ОРГАНИКАЛЫҚ ХИМИЯ
ОРГАНИЧЕСКАЯ ХИМИЯ
ORGANIC CHEMISTRY

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Determination of the microstructure, the swelling degree and dynamics of cryogels based on methacrylic acid, dimethylaminoethylmethacrylate and acrylamide

By the method of radical polymerization, cryogels were synthesized on the basis of methacrylic acid, acrylamide and dimethylaminoethylmethacrylate in proportions of cryogels (%) 20:20:60, 20:60:20, 60:20:20, 40:40:20, 15:45:40, 45:15:40. The microstructure of cryogel was studied by the method of electrone microscopy. It was revealed that cryogels have super macroporous. The degree and dynamics of cryogel swelling in water solutions was identified, fluid diffusion mechanism in the scope of cryogel was identified as well. It was determined that the diffusion of liquids in cryogels obeys Fick's law.

Key words: macroporous amphoteric cryogels, methacrylic acid, acrylamide, dimethylaminoethylmethacrylate, microstructure.

Introduction

Due to the adequate respond to changes in the external environment (temperature, pH, ionic strength of the solution, a mixture of water and organic solvents, the electric and magnetic fields, etc.) amphoteric gels refer to the «intelligent» materials [1–4].

In recent years, most attention of researchers is paid to the amphoteric nanogels [5–12] and microgels [13–17], however, the literature provides few information about polyampholytes with macroporous structure, which synthesized at low temperatures, i.e., under cryo conditions.

Macroporosity is a characteristic morphological feature of the cryogels. Depending on the synthesis conditions cryogels may have a macroporous structure with pore sizes ranging from 0.1 to 10 microns, or over macroporous with pore sizes from 10 to 1000 microns, which impart a unique set of physical and chemical properties to these materials, and it also allows to use them to solve a number of biomedical, biotechnological and catalytic problems [18].

The cryogel characteristic structure is formed during freezing, when the formation of sufficiently large crystals of solvent, usually ice, results in the displacement of solid particles into the space between them and in concentration of the suspension. In freezing of colloidal solutions the concentrating leads to the formation of a gel. Removal of the frozen solvent by sublimation leads to the formation of frame structures with large pores in place of the removed ice crystals. The structural elements of the frame structure are composed of solid particles of the suspension, usually nanosized particles. As a result, inorganic cryogels, in contrast to the polymer cryogels, are characterized by a bimodal distribution of porosity, in which the second peak corresponds to mesopores. Target-specific ice crystallization creates the materials with large cylindrical pores and mesoporous frame walls, such carriers are promising for the creation of highly effective catalysts [19, 20].

The purpose of this study is a synthesis of amphoteric cryogels based on methacrylic acid (MAA), dimethylaminoethylmethacrylate (DMAEM) and acrylamide (AA) monomers and study their microstructure, the kinetics and degree of swelling.

Experimental section

Materials and Methods. The synthesis of amphoteric MAA/DMAEMA/AA cryogels is based on acid monomer methacrylic acid, dimethylaminoethylmethacrylate as a basic monomer, and acrylamide, as a non-ionic monomer. Cryogels by free radical polymerization with the degree of crosslinking of 10 % were synthesized.[*] Methylenbisacrylamide (MBA) is used as a coupling agent.

Acid (MAA) and basic (DMAEMA) monomers were added in various ratios, with increasing acidic or basic monomers. Acrylamide was added to improve the mechanical properties of cryogels. In the result a series of gels were obtained by the following composition (Table 1).

T a b l e 1

Ratio of monomers

Concentration of MBA, %	Amphoteric cryogels [MAA]/[DMAEMA]/[AA], %
10	20:20:60
10	20:60:20
10	60:20:20
10	40:40:20
10	45:15:40
10	15:45:40

The reaction mixture consisting of MAA, AA and DMAEMA in 10 ml of water was dissolved. The obtained initial monomer mixture (IMM) was cooled until 0°C and then was purged with argon for 10 min. Afterwards, the coinitiator — N,N,N,N-tetramethylethylene diamine (TMED) and 0.1 ml of a 10 % solution of ammonium persulfate as an initiator were added. The obtained IMM in a cylindrical shaped container was placed and cryo polymerization in a cryostat at −12 ℃ for 48 hours was carried out.

