cars, boat hulls, artificial facing stone, tabletops, cisterns, figurines, buttons, all kinds of boxes, containers and tanks. Polyesters are also used in the manufacture of armor for the hulls of amphibious assault ships, aircraft skin, in various metal structures with high loads applied to them. However, the polyfunctionality of unsaturated polyesters allows a systematic search for new areas of their

application. Thus, an innovative direction is the possibility of producing «intelligent»-polymers based on unsaturated polyesters cured with vinyl ionic monomers. Currently, it is «smart»-polymers that are the most demanded development due to their ability to purposefully and quickly respond to changes in external factors. This «stimulus sensitivity» allows the use of copolymers of unsaturated polyesters with vinyl monomers as polymer gels, which can significantly expand the areas of their practical application.

The studies carried out in the dissertation work indicate the possibility of using unsaturated polyesters as co-reagents in the synthesis of «smart»-copolymers capable of responding to the slightest change in external conditions by transitioning to a swollen or collapsed state, which indicates the relevance of the studies.

The subject of the study is the radical co- and terpolymerization of p-PGMPH with AA, MAA, and AAm, the regularity of probabilistic structures in the macromolecule depending on the composition of co- and terpolymers, the susceptibility of synthesized co- and terpolymers to changes in external factors (pH value of the medium, temperature, presence of mono- and bivalent low-molecular salts and organic solvents of different polarity), as well as radical copolymerization of p-PGMPH with styrene, study of the properties of styrene solutions of p-PGMPH depending on the composition of the initial mixture in the presence of a filler and without it.

The aim of this work is to synthesize new copolymers based on polypropylene glycol maleate phthalates with some vinyl monomers obtained by radical co- and terpolymerization, to determine a number of physicochemical properties of the obtained co- and terpolymers, as well as the possibility of their use as “smart” polymers.

In accordance with the set goal, the following tasks were identified in the dissertation work:

- synthesis of new ionic co- and terpolymers based on polypropylene glycol maleate phthalate with acrylic and methacrylic acids and acrylamide;

- study of the kinetic parameters of radical co- and terpolymerization of the following binary systems: p-PGMPH-AA, p-PGMPH-MAA and p-PGMPH-AAm and ternary systems p-PGMPH-AA-AAm and p-PGMPH-MAA-AAm according to the data qualitative and quantitative analysis of the composition of the presented samples;

- investigation of the behavior of synthesized samples of co- and terpolymers with varying temperature factor, pH values of the medium, low molecular weight polyelectrolyte or organic solvent in an external solution;

- search for promising areas of practical application of synthesized copolymers based on polypropylene glycol maleate phthalate with acrylic acid;

- investigation of some physicochemical properties of styrene solutions of p-PGMPH, depending on the composition of the initial mixture in the presence of a filler and without it.

Scientific novelty of the research. In the dissertation work for the first time:

– by the method of radical co- and terpolymerization, new co- and terpolymers of a network structure based on polypropylene glycol maleate phthalate with hydrophilic vinyl monomers – acrylic and methacrylic acids and acrylamide were obtained;

–the constants and parameters of the process of radical co- and terpolymerization have been determined;

– the dependences of the swelling of the synthesized co- and terpolymers on varying external conditions: pH of the medium, temperature, the presence of low molecular weight electrolytes in solution and the quality of organic solvents were studied;

– the possibility of using copolymers of p-PGMPh with AA as a moisture sorbent in open and closed ground conditions has been established;

–data are presented on the study of the physicochemical properties of styrene solutions of p-PGMPh with the aim of using the obtained hardened copolymers – PGMPh–St. as materials for structural purposes.

Thus, by carrying out the polycondensation of maleic and phthalic anhydrides with propylene glycol, the initial unsaturated polyester, polypropylene glycol maleate phthalate, was obtained. The qualitative composition of the obtained polyester was established by IR and ^1H NMR spectroscopy, and the molecular weight was determined by turbidimetry and gel permeation chromatography.

Crosslinked polymers with a network structure were obtained by radical co- and terpolymerization, which was confirmed by further studies of their swelling, as well as by scanning electron microscope images MIRA 3 from TESCAN at an accelerating voltage of 20 kV, which also made it possible to study the surface morphology of the obtained co- and terpolymers. The identification of the structures of the samples under study was carried out by means of IR spectroscopy. The study of the influence of various factors (varying the temperature factor and pH values of the environment, placing the studied polymer samples in a solution containing a low molecular weight electrolyte or thermodynamically «bad» solvent) showed the sensitivity of the obtained co- and terpolymers even to insignificant changes in the external environment, which makes it possible to classify the polymers synthesized by us in the category of «intellectual».

Together with the staff of the biological faculty of the Karaganda University named after academician E.A. Buketov, a number of tests of the obtained copolymers of polypropylene glycol maleate phthalate with acrylic acid as moisture sorbents in the cultivation of vegetable crops were carried out in indoor and outdoor conditions. It was found that the use of a copolymer of polypropylene glycol maleate phthalate with acrylic acid as a sorbent introduced into the soil promotes an increase in seedling germination and productivity, which is due to the retention of irrigation water in the soil, followed by its dosed release and nutrition of the plant root system.

