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*Article*

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M.Zh. Burkeyev[1], M.S. Zhunissova[1*], J. Plocek[2],
A.T. Kazhmuratova[1], T.S. Zhumagalieva[1]

[1]*Karagandy University of the name of academician E.A. Buketov, Kazakhstan;*
[2]*Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Rez, Czech Republic*
*([*]Corresponding author`s e-mail: meruert_zhunusova@mail.ru)*

# Properties of cross-linked copolymers of polypropylene glycol maleate with acrylic acid obtained at various concentrations of the RAFT agent

The initial polypropylene glycol maleate has been obtained by the polycondensation reaction of maleic anhydride and propylene glycol. The molecular weight of the synthesized unsaturated polyester resin has been determined. The copolymers under study have been obtained by radical copolymerization of p-PGM. The possibility of synthesizing new polymers based on p-PGM with acrylic acid in the presence of a RAFT agent has been shown. The effect of RAFT agent concentration on the network density and product yield has been studied. It has been found that the yield of the cross-linked polymer decreases, its swelling capacity increases, and the yield of the linear polymer increases with an increase in the RAFT agent concentration. The effect of organic solvents, pH, and low-molecular-weight salts on the swelling degree of the synthesized copolymers has been investigated. The research results demonstrate that the susceptibility of polymer hydrogels to organic solvents and changes in pH, and low molecular weight salts, is affected by the amount of RAFT agent in the polymer. The synthesized objects have been characterized by infrared spectroscopy. Scanning electron microscopy has estimated the polymer surface morphology and pore sizes.

*Keywords:* unsaturated polyester resin, polypropylene glycol maleate, RAFT-polymerization, swelling, collapse.

## *Introduction*

Currently, the search for materials with controllable properties and sensitivity to environmental changes is one of the key issues in macromolecular compound chemistry [1, 2]. Such polymers' ability feature is to sorb a huge amount of water and bind low molecular weight substances dissolved in it [3, 4]. Unsaturated polyesters are among promising co-monomers for synthesizing these materials [5].

Unsaturated polyester resins (UPRs) are increasingly being used. They occupy leading positions among composite materials due to the ease of production the availability of raw materials [6]. Prior to our research, a literature-patent search showed [7] the absence of data on radical copolymerization of UPRs with ionic monomers, which opens prospects for the synthesis of new "smart-systems" [8].

As practice shows, when UPRs interact with vinyl monomers, the reaction is not controllable and leads to an insoluble product with a chaotic network arrangement in space. The solution to this problem becomes possible due to the creation of a general concept of macromolecules controlled synthesis [9]. "Pseudo-living" radical polymerization is of considerable interest from this point of view. This assists in replacing uncontrolled chain termination reactions with reversible reactions by adding RAFT agents, allowing regulation of the quadratic chain termination [10].

Using radical polymerization reactions under such conditions makes it possible to design a macromolecule as part of a polymer matrix to obtain (co-)polymers with a given molecular weight, block, and graft copolymers with a controlled length, predictable properties [11].

In this regard, an attempt was made to change the copolymerization reaction of polypropylene glycol maleate (p-PGM) with acrylic acid (AA) in the presence of a RAFT agent at various concentrations. The sorption properties of new polymers were analyzed as a function of changes in the pH of the medium, the concentration of low molecular weight salts, and the choice of organic solvents.

## *Experimental*

The following reagents were used: Propylene glycol, maleic anhydride, acrylic acid, benzoyl peroxide, zinc chloride, 1,4-dioxane, RAFT-agent (2-Cyano-2-propyl dodecyl trithiocarbonate/CPDT) from Sigma-Aldrich.

According to the standard procedure [12], initial p-PGM was obtained by the polycondensation reaction of maleic anhydride and propylene glycol at 423–453 K. The molecular mass of the synthesized p-PGM was determined indirectly by the amount of released water and the content of acid and hydroxyl numbers by the titrimetric method. The p-PGM molecular mass obtained by these methods averaged 2442 a.m.u.

Radical copolymerization of p-PGM with AA was carried out under the following conditions: 50:50 mol% co-monomer ratio, 333 K. Dioxane (1:1 weight ratio) was used as a solvent, and benzoyl peroxide was used as an initiator. After purging with an inert gas for 30 minutes, the radical copolymerization was carried out for 52 hours. The resulting copolymers were washed with dioxane and dried to constant weight in a vacuum drying oven.

Controlled polymerization was carried out similarly to the synthesis of p-PGM-AA, but with the addition of the calculated amount of the RAFT agent (2-Cyano-2-propyl dodecyl trithiocarbonate CPDT) in dioxane solution to initiate the “fluid” polymerization process. The reaction mixtures were poured into ampoules, degassed in a vacuum unit, and sealed. Then the ampoules were placed in a thermostat and incubated for 52 hours at a temperature of 70 °C. The ampoules were cooled at the end of the polymerization and opened. The resulting reaction products were separated quantitatively, and then the cross-linked copolymers filtered from the mother liquor were dried in a vacuum drying oven until a constant weight was established.