After thawing cryogels were washed with bidistilled water for 2 days with replacement of water every 4 hours. For the purpose of lyophilization 1 cm of ready cryogel samples were placed in solutions of ethyl alcohol with a mass fraction of 25 %, 50 % and 75 % within 2 hours. Subsequently cryogel samples were placed in a 90 % ethanol solution and allowed to stand for 1 day. Prepared samples were freeze dried at room temperature until constant mass by using freeze-dryer JED-320 of «JEOL» company (Japan) [21].

The microstructures of prepared cryogels were investigated by JSM-6390 LV low vacuum scanning electron microscope of «JEOL» company (Japan)[1] due to its macroporous structure the cryogels swelling much better than the analog polymer networks.

The degree of swelling (α) of cryogels was calculated according to the formula 1:

$$\alpha = (m - m_0)/m_0, \tag{1}$$

where m — mass of equilibrium swollen polymer, g; m_0 — mass of the dry polymer, g. The value of the degree of swelling was determined as the average value of three parallel experiments.

According to [22], the swelling ratio of cryogel in aqueous solutions was calculated. The swelling rate was calculated by the formula 2:

$$kt^n = m_t/m_\infty, \tag{2}$$

where k — constant of swelling rate; n — characteristic exponent describing the mechanism of liquid transport; t — absorption time; m_t — cryogel mass (g) against time t; m_∞ — limiting mass of cryogel (g) for an infinite time t_∞. Constant k was defined as the intersection point of the tangent to curve of the dependence $\ln(m_t/m_\infty)$ on the ordinate axis $\ln t$ c, constant n as the slope of the tangent to the curve $\ln(m_t/m_\infty)$ from $\ln t$, provided that the $m_t/m_\infty < 0,6$.

Results and discussion

Cryogels based on MAC/DMAEMA synthesized by free radical polymerization were obtained in the following proportions (%) — 20:20:60, 40:40:20, 20:60:20, 45:15:40, 60:20:20, 15:45:40. The microstructures of cryogels observed by electron microscopy are shown in figures 1–6.