Scientific and practical significance of the research. The work carried out within the framework of the dissertation research allows one to obtain «smart»–polymers with desired properties by varying the composition of the initial polymer–monomer mixture, which determines the areas of their practical

application. Thus, for example, hydrogels based on copolymers of p-PGMPh with AA can be used as moisture sorbents.

Conclusions based on the results of the dissertation research:

1. For the first time, new co- and terpolymers based on polypropylene glycol maleate phthalate with acrylic and methacrylic acids and acrylamide were obtained by the reaction of radical co- and terpolymerization in solution at various molar ratios. Dioxane was used as a solvent, and benzoyl peroxide was used as an initiator. The reaction was carried out at a temperature of 333 K at various molar ratios of the co-reactants;

2. The integral Mayo-Lewis method was used to calculate the co- and terpolymerization constants. It was found that p-PGMPh is less active in the above reactions;

3. It was found that the obtained co- and terpolymers have a spatially crosslinked structure, since the obtained terpolymers were found to be insoluble in organic solvents such as benzene, ethyl acetate, dimethylformamide, isopropyl alcohol, hexane, as well as in a mixture of these solvents in various respects. The synthesized terpolymers showed the ability to absorb a certain amount of water, i.e. they are swellable;

4. Compositions of co- and terpolymers of p-PHMP with AA, MAA and AAm, synthesized at various molar ratios of co-reactants, were determined by HPLC. It was found that the composition of terpolymers at any ratios of the initial polymer-monomer mixture is enriched with units of vinyl monomers - acrylic and methacrylic acids and acrylamide;

5. The degrees of saturation of the starting polyester, as well as co- and terpolymers based on p-PGMPh with AA, MAA, and AAm, were determined by the bromide-bromate method. It was found that the degree of unsaturation of the studied co- and terpolymers increases with an increase in the content of unsaturated polyester in the initial mixture;

6. It has been established that the increase in the degree of swelling of the synthesized terpolymers p-PGMPh-AA-AAm and p-PGMPh-MAA-AAm (mol.%) is facilitated by an increase in the content of the same type of vinyl monomer units (units of acrylic and methacrylic acids and acrylamide) in the terpolymer, which gives the right to assume about the partial occurrence of the homopolymerization reaction, which promotes the elongation of intermediate bridges during the formation of a polymer network;

7. The structure of the obtained co- and terpolymers was confirmed by IR and ^1H NMR spectroscopy;

8. The influence of external factors (varying the temperature and pH values of the medium, the presence of mono- and bivalent salts and organic solvents of different polarity in the external solution) on the behavior of the obtained gels based on p-PMGPh with AA, MAA and AAm was studied. As a result of the study, it was found that co- and terpolymers based on p-PGMPh with AA, MAA, and AAm synthesized at molar ratios of the starting reagents are sensitive to the influence of the above external factors, which indicated that the synthesis of co- and terpolymers based on these coreagents is promising, but taken in mass ratios;

9. For the first time, new co- and terpolymers based on p-PGMPh with AA, MAA and AAm were obtained by the reaction of radical co- and terpolymerization in bulk at various mass ratios. Benzoyl peroxide was also used as an initiator, and the reaction was carried out at a temperature of 333 K;

10. The composition of the co- and terpolymers was determined by HPLC. It was found that the highest degree of swelling is observed in the p-PGMPh-AA-AAmterpolymer with a ratio of 3.91:75.14:20.95 mol.%, which is 10 189.43%;

11. By means of scanning electron microscopy, as well as IR and ^1H NMR spectroscopy, the structure of the obtained co- and terpolymers based on p-PGMPh with AA, MAA and AAm was established;

12. The influence of external factors (variation in temperature and pH values of the medium, the presence of mono- and bivalent salts and organic solvents of different polarity in an external solution) on the behavior of synthesized gels based on p-PGMPh with AA, MAA, and AAm, synthesized at different mass ratios co-reactants;

13. In the course of studying the effect of temperature changes, a mixed behavior of the synthesized gels based on p-PGMPh with AA, MAA and AAm was established. Thus, an increase in temperature up to 30–35° C leads to the collapse of synthesized co- and terpolymers. A further increase in temperature to 45° C, on the contrary, promotes an increase in the size of the polymer network, i.e. samples swell;

14. When studying the effect of pH on the co- and terpolymers of p-PGMPh with AA, MAA, and AAm, it was found that an acidic environment suppresses the ionization of the carboxyl and amide groups, which leads to the collapse of the gels. On the contrary, a shift in pH towards an increase (alkaline medium) leads to an increase in the size of the polymer network, that is, to swelling of the investigated co- and terpolymers. This circumstance indicates that the compounds we synthesized are polyelectrolyte gels. Also, in all the samples of co- and terpolymers studied by us, an increase in the degree of swelling was observed with an increase in the alkalinity of the medium, while the swelling curves showed a jump in the pH range 4–7;