The composition of the synthesized copolymers was determined on a Shimadzu chromatograph (Japan) using HPLC by the number of unreacted monomers.

IR spectra of these samples were recorded in KBr pellets on a FSM 1201 spectrometer. Samples for IR spectroscopy were prepared by long-term grinding of 2 ± 0.1 mg of a sample with 200 ± 0.1 mg of dry KBr. The samples were pressed at 200 atm. The IR spectra of the obtained materials were recorded on a device with the best possible resolution of 1 $cm^{-1}$ to measure the relative transmittance. The number of re-scans was increased to a maximum of 50.

The surface morphology of the samples was investigated on a scanning electron microscope MIRA3 (TESCAN, Czech Republic).

Equilibrium swelling of the obtained copolymers was achieved within 1-2 days. The swelling degree $\alpha$ (%) of the polymers was measured gravimetrically. The calculation of $\alpha$ (%) was performed as the ratio of the absolute mass of the swollen hydrogel at the point of equilibrium swelling to its initial mass in the dry state.

Aqueous solutions of low molecular weight salts (LMWS) $CuSO_4$, $FeCl_3$, $Pb(NO_3)_2$ were prepared in calculated amounts from 0.001 to 1 volume fraction to determine the swelling of copolymers in solutions. Buffer solutions of working ethanol pH of the third category ST-pH-04.3 were used to determine the swelling ability of the synthesized copolymers with a change in the pH of the medium.

The following solvent mixtures were chosen as model systems: water – ethanol, water – DMF, water – DMSO, the content of which varied from 0 to 1 volume fractions.

## *Results and Discussion*

As already noted [8, 9], refractory spatially cross-linked copolymers are formed during copolymerization of unsaturated polyester resins at all ratios of the monomer mixture. In this regard, it seemed interesting to follow the change during the copolymerization reaction to the addition of a RAFT agent. Data on the synthesis of copolymers, as well as with the addition of CPDT various concentrations, are shown in Table 1.

Table 1

**Influence of the RAFT agent concentration on the mechanism of copolymerization of p-PGM with AA in dioxane solution, T = 343 K, $[I] = 8\cdot10^{-3}$ mol/L, $[M_1+M_2]$=49.9:50.1 mol.%, the solvent ratio $[M_1+M_2]$=1:1 by weight**

| $[RAFT]\cdot10^3$, mol/L | Cross-linked polymer yield, % | Swelling of the cross-linked polymer, α, % | Linear polymer yield, % |
|---|---|---|---|
| – | 96.93 ± 1.78 | 187.12 ± 6.56 | – |
| 10.02 | 94.15 ± 6.24 | 201.16 ± 3.70 | 3.87 ± 1.59 |
| 30.01 | 78.21 ± 6.62 | 267.21 ± 4.96 | 13.52 ± 1.65 |
| 50.01 | 49.42 ± 2.72 | 314.17 ± 4.92 | 47.45 ± 2.51 |
| 80.03 | 4.96 ± 3.24 | 385.11 ± 6.44 | 92.26 ± 6.11 |

Data in Table 1 demonstrate that the copolymerization reaction proceeds in two directions with the formation of spatially cross-linked and linear copolymers. Each obtained product swells or dissolves in polar solvents, respectively, while antibaticity is observed in the product yield. It should be noted that there is an increase in the swelling degree of the copolymers obtained at high concentrations of RAFT agent. This phenomenon can be explained by a reduction in the network density due to a decrease in the reaction of bimolecular chain termination with the addition of the chain transfer agent.

IR spectral analysis of the copolymers (Fig. 1*a*) shows absorption band in the region of 775 cm$^{–1}$ caused by pendulum vibrations of –CH$_2$– bonds, as well as an absorption band at 1153 cm$^{–1}$, confirming the presence of –C–O–C– ester bonds. An intense peak at 1300 cm$^{–1}$ in the spectrum indicates the presence of the –C=C– polyester group. Absorption bands at 1736 cm$^{–1}$ and 2986 cm$^{–1}$ are characteristic of the presence of –C=O and symmetrically located –CH bonds in the CH$_2$ and COOH groups, respectively. It should also be noted the presence of signals at 2866 cm$^{-1}$ indicates the presence of the =C–H group of the aromatic hydrocarbon.