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[*] Testing laboratory of engineering profile of KazNRTU named after K.I. Satpayev in Almaty.
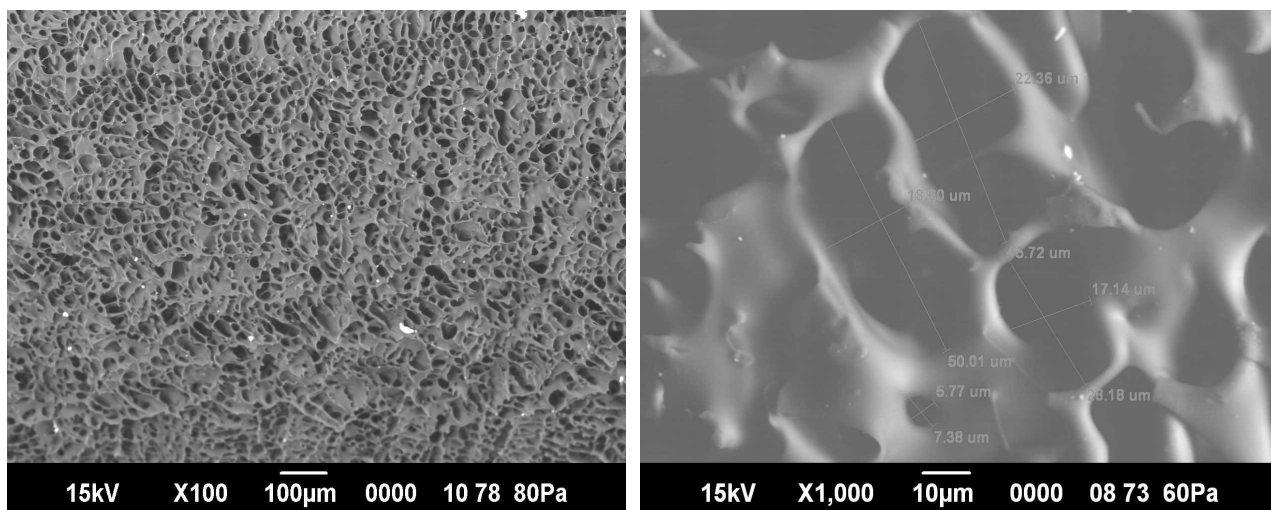
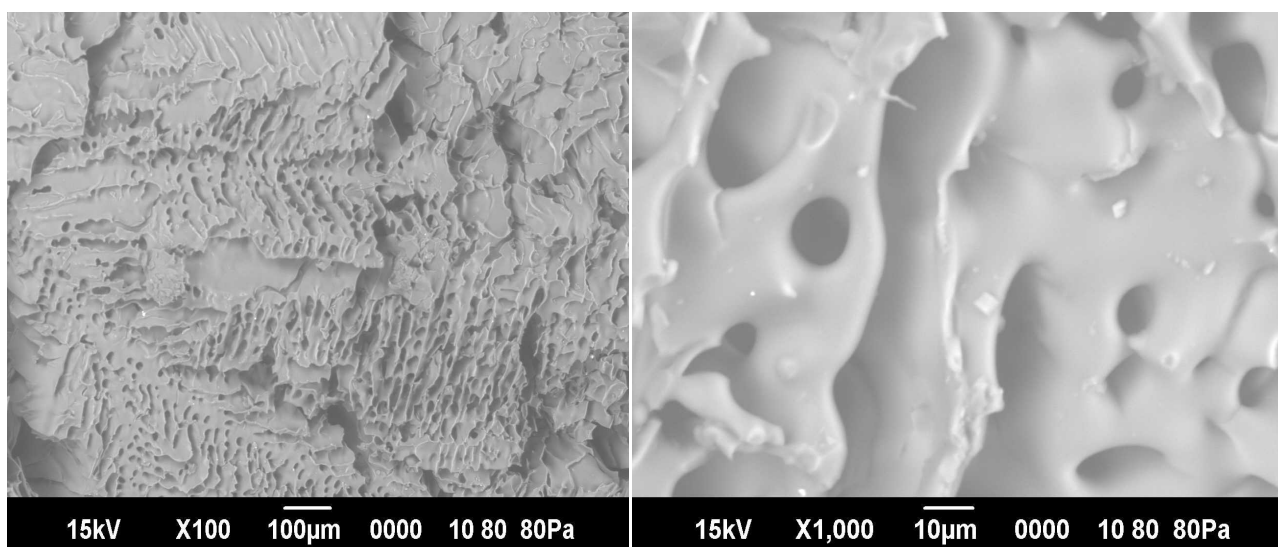Figure 1. Microstructure of cryogel MAA/DMAEMA/AA in the ratio 20:20:60

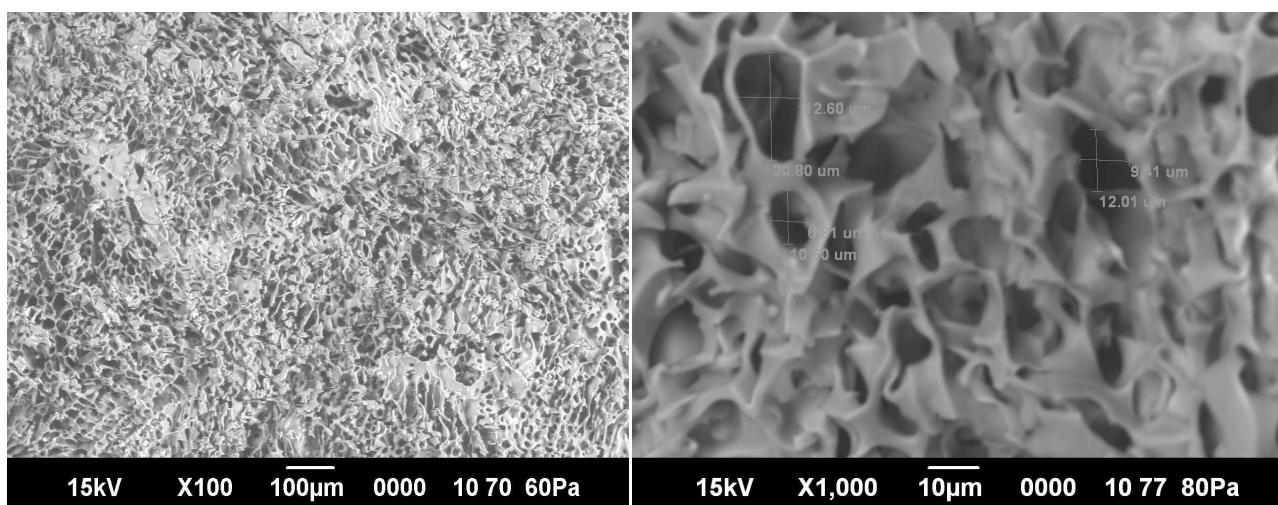Figure 2. Microstructure of cryogel MAA/DMAEMA/AA in the ratio 20:60:20

