

ABSTRACT

of the dissertation submitted for the degree of Doctor of Philosophy (PhD) in the specialty «6D060600 – Chemistry»

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Controlled RAFT copolymerization of polypropylene glycol fumarate phthalates with vinyl monomers: synthesis, structure and properties

The dissertation is devoted to the synthesis of new copolymers of poly(propylene glycol fumarate phthalate) with varying molecular weights and acrylic and methacrylic acids, as well as to the investigation of the possibility of controlling the radical copolymerization reaction by introducing a RAFT agent into the reaction mixture in order to obtain both crosslinked and linear copolymers and to vary their yield depending on the RAFT agent concentration.

The industrialization of the country involves various approaches, including the intensification of the development of Kazakhstan's industrial complex, the introduction of new technologies and materials with unique properties, and the modification of these materials to impart new functionalities.

Modern industrial development is continuously challenged by the need for high-quality yet cost-effective materials with superior performance characteristics. This underscores the importance of developing alternative raw material sources and innovative materials. In this context, the synthesis of unsaturated polyesters of various compositions as initial co-reactants and the creation of polymeric materials based on them with valuable practical properties is considered a promising direction. Due to their polyfunctionality, unsaturated polyesters are widely used in various sectors. Industrial-scale production is primarily directed toward the construction industry, where they are utilized as reinforced and unreinforced structural materials and fiberglass products. Certain unsaturated polyesters are employed as impregnating agents and polymer coatings for wood, providing anticorrosive and flame-retardant properties.

The demand for products made from unsaturated polyesters is steadily growing each year. These materials are used to manufacture both specialized and general-purpose items, including machine bumpers, boat hulls, artificial facing stone, countertops, tanks, buttons, containers, and decorative figurines. Specialized applications also include the production of armor for amphibious vehicles, aircraft paneling, and metal structures subjected to high mechanical loads. The inherent polyfunctionality of these materials enables a systematic search for new application areas.

An innovative direction in macromolecular science aimed at solving specific practical problems involves the synthesis of "smart" polymers based on unsaturated polyesters crosslinked with vinyl monomers. The ionogenic nature of vinyl monomers imparts water sorption capacity to the resulting materials. Today, "smart"

polymers occupy a leading role in applied research due to their ability to respond rapidly and selectively to minor environmental changes. Their stimuli-responsiveness opens up new applications for unsaturated polyester-based copolymers as polymer gels, significantly broadening their practical utility.

The research conducted in this dissertation demonstrates the feasibility of using unsaturated polyesters as co-reactants for the synthesis of "smart" copolymers capable of undergoing transitions between swollen and collapsed states in response to slight environmental changes.

Additionally, the linear copolymers obtained may be applied as sorbents for wastewater and industrial effluent treatment.

Aim of the Research. The aim of the study is to synthesize new copolymers based on poly(propylene glycol fumarate phthalate) of various molecular weights with acrylic and methacrylic acids; to investigate the physicochemical properties of the obtained copolymers; to explore the possibility of controlling the radical copolymerization reaction by introducing a RAFT agent into the reaction mixture in order to obtain both crosslinked and linear structures; and to evaluate the variation in yield depending on the RAFT agent concentration.

In accordance with the stated aim, the following **objectives** were defined:

- Synthesis of unsaturated polyester – poly(propylene glycol fumarate phthalate) with different molecular weights;
- Preparation of new ionogenic copolymers based on poly(propylene glycol fumarate phthalate) with acrylic and methacrylic acids;
- Investigation of the kinetic parameters of radical copolymerization for binary systems p-PGFPh–AA and p-PGFPh–MAA based on qualitative and quantitative analysis of the sample compositions;
- Study of the influence of external factors on the behavior of the synthesized copolymer samples;
- Conducting radical copolymerization reactions in the presence of a RAFT agent;
- Examination of the properties of the obtained crosslinked and linear copolymers;
- Identification of promising practical applications for the synthesized copolymers based on poly(propylene glycol fumarate phthalate) and unsaturated carboxylic acids.