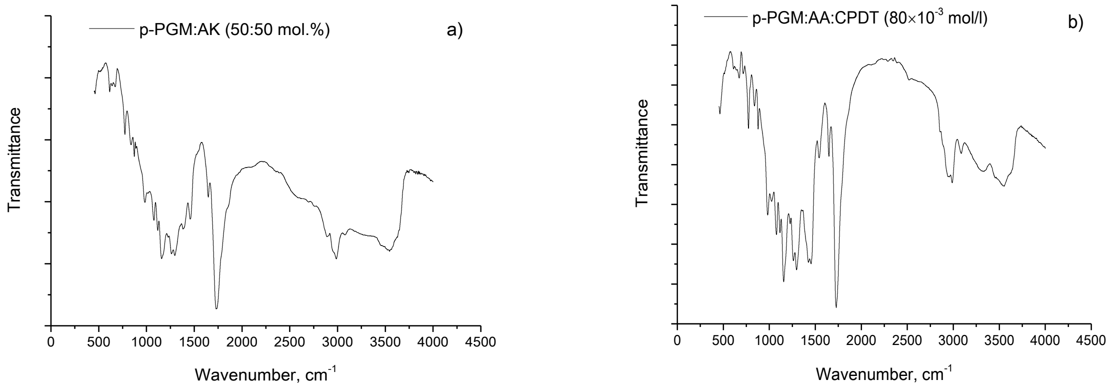


Figure 1. IR spectra of copolymers of the p-PGM-AA (*a*); p-PGM-AA-[CPDT] = 80·10$^{–3}$ mol/L (*b*)

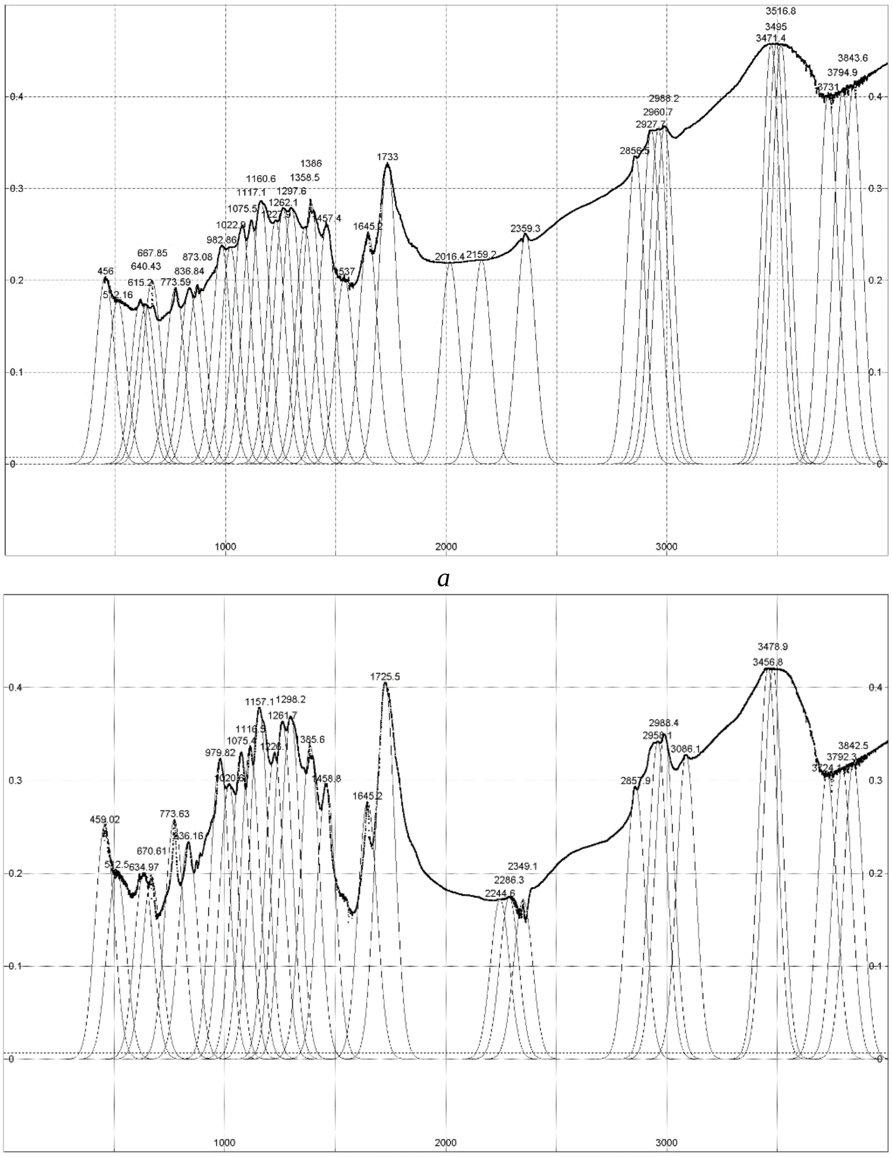
Furthermore, the obtained IR spectra (Fig. 1*b*) of the p-PGM-AA-CPDT copolymers have been analyzed. There is an absorption band in the region of 3545 cm$^{–1}$, which is characteristic of the O–H bonds. There is an absorption band in the region of 3082 cm$^{-1}$, which is responsible for the stretching vibration of the =C–H bond of the aromatic compound, and a weak stretching vibrations band of the C–H groups of the aliphatic hydrocarbon in the region of 2997 cm$^{–1}$. In addition, there is the manifestation of symmetrical vibrations of CH$_3$ groups in the region of 1381 cm$^{-1}$ and scissor bending vibrations of CH$_2$ groups in the region of 1466 cm$^{-1}$ and 1454 cm$^{-1}$, which indicates the presence of branched hydrocarbons. In the spectra of copolymers with an increased RAFT agent concentration, signals are observed at 2244 cm$^{–1}$, which indicates the presence of CN. The data was exported in the form of tables for processing in third-party software.