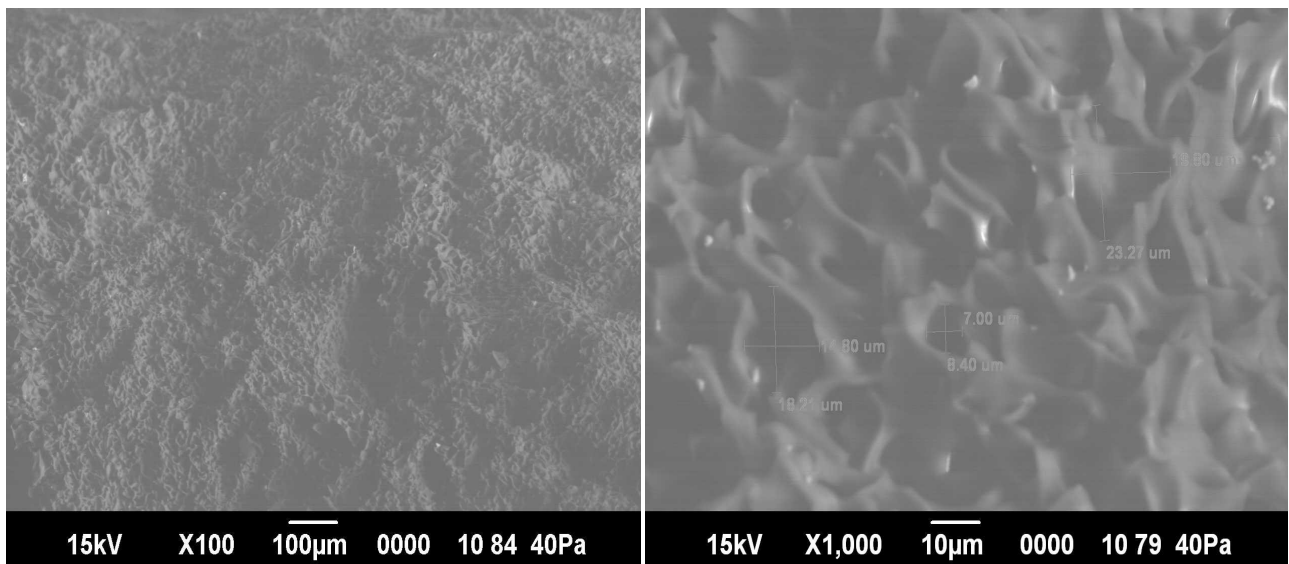Figure 3. Microstructure of cryogel MAA/DMAEMA/AA in the ratio 40:40:20