15. The effect of the presence of low molecular weight polyelectrolytes (mono- and bivalent salts) on the size of the polymer network of the gels we synthesized was investigated. Thus, it was found that low concentrations of low-molecular-weight salt have an insignificant effect on the size of the polymer network of the gel, while a smooth contraction is observed. An increase in the concentration of the introduced low-molecular-weight electrolyte to a certain limit leads to an abrupt collapse, as a result of which the size of the polymer gel sample is significantly reduced. A further increase in the content of mono- and bivalent salts in the solution has no significant effect on the course of the curves of the collapse of the copolymers. In this case, in the case of adding a bivalent CaCl_2 salt, the collapse of co- and terpolymers based on p-PGMPh with AA, MAA, and AAm is observed even at an electrolyte concentration of 10^{-2} degrees;

16. It has been established that the synthesized co- and terpolymers based on p-PGMPh with AA, MAA, and AAm are sensitive to the presence of organic

solvents in an external solution. Thus, the effect of organic solvents of various polarities (DMSO, DMF, ethanol) on the behavior of the co- and terpolymers synthesized by us was investigated, as a result of which it was found that an increase in the content of the organic component in the external solution leads to the collapse of the gels. In this case, the dependence of the degree of swelling on the concentration of the organic solvent is extreme;

17. The use of a copolymer of p-PGMPH with AA of a ratio of 13.93: 86.07 mol.% As a moisture sorbent on a number of vegetable crops was tested. The experiments carried out made it possible to reduce the frequency of watering by 3 times, to reduce the volume of irrigation water by half, and also to 3 times to reduce the death of seedlings. Thus, the copolymer synthesized by us has proven itself well as a moisture sorbent;

18. Carried out copolymerization of p-PGMPH with styrene in order to obtain materials for structural purposes. In the course of the study, the viscosity characteristics of solutions of p-PGMPH in styrene were established at various mass ratios of co-reactants, as well as similar solutions with the addition of an impurity – chalk. It was found that the most optimal parameters are possessed by a solution with a component ratio of p-PGMPH–St. ~70: 30 mol.%.

Thus, the co- and terpolymers synthesized by us based on polypropylene glycol maleate phthalate with acrylic and methacrylic acids and acrylamide have good moisture absorption properties and are sensitive to the influence of external factors, which makes it possible to control their behavior by changing external conditions, thereby increasing the efficiency of their use in various industries in the future. At the same time, copolymers of p-PGMPH with styrene exhibit structural properties, which makes it possible to hope for their use in the construction industry, automobile and machine-tool industry.

The main provisions for the defense.

–establishment of optimal ratios of coreagents in the synthesis of co- and terpolymers of polypropylene glycol maleate phthalate with hydrophilic vinyl monomers – acrylic and methacrylic acids and acrylamide;

–determination of the constant and parameters of the process of radical co- and terpolymerization;

– study of the dependence of the swelling of synthesized co- and terpolymers on varying external conditions: pH of the medium, temperature, the presence of low molecular weight electrolytes in solution and the quality of organic solvents;

– establishing the possibility of using copolymers p-PGMPH with AA as a moisture sorbent in open and closed ground;

– establishment of the optimal ratio of co-reagents of styrene solutions of p-PGMPH and study of their physicochemical properties with the aim of using the obtained cured copolymers-PGMPH–St. as materials for structural purposes.

Communication of dissertation work with the research plan and state programs. The dissertation work was carried out in the laboratory «Synthesis and research of physical and chemical properties of polymers» on the basis of the Scientific Research Institute of Chemical Problems of the Karaganda University. academician E.A. Buketov within the framework of grant financing of the Ministry

of Education and Science of the Republic of Kazakhstan for research work on the topic No. 0713/GF4 (state registration No. 0115RK00932) «Creation of technology for obtaining new superhydro-absorbents, ion exchangers and construction materials based on polypropylene glycol maleate, polypropylene glycol maleate phthalate».

Approbation of work. The main provisions of the dissertation work were published in peer-reviewed journals recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan (4 articles), and reported and discussed at international conferences of the Republic of Kazakhstan (2 theses), near (9 theses) and far (3 theses) abroad. The main results of the dissertation research. The main provisions of this dissertation work were presented in peer-reviewed journals recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, where 4 articles were published. To confirm the relevance of the research, 2 articles were published in international peer-reviewed journals included in the Thomson Reuters and Scopus databases. Also in co-authorship, based on the results of the tasks of the dissertation work, 14 theses were published and discussed at international conferences of near and far abroad and 1 patent for an invention was received at the Kazakhstan Patent Bureau.

Thesis structure. The dissertation work is presented on 159 pages of typewritten text and includes standard sections: an introduction, three chapters, including 19 tables, 45 figures, a conclusion, a list of used literature, consisting of 197 titles of domestic and foreign authors, and applications.