The spectra were inverted by subtracting the relative transmittance from unity. The positions of the absorption maxima were detected by the program, after which the amplitudes of the maxima were refined by approximating the Gaussian contours (Fig. 2 *a*, *b*).

The polymer's surface morphology was determined by scanning electron microscopy. As shown in Figure 3, the surface of the p-PGM-AA polymer particles (a) has cleavage points characteristic of hard, brittle materials.

The predominance of a layered, loose structure and the appearance of pores are seen in the image for samples containing p-PGM-AA-CPDT (b). The chipping of particles is more plastic in comparison with the p-PGM-AA polymer. The results of electron microscopy confirm that an increase in the CPDT content in the composition of the polymer-monomer mixture affects the distribution and size of the formed pores, which causes a high swelling degree.

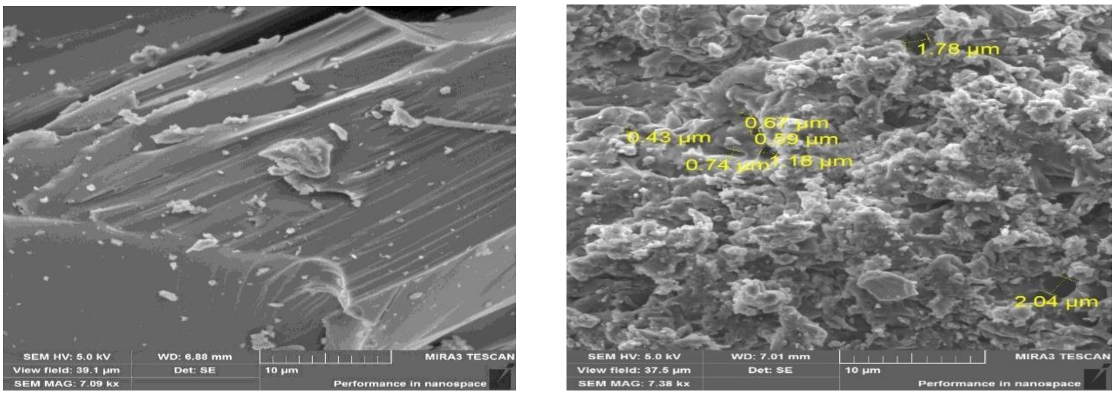
The presence of functional units in the hydrogel structure, which is capable of ionization, increases their sensitivity to various changes in the parameters of the external environment.



*a*

*b*

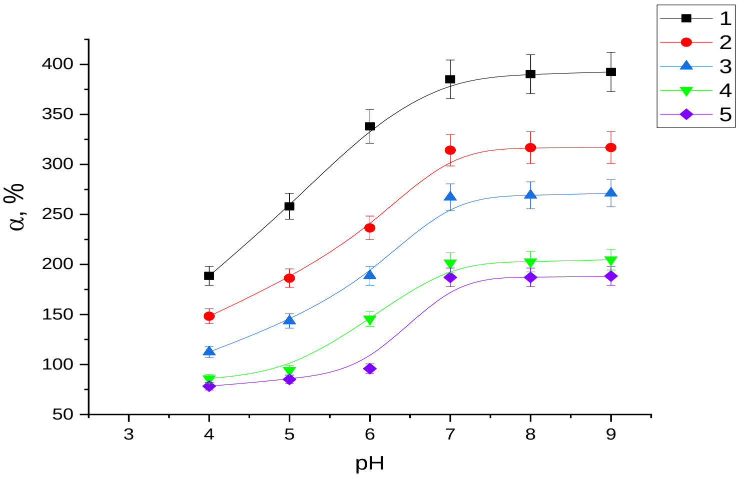
Figure 2. IR spectra of copolymers of p-PGM-AA (*a*); p-PGM-AA-[CPDT] = $80{\cdot}10^{-3}$ mol/L (*b*)



*a* *b*

Figure 3. Surface morphology of the polymer p-PGM-AA (*a*);
surface morphology of the polymer p-PGM-AA-[CPDT]=$80{\cdot}10^{-3}$ mol/L (*b*)

The pH of the medium is one of the external environment parameters that can significantly affect the polymer gels properties. In this section, the swelling ability of the synthesized copolymers based on p-PGM:AA and p-PGM-AA-CPDT was evaluated with a change in the pH of the medium (Fig. 4).