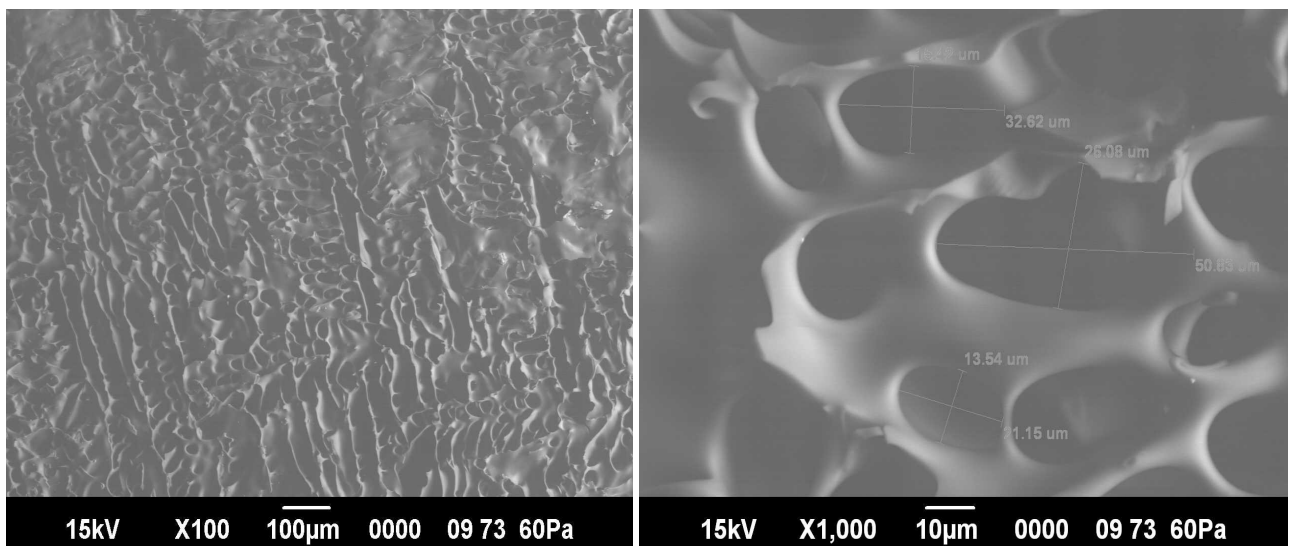Figure 4. Microstructure of cryogel MAA/DMAEMA/AA in the ratio 45:15:40

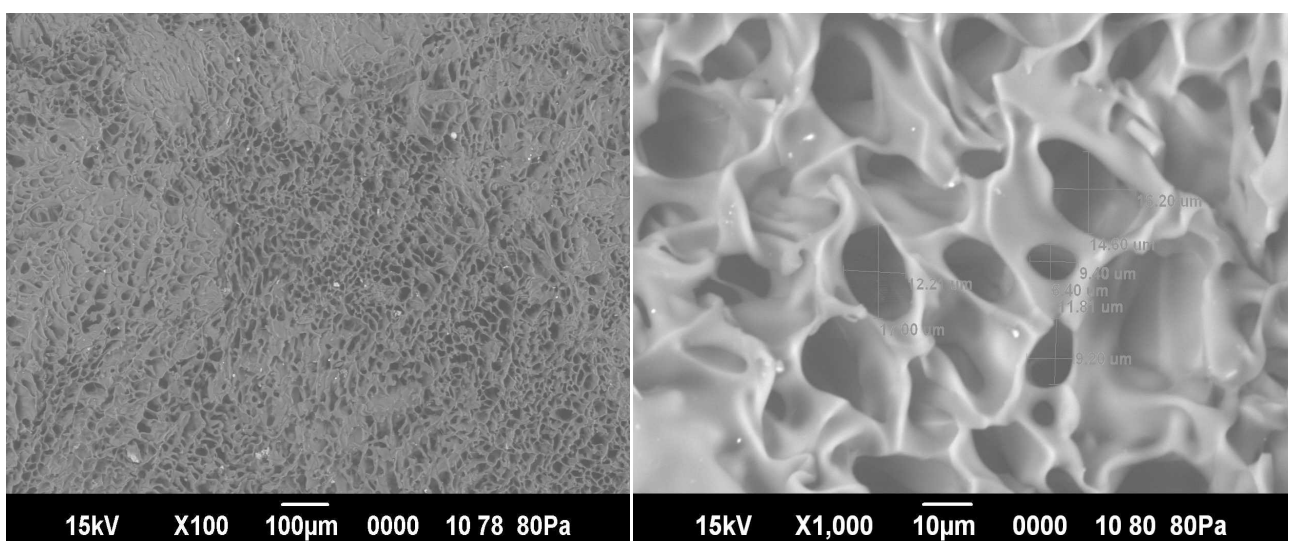Figure 5. Microstructure of cryogel MAA/DMAEMA/AA in the ratio 60:20:20


Figure 6. Microstructure of cryogel MAA/DMAEMA/AA in the ratio 15:45:40

Figures 1–6 show that the microstructures of cryogels at different component ratio are homogeneous in pore size and wall thickness. The minimum pore size was 6 microns, a maximum was 60 microns or more.

