



Investigation of the Properties of Hydrogels Based on Acrylic Acid and Diamines

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ABSTRACT

The electrochemical properties and swelling abilities of new hydrogels of acrylic acid derivatives in an aqueous solution, as well as their conformational transformations during the transition from one state to another, have been studied. The mutual influence of the physicochemical parameters of aqueous solutions, including electrical conductivity, pH media, and the swelling coefficient of hydrogels, has been studied. It has been established that during the ionization of hydrogels in an aqueous medium, intramolecular associates are formed with the participation of a proton and carboxylate anions, stabilized by hydrophobic interactions of the network structure of a sparsely crosslinked polyelectrolyte. It is shown that this process is accompanied by a sharp change in the pH values of the medium, an increase in the electrical conductivity and the swelling coefficient of the hydrogel in water.

Keywords:

hydrogel, electrical conductivity, aqueous solution, swelling coefficient, intramolecular associates, rare cross-linked structure

Introduction

Recently, polymer hydrogels (three-dimensional cross-linked systems based on polymers) have found wide application in various industries: construction, oil production, and agriculture as sorbents, filters, catalytic systems, and as hydro-swelling sealants [1–6]. Rarely crosslinked polymer hydrogels are chemical compounds consisting of a hydrophilic polymer network with long internodal chains and an aqueous component, the amount of which can vary over a wide range. One of the most unique properties of lightly crosslinked polymer hydrogels is their ability to swell strongly in water and aqueous solutions. The advantage of hydrogels is the possibility of preparing polymer-carriers with desired properties and their easy controllability by combining various types of active functional groups along macromolecular chains.

It is known [7–12] that some synthetic polymers, such as polyacrylic acid and its derivatives, are polyelectrolytes. The identification of regularities that relate the physicochemical properties of chain molecules with their structure, as well as the parameters characterizing the state of macromolecules in solution, can be useful in choosing a specific area of application of polymers.

A review of publications [7-12] showed that the attention of many scientists is focused on the study of the physicochemical properties of synthetic polymers, but very little has been studied, and there is no single approach to discussing the mutual influence of the obtained characteristics [13-17].

Cross-linked polyelectrolytes have several features. The high density of charged groups along the macro chain imparts certain electrochemical, hydrodynamic, and conformational properties to them [18], for

example, the mutual electrostatic repulsion of fixed charges unfolds the coils of macromolecules and increases their hydrodynamic dimensions. In this regard, it is important to study the mutual influence of the physicochemical properties and characteristics of rare cross-linked polyelectrolytes in an aqueous solution. The purpose of this work is to establish patterns of change and mutual influence of physicochemical properties and characteristics (electrical conductivity, pH environment, swelling and conformational transitions) of new rarely cross-linked polyelectrolytes based on acrylic acid and diamines in aqueous solution, as well as to study the water-retaining capacity and efficiency of new hydrogels in construction and agriculture.

Materials and methods

A copolymer of polyethylenediamidacrylate, acrylic acid, and ammonium acrylate (GPEA) was synthesized in an aqueous medium by radical polymerization of an acrylic acid monomer in the presence of a crosslinking agent of ethylenediamine and at a temperature of 343K. A redox system ($\text{Na}_2\text{S}_2\text{O}_3$ and $\text{K}_2\text{S}_2\text{O}_8$) was used as an initiator. A copolymer of hexamethylenediamidacrylate, acrylic acid, and ammonium acrylate (HPHA) was synthesized in an aqueous medium by radical polymerization of an acrylic acid monomer in

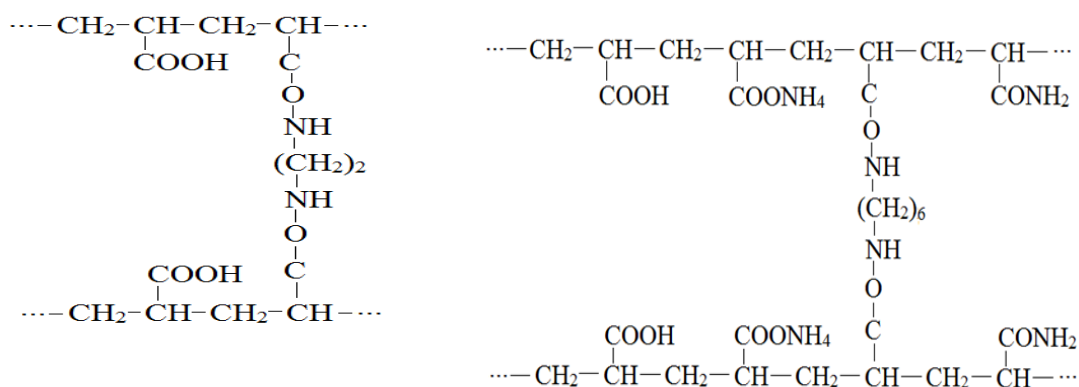
the presence of a crosslinking agent, hexamethylenediamine, at a temperature of 353K. The redox system ($\text{Na}_2\text{S}_2\text{O}_3$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$) was used as an initiator. The resulting hydrogels were purified from impurities, unreacted products, and soluble fractions of polymers by long-term washing in water under stationary conditions. In this case, polymer hydrogels are subjected to washing in washing columns.

Swellings (K_n) of hydrogels in an aqueous medium were determined by the gravimetric method, while the swelling coefficient was calculated using the formula $K_n = m_2 - m_1/m_1$. The electrical conductivity of aqueous solutions was measured on a Bante 510-DH digital stationary conductometer (Bante instruments). The pH of aqueous solutions was measured using a Metrohm 827 lab pH meter (Switzerland).

Results and discussions

The task of the study was to study the electrochemical and swelling properties hydrogels GPEA and GPHA in an aqueous solution, and also, based on the discovered relationship of the studied parameters, to characterize their conformational transformations in an aqueous medium.

The structure of rare cross-linked hydrogels can be represented as follows:



GPEA GPGA

GPEA and GPHA hydrogels are polyelectrolytes with the ability to conformational changes, due to the flexibility of their chains and the significant charge density of the chain in the ionized state. The specific electrical conductivity and pH media in the presence of a

hydrogel were studied GPEA in an aqueous solution as a function of time. The results of changes in the specific electrical conductivity and pH of the medium in the presence of GPEA hydrogel in an aqueous solution depending on time are shown in Figure 1 a, b.