*1* — p-PGM-AA-[CPDT] = $80\cdot10^{-3}$ mol/L; *2* — p-PGM-AA-[CPDT] = $50\cdot10^{-3}$ mol/L;
*3* — p-PGM-AA-[CPDT] = $30\cdot10^{-3}$ mol/L; *4* — p-PGM-AA-[CPDT] = $10\cdot10^{-3}$ mol/L; *5* — p-PGM-AA

Figure 4. Effect of the medium pH on the volume of hydrogels based on p-PGM-AA and p-PGM-AA-CPDT copolymers

In Figure 4, the shape of the swelling curves of p-PGM-AA copolymer samples is similar to the networks containing a chain transfer agent. However, lower sensitivity to changes in the pH of the medium appears with an increase in the RAFT agent content in the composition of the initial polymer-monomer mixture at the same content of p-PGM-AA. The network density fundamentally affects the pH dependence of the swelling of p-PGM-AA and p-PGM-AA-CPDT.

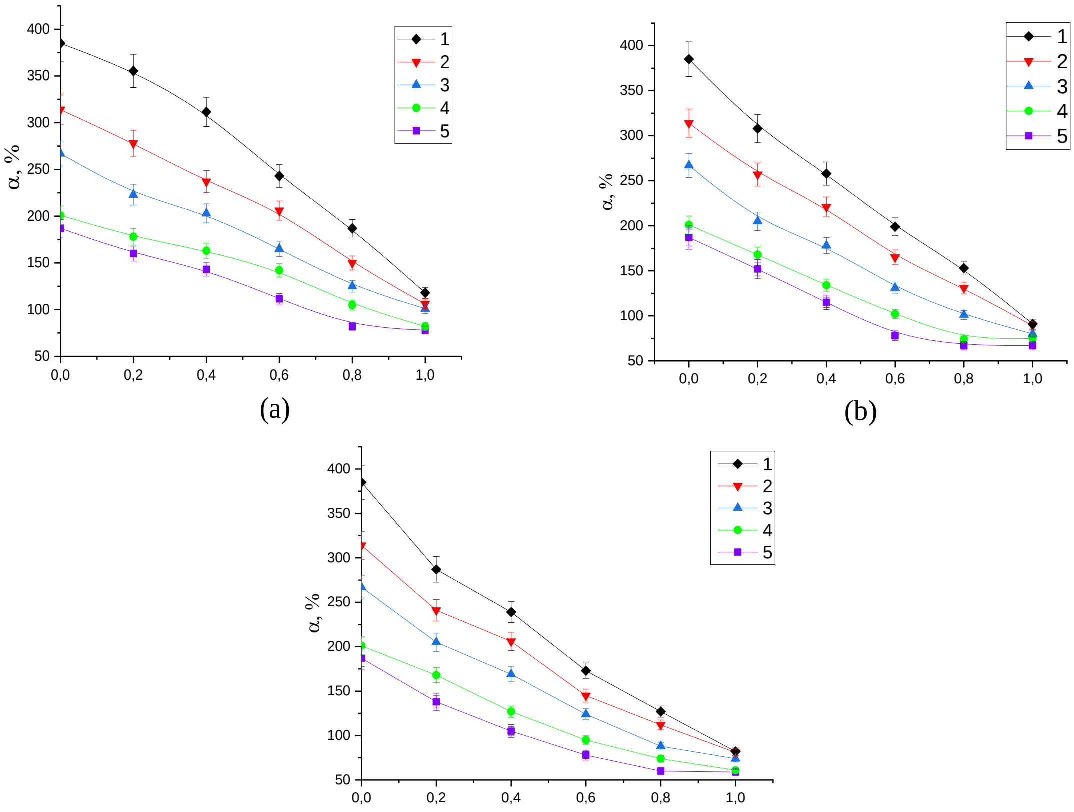
The chain of the non-dissociated p-PGM-AA macromolecule tends to curl up at low pH values compared to p-PGM-AA-CPDT. As the pH rises, the dissociation of ionogenic groups (–COOH… HOOC–) of the p-PGM-AA macromolecule increases, which contributes to the straightening of the folded chain as an effect of mutual repulsion, resulting in smooth polymer swelling. A further shift of the solution pH to an alkaline region has no significant effect on the polymer macromolecules conformation.