It should be noted that the concentration of crosslinking agent was 10 %, since this ratio gel will be obtained very elastic and strong. The high concentration of the crosslinking agent results in weak swelling of cryogels and deterioration of their mechanical properties.

Figure 7 shows curves of swelling of cryogels MAA/DMAEMA/AA in water.
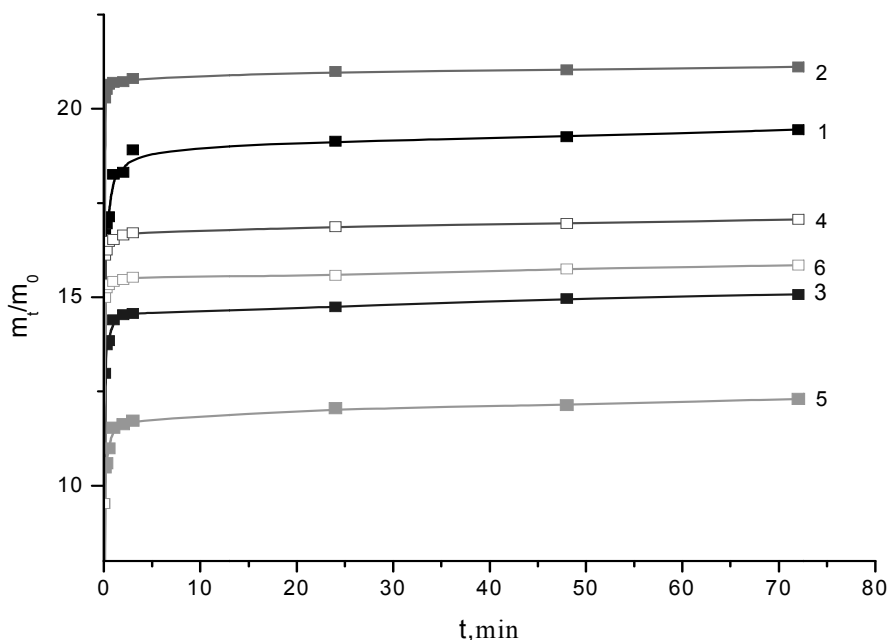
1 — 40:40:20; *2* — 60:20:20; *3* — 20:20:60; *4* — 20:60:20; *5* — 45:15:40; *6* — 15:45:40

Figure 7. Rate change of swelling of cryogels samples in water

Figure 7 shows that the swelling of cryogels proceeds in a short time for 1–2 minutes. This indicates the high porous structure of cryogels.

Figures 8–13 present the curves of swelling kinetics of cryogels in dependence $\ln(m_t/m_\infty)$ to $\ln t$.
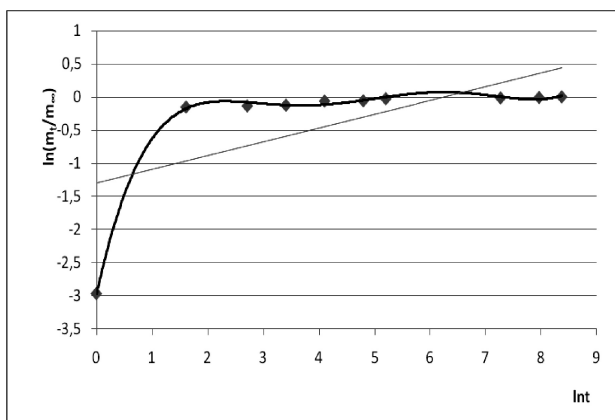