Methods of the research. Modern analytical instruments were employed for the studies, located at the Chemical Research Institute of Karaganda University, the engineering laboratory “Physicochemical Methods of Research,” Nazarbayev University, Ualikhanov University, and Charles University: the MIRA 3 TESCAN scanning electron microscope equipped with an X-Act detector from Oxford Instruments (UK, 2012), the LabSYSEvo thermogravimetric/differential thermal/differential scanning calorimeter (2014), the Agilent 7890A gas chromatograph with a 5975 C mass selective detector, the Jeol JNN-ECA-500 NMR spectrometer for recording ^{13}C and ^1H spectra, combined thermal analyzers TGA DSC-IR and TGA-DSC-MS Netzsch Jupiter STA 449 F3 integrated with an IR analyzer and mass spectrometer, the Bruker FTIR Alpha II infrared spectrometer, the Auriga Crossbeam 540 scanning electron microscope from Carl Zeiss, among others.

Main Points to be Defended

- to evaluate the influence of the molecular weight of poly(propylene glycol fumarate phthalate) (p-PGFPh) on the sorption properties of copolymers synthesized with acrylic acid (AA) and methacrylic acid (MAA);
- to investigate the possibility of controlling the radical copolymerization of p-PGFPh with AA and MAA in the presence of a RAFT agent by altering the yield ratio of crosslinked and linear copolymer structures;
- to study the relationship between the RAFT agent concentration and the sorption properties of crosslinked p-PGFPh-AA and p-PGFPh-MAA copolymers;
- to conduct thermogravimetric analysis of crosslinked p-PGFPh-AA and p-PGFPh-MAA copolymers in order to assess their thermal stability range;
- to evaluate the sorption capacity of linear p-PGFPh copolymers with AA and MAA toward transition metals, with the aim of using them as sorbents for the purification of wastewater and industrial effluents.

The results of the research:

The initial unsaturated polyester—poly(propylene glycol fumarate phthalate)—was synthesized by polycondensation of fumaric acid, phthalic anhydride, and propylene glycol. The qualitative composition of the resulting polyester was confirmed by IR and ¹H NMR spectroscopy, while its molecular weight was determined by turbidimetry and gel permeation chromatography.

Crosslinked p-PGFPh-AA and p-PGFPh-MAA polymers were synthesized via radical copolymerization, as confirmed by their swelling behavior and scanning electron microscopy (MIRA 3 from TESCAN, 20 kV accelerating voltage), which enabled detailed analysis of their surface morphology. Structural identification of the copolymers was performed using IR spectroscopy. Studies on the influence of various factors (temperature, pH, presence of low-molecular-weight electrolytes of different valency, and thermodynamically «poor» solvents) revealed that the investigated binary systems were highly responsive to even slight environmental changes, which qualifies the synthesized crosslinked copolymers as "smart" polymers.

Radical copolymerization of p-PGFPh with AA and MAA in the presence of a RAFT agent enabled the simultaneous formation of copolymers with crosslinked and linear architectures. By adjusting the RAFT agent concentration, the proportion of copolymers with different structures can be effectively controlled.

A series of tests on the linear p-PGFPh copolymers with AA and MAA demonstrated their high sorption capacity toward transition metals, highlighting their potential for use in industrial and wastewater treatment applications.

Scientific Novelty of the Research

In this dissertation, for the first time:

- Novel copolymers with both crosslinked and linear structures based on poly(propylene glycol fumarate phthalate) (p-PGFPh) and hydrophilic vinyl monomers—acrylic acid (AA) and methacrylic acid (MAA)—were synthesized via radical copolymerization in the presence of a RAFT agent;
- The constants and parameters of the radical copolymerization process were determined;
- The swelling degree of the synthesized copolymers was studied under varying external conditions such as pH, temperature, presence of low-molecular-weight electrolytes of different valency, and quality of organic solvents;
- The thermal degradation kinetics of p-PGFPh-AA copolymers with

varying molar compositions was investigated;

– It was demonstrated that the ratio of crosslinked to linear p-PGFPh-AA and p-PGFPh-MAA copolymers can be controlled by adjusting the concentration of the RAFT agent;

–The potential application of linear p-PGFPh-AA and p-PGFPh-MAA copolymers as flocculants for the treatment of industrial and wastewater was established.

The main findings of this dissertation have been presented in peer-reviewed journals recommended by the Committee for Quality Assurance in the Sphere of Science and Higher Education of the Republic of Kazakhstan, with a total of 4 articles published. To further confirm the relevance of the research, 3 articles have been published in international peer-reviewed journals indexed in international databases Web of Science and Scopus. Additionally, 3 abstracts based on the dissertation research objectives were co-authored, published, and discussed at international conferences held both in near and far abroad countries.