The swelling degree in the acidic region does not change noticeably when the RAFT agent concentration is up to $30\cdot10^{-3}$ mol/L. However, a more significant change in the swelling degree depends on the pH when the RAFT agent content is over $30\cdot10^{-3}$ mol/L.

Thus, the data presented shows that hydrogels based on copolymers p-PGM-AA and p-PGM-AA-CPDT behave as typical polyelectrolytes containing ionized acid groups covalently attached the main chain. Furthermore, we studied the effect of the presence of solvents binary mixtures (DMSO, DMF, and ethanol) on the sorption properties of the synthesized polymers (Figure 5).

Figure 5 demonstrates p-PGM-AA and p-PGM-AA-CPDT-based gels in the fraction range of 0.2 to 0.8 vol. in the water — DMSO mixture are gradually compressed. This may be because carboxyl groups' dissociation degree, providing electrostatic repulsion of the subchains from each other, decreases, and a collapse occurs. When DMF and ethanol are added to the system, the volume-phase transition occurs at lower values of the added solvent, which is associated with a lower dielectric constant of the last one.

The smallest swelling degree of the p-PGM-AA and p-PGM-AA-CPDT copolymers is observed in the case of ethanol as the least polar solvent in the DMSO>DMF>ethanol series. It should be noted that the copolymers swelling degree, depending on the solvent concentration, reduces with a decrease in the RAFT agent concentration. It follows from the above that practically all hydrogels are characterized by a high degree of sensitivity to the quality of the solvents used and behave in the same manner.



(a)

(b)

(c)

*1* — p-PGM-AA-[CPDT] = 80·10$^{-3}$ mol/L; *2* — p-PGM-AA-[CPDT] = 50·10$^{-3}$ mol/L;
*3* — p-PGM-AA-[CPDT] = 30·10$^{-3}$ mol/L; *4* — p-PGM-AA-[CPDT] = 10·10$^{-3}$ mol/L; *5* — p-PGM-AA

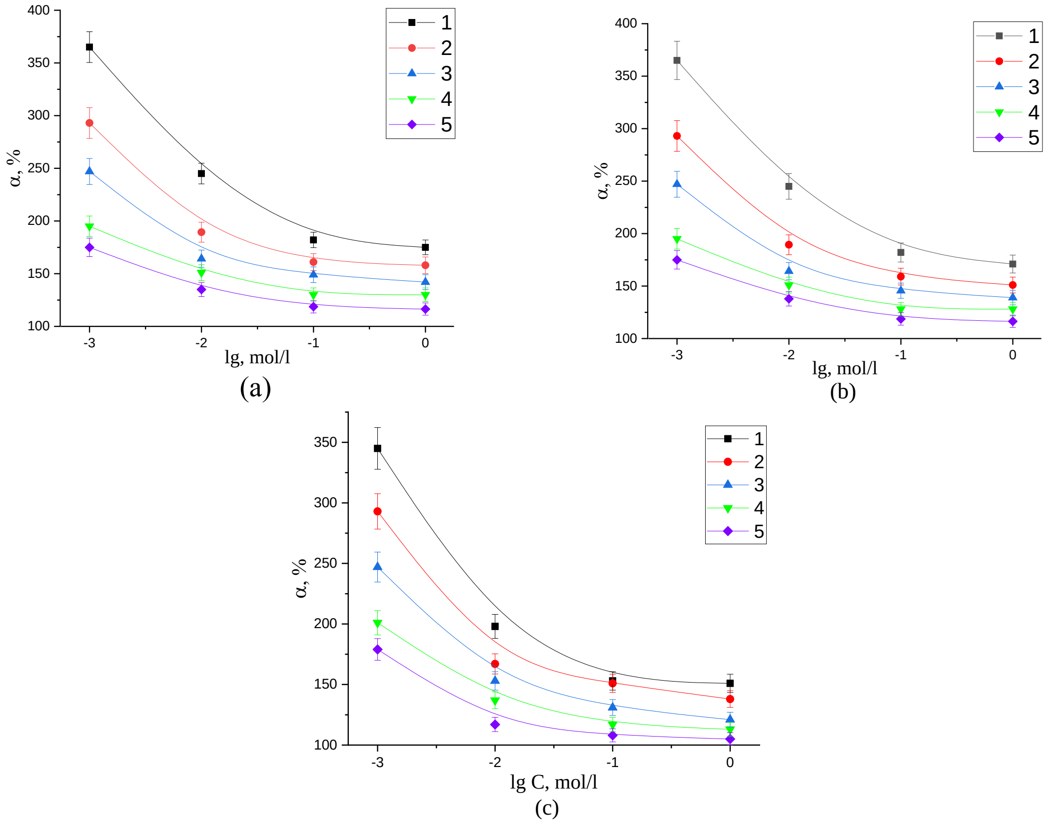
Figure 5. Effect of the volume fraction of DMSO (*a*), DMF (*b*), ethanol (*c*) on the hydrogels swelling based on p-PGM-AA and p-PGM-AA-CPDT copolymers