Figure 8. Kinetics of swelling of cryogels in the ratio 40:40:20
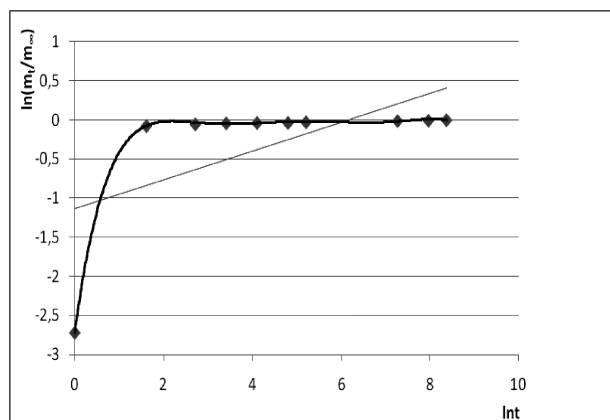

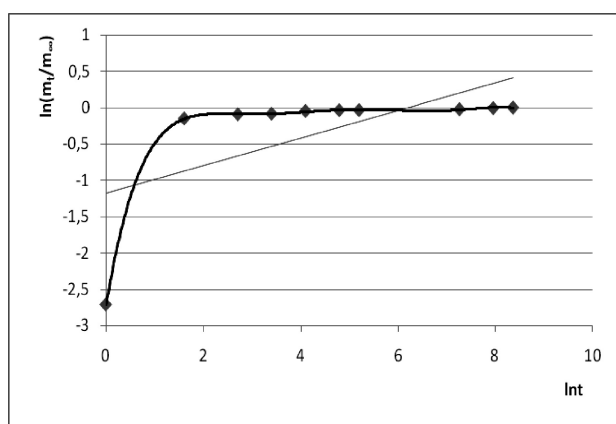Figure 9. Kinetics of swelling of cryogels in the ratio 60:20:20

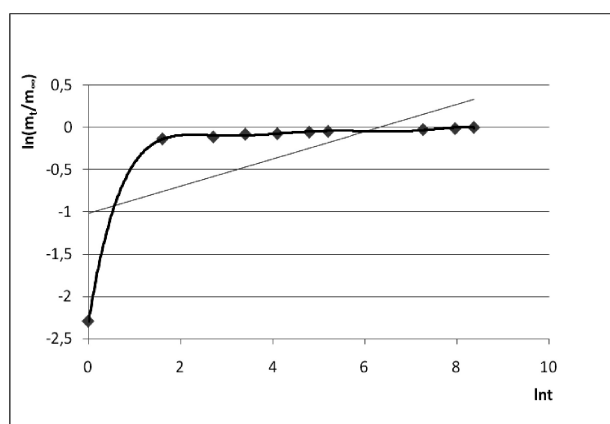Figure 10. Kinetics of swelling of cryogels
in the ratio 20:20:60

Figure 11. Kinetics of swelling of cryogels
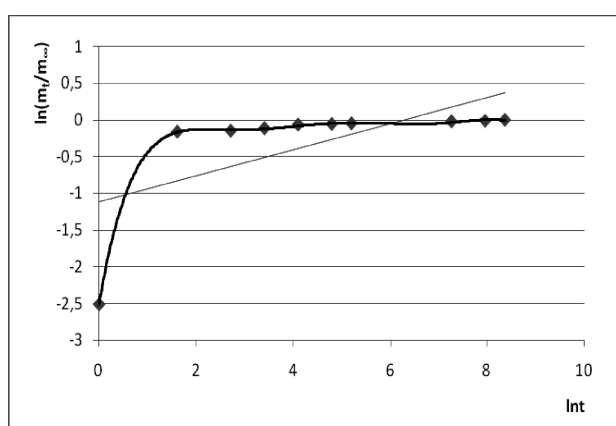in the ratio 20:60:20

Figure 12. Kinetics of swelling of cryogels
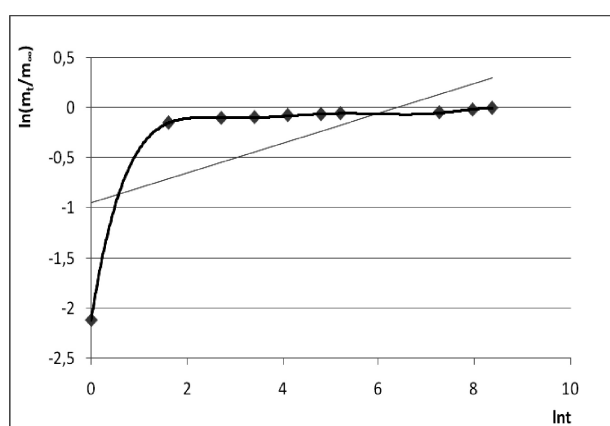in the ratio 45:15:40

Figure 13. Kinetics of swelling of cryogels
in the ratio 15:45:40

From these curves characteristic constants k of cryogels and characteristic exponents n, describing the mechanism of liquid diffusion in gel volume (Table 2) were determined.