Compliance with the directions of scientific development or state programs. The work was carried out within the framework of program-targeted funding under the topic: «Development of new sealants and adhesives based on unsaturated polyester resins for the needs of the construction and defense industries» (2021–2023, BR10965249-OT-23), and under the «Zhas Galym» program of the Ministry of Science and Higher Education of the Republic of Kazakhstan on the topic: «Application of computational methods for the effective study of thermal degradation processes of copolymers based on polypropylene glycol fumarate phthalate» (IRN AP15473241).

The author's personal contribution consists in the direct implementation of experimental work within the framework of the dissertation research, processing and interpreting the obtained results, formulating scientific conclusions, as well as preparing scientific articles and conference presentations to disseminate the research findings.

Description of the Doctoral Student's Contribution to Each Publication:

The doctoral student is the first author or corresponding author in all articles written within the framework of the dissertation.

1. Study of Mathematical Models Describing the Thermal Decomposition of Polymers Using Numerical Methods // *Polymers*. – 2025. – Vol. 17. – №. 9. – P. 1197. (Q1, IF-4.7) The research topic was initiated by the doctoral student, numerical calculations were carried out, and the full text of the article was prepared and formatted.

2. Research on the Thermal Decomposition Processes of Copolymers Based on Polypropyleneglycolfumaratephthalate with Acrylic Acid // *Polymers*. – 2023. – Vol. 15. – №. 7. – P. 1725. (Q1, IF-4.7) The doctoral student conducted thermogravimetric analysis of the synthesized copolymers, processed experimental data, calculated kinetic parameters and thermodynamic characteristics, and prepared and formatted the article text.

3. RAFT Agent Effect on Graft Poly(acrylic acid) to Polypropylene Glycol Fumarate Phthalate // *Chemical Papers*. – 2024. – Vol. 78. – №. 6. – Pp. 3831–3843. (Q3, IF-2.1) The doctoral student performed the full cycle of work — from resin synthesis and RAFT polymerization to detailed structural analysis of the resulting polymers using FT-IR, ¹³C, ¹H NMR and SEM, including spectral

interpretation, thermogravimetric studies, and independent preparation of the manuscript.

4. Research of the Influence of External Factors on Copolymers Based on Unsaturated Polyester Resins // Bulletin of Karaganda University. Chemistry Series. – 2020. – №. 2. – Pp. 51–57. The doctoral student synthesized the copolymers, organized experiments to study the influence of pH and organic solvents on swelling behavior, conducted IR spectroscopy and HPLC analysis, processed and interpreted results, and prepared and wrote the main text of the article.

5. Poly(propylene fumarate phthalate) and Acrylic Acid Radical Copolymerization Constants and Parameters // Bulletin of Karaganda University. Chemistry Series. – 2020. – №. 1. – Pp. 68–74. The doctoral student synthesized unsaturated polyester resin, performed radical copolymerization with acrylic acid, calculated copolymerization constants using the Mayo–Lewis method and Q-e parameters using the Alfrey–Price equation, and interpreted the data and wrote the article.

6. The Effect of Liquid Active Media on the Character of Equilibrium Swelling of Copolymers Based on Polypropylene Fumarate Phthalate with Acrylic Acid // Eurasian Journal of Chemistry. – 2023. – Vol. 28. – №. 1. The doctoral student conducted studies on equilibrium swelling in the presence of low-molecular-weight salts, interpreted the effect of ionic strength on the properties of the polymer network, and wrote and formatted the article text.

7. Influence of External Factors on Binary Systems During RAFT Polymerization // Chemical Journal of Kazakhstan. – 2024. – №. 2. The doctoral student synthesized polymer gels using RAFT polymerization based on polypropylene glycol fumarate phthalate and vinyl monomers, studied the effect of pH and temperature on equilibrium swelling, analyzed the thermoresponsive and polyelectrolyte properties of the resulting copolymers, and prepared and formatted the article.

8. Conference Abstracts: The doctoral student synthesized the studied polymer samples, calculated molecular characteristics, interpreted the obtained data, and carried out preparation, formatting, and presentation of all abstracts.

Structure of the Dissertation. The dissertation consists of 126 pages. The structure includes the standard sections: introduction, three chapters (literature review, experimental part, and discussion of the obtained results), conclusion, and a list of references comprising 177 works of domestic and foreign authors. The text of the dissertation contains 12 tables and 33 figures.