The study of the metal ions interaction processes with cross-linked polymers is of interest to researchers in this field, and many works of both foreign and domestic scientists are devoted to them [13]. According to the literature [14–17], polymer networks can both swell and undergo collapse in solutions of low molecular weight salts (LMWS). Previously, we carried out experiments to determine the influence of external factors on the behavior of hydrogels in inorganic salts solutions [18, 19]. However, the obtained results do not allow for creating a unified theory of the interaction of low molecular weight compounds with polymer macromolecules. In this regard, in the continuation of research in this direction, it seemed interesting to study the behavior of RAFT polymers based on p-PGM-AA in solutions with an increase in the concentration of mono-, bi- and trivalent salts (Figure 6).

Figure 6 (*a*, *b*, *c*) shows the swelling behavior of p-PGM-AA and p-PGM-AA-CPDT copolymers depending on the concentration of added low molecular weight electrolytes, namely $Pb(NO_3)_2$, $CuSO_4$, and $FeCl_3$.

The graphical dependence shows that an increase in the salt concentration to a certain value (about 10$^{-3}$ mol/L) does not have a significant effect on the size of hydrogel. A further increase in the ionic strength has practically no effect on the α value. It can be seen that with an increase in the salt concentration (from 10$^{-2}$ mol/L), the ions osmotic pressure in the solution increases, resulting in the contraction of the polyelectrolyte hydrogel.

The contraction of hydrogels in LMWS solutions during the alteration from trivalent to bivalent is observed at high values of the salt concentration, respectively. Thus, an increase in the LMWS content in the network leads to the contraction of the copolymer. This may be due to several reasons: first, an increase in the concentration of salts in the solution worsens the thermodynamic quality of water, and secondly, the polyelectrolyte effect may be suppressed by the addition of low molecular weight substrates in the surrounding solution.



(a) (b) (c)

*1* — p-PGM-AA-[CPDT] = $80\cdot10^{-3}$ mol/L; *2* — p-PGM-AA-[CPDT] = $50\cdot10^{-3}$ mol/L;
*3* — p-PGM-AA-[CPDT] = $30\cdot10^{-3}$ mol/L; *4* — p-PGM-AA-[CPDT] = $10\cdot10^{-3}$ mol/L; *5* — p-PGM-AA

Figure 6. Effect of the volume fraction of $CuSO_4$ (*a*), $Pb(NO_3)_2$ (*b*), $FeCl_3$ (*c*) on the swelling of hydrogels based on p-PGM-AA and p-PGM-AA-CPDT copolymers

## *Conclusions*

For the first time, copolymers based on p-PGM-AA with the addition of a RAFT agent (CPDT) in various concentrations were obtained by the method of controlled radical polymerization.

The study of the copolymerization reactions of unsaturated polyester resin, namely polypropylene glycol maleate with acrylic acid, showed that the addition of small amounts of RAFT agents significantly affected not only the network density but also the product yield.

Based on the results of scanning electron microscopy, it was found that copolymer samples with the addition of a RAFT agent have a loose, porous surface with average pore size in the range from 0.39 nm to 2.04 nm.

The gravimetric method for determining the swelling degree of the synthesized hydrogels proves that an increase in the CPDT content in the initial polymer-monomer mixture at the same p-PGM-AA content makes it possible to obtain a product capable of absorbing a significantly larger volume of water.

The effect of external factors (pH of the medium, quality of the organic solvent, and the solution ionic strength) on the swelling ability of copolymers without the addition of a chain transfer agent and samples containing various concentrations of the RAFT agent has been established.

Thus, understanding the dependence of the density and the network range on the RAFT-agent concentration makes it possible to “regulate” the structure of the copolymers, thereby avoiding chaos in the structure. Besides, varying the concentration of the RAFT agent will allow purposefully synthesizing copolymers with desired properties based on experimental and mathematical methods, as well as to control the cross-linking degree and the swelling degree of polymers.

Considering the fact that the concentration of the RAFT agent contributes to a decrease in the polymer network density, it is possible to obtain new “smart” systems with desired properties that can change the swelling capacity under the influence of various external factors.