T a b l e 2

The values of n and k of cryogels MAA/DMAEMA/AA

Amphoteric cryogels [MAA]/[DMAEMA]/[AA], %	n	k
20:20:60	0.31	1.72
20:60:20	0.26	1.57
60:20:20	0.27	1.52
40:40:20	0.27	1.42
45:15:40	0.23	1.62
15:45:40	0.27	1.77

According to [23], hydrogels swelling profile depends on the relative contribution of diffusion of liquid molecules and the relaxation processes of crosslinked polymer chains. If $n = 0.5$ the process of diffusion into the gel obeys Fick's law, if $n > 0.5$ then the abnormal liquid movement is happened, and for $n = 1$ the relaxation-controlled transport of water molecules to the volume of network. The abnormal value $n < 0.5$ indicates the applicability of Fick's law to describe the diffusion of water into the porous structure of cryogel. From the presented data of n and k (Table 2), it is determined that the diffusion mechanism of liquid diffusion in cryogels in ratios (%) 20:20:60, 20:60:20, 60:20:20, 40:40:20, 15:45:40, 45:15:40 obeys Fick's law.

Conclusion

Amphoteric cryogels based on methacrylic acid, dimethylaminoethylacrylamide and acrylamide monomers in ratios (%) 20:20:60, 20:60:20, 60:20:20, 40:40:20, 15:45:40, 45:15:40 were obtained.

The structure of cryogels by scanning electron microscopy was studied. The pore size varies from 6 and more microns.

The swelling degree and kinetics of cryogels were investigated. MAA/DMAEMA/AA cryogels is swelling up within 1–2 minutes. The diffusion mechanism of MAA/ DMAEMA/AA cryogels obeys Fick's law.

Obtained data represent scientific and practical interest. Cryogels based on methacrylic acid, dimethylaminoethylmethacrylate, acrylamide monomers exhibit high macroporosity, which is enabled to be used as catalysts in nanotechnology.

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Б.Х. Мұсабаева, С.Е. Құдайбергенов, Л.К. Оразжанова,
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Метакрил қышқылы, диметиламиноэтилметакрилат және акриламид негізіндегі криогельдердің микроқұрылымын, ісіну дәрежесі және динамикасын анықтау

Радикалдық полимерлену әдісімен 20:20:60, 20:60:20, 60:20:20, 40:40:20, 15:45:40, 45:15:40 (%) қатынастарда метакрил қышқылы, диметиламиноэтилметакрилат және акриламид негізінде крио-гельдер алынды. Электронды микроскопия әдісімен криогельдердің микроқұрылымдары зерттелді. Криогельдер жоғары макрокеуекті қасиетке ие. Криогельдердің сулы ерітіндідегі ісіну дәрежесі, динамикасы және судың криогель көлеміне диффузиялануы Фик заңына бағынатындығы анықталды.

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Определение микроструктуры, степени и динамики набухания криогелей на основе метакриловой кислоты, диметиламиноэтилметакрилата и акриламида

Методом радикальной полимеризации были синтезированы криогели на основе метакриловой кисло-ты, диметиламиноэтилметакрилата и акриламида в соотношениях (%) 20:20:60, 20:60:20, 60:20:20, 40:40:20, 15:45:40, 45:15:40. Исследована микроструктура криогелей методом электронной микроско-пии. Выявлено, что криогели обладают сверхмакропористостью. Определены степень и динамика на-бухания криогелей в водных растворах, выявлен механизм диффузии жидкости в объем криогеля. До-казано, что диффузия жидкостей в криогели подчиняется закону Фика.