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М.Ж. Бүркеев, М.С. Жүнісова, Ю. Плоцек, А.Т. Қажмұратова, Т.С. Жұмағалиева

# РАФТ агентінің әртүрлі концентрацияларында алынған акрил қышқылымен полипропиленгликольмалеинатының тігілген сополимерлерінің қасиеттері

Бастапқы полипропиленгликольмалейнаты малеин ангидриді мен пропиленгликольдің поликонденсациялану реакциясы арқылы алынды. Синтезделген қанықпаған полиэфир шайырының молекулалық салмағы анықталды. Зерттелетін сополимерлер радикалды сополимерлену реакциясы арқылы п-ПГМ пен қанықпаған карбон қышқылының негізінде алынды. RAFT-агентінің әртүрлі концентрациясының қатысуымен п-ПГМ мен акрил қышқылы негізінде жаңа полимерлерді синтездеу мүмкіндігі көрсетілді. RAFT-агентінің концентрациясы полимер торының тығыздығына және өнім шығымына әсері зерттелді. RAFT-агентінің концентрациясының жоғарылауымен тігілген полимердің шығымы төмендейтіні және оның ісіну қабілеті жоғарылайтыны, сонымен қатар сызықты полимердің шығымы жоғарылайтыны анықталды. Синтезделген сополимерлердің ісіну дәрежесіне органикалық еріткіштердің, pH ортаның және төмен молекулалы тұздардың әсері зерттелді. Зерттеу нәтижелері полимерлі гидрогельдердің органикалық еріткіштердің концентрациясының өзгеруіне және pH ортаның өзгеруіне, сондай-ақ төмен молекулалық тұздар ерітінділерінің сезімталдығына полимердегі RAFT-агенттің мөлшері әсер ететіндігін көрсетті. Полипропиленгликольмалеинат пен акрил қышқылы негізіндегі объектілер инфрақызыл спектроскопиясы арқылы сипатталады. Сканерлеуші электронды микроскоптың көмегімен полимерлердің беткі морфологиясы зерттелген, сонымен қатар тор өлшемдері бағаланған.

*Кілт сөздер*: қанықпаған полиэфир шайыры, полипропиленгликольмалеинат, RAFT-полимеризация, ісіну, коллапс.

М.Ж. Буркеев, М.С. Жунисова, Ю. Плоцек, А.Т. Қажымұратова, Т.С. Жұмағалиева

# Свойства сетчатых сополимеров полипропиленгликольмалеината с акриловой кислотой, полученных при различных концентрациях RAFT-агента

Реакцией поликонденсации малеинового ангидрида и пропиленгликоля получен исходный полипропиленгликольмалеинат. Определена молекулярная масса синтезированной ненасыщенной полиэфирной смолы. Путем радикальной сополимеризации п-ПГМ с ненасыщенной карбоновой кислотой получены исследуемые сополимеры. Показана возможность синтеза новых полимеров на основе п-ПГМ с акриловой кислотой в присутствии RAFT-агента. Изучено влияние концентрации RAFT-агента на плотность сетки и выход продукта. Установлено, что с увеличением концентрации RAFT-агента уменьшается выход сетчатого полимера, увеличивается его набухающая способность, а выход линейного полимера возрастает. Исследовано влияние органических растворителей, pH среды, низкомолекулярных солей на степень набухания синтезированных сополимеров. Результаты исследований показали, что на восприимчивость полимерных гидрогелей к присутствию органических растворителей и к изменению pH среды, а также низкомолекулярных солей влияет количество RAFT-агента в полимер-мономерной смеси. Синтезированные объекты охарактеризованы методами инфракрасной спектроскопии. Посредством сканирующей электронной микроскопии исследована морфология поверхности полимера и оценены размеры пор.

*Ключевые слова:* ненасыщенная полиэфирная смола, полипропиленгликольмалеинат, RAFT-полимеризация, набухание, коллапс.

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## Information about authors

**Burkeyev, Meyram Zhunusovich** — Full Professor, Doctor of Chemical Sciences, Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: m_burkeev@mail.ru; https://orcid.org/0000-0001-8084-4825;

**Zhunissova, Meruyert Serikhanovna** — 2nd year PhD student, Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: meruert_zhunusova@mail.ru; https://orcid.org/ 0000-0001-6376-8955;

**Plocek, Jiri** — PhD., CSc. Institute of Inorganic Chemistry of the Czech Academy of Sciences, Czech Republic, Husinec-Rez 1001 25068 Rez; e-mail: plocek@iic.cas.cz; https://orcid.org/0000-0001-6082-5766;

**Kazhmuratova, Akerke Temirgalievna** — Candidate of chemical sciences, Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: kazhmuratova@mail.ru; https://orcid.org/0000-0003-4044-8419;

**Zhumagalieva, Tolkyn Sergazyevna** — Candidate of chemical sciences, Professor, Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: Zhumagalieva79@mail.ru; https://orcid.org/0000-0003-1765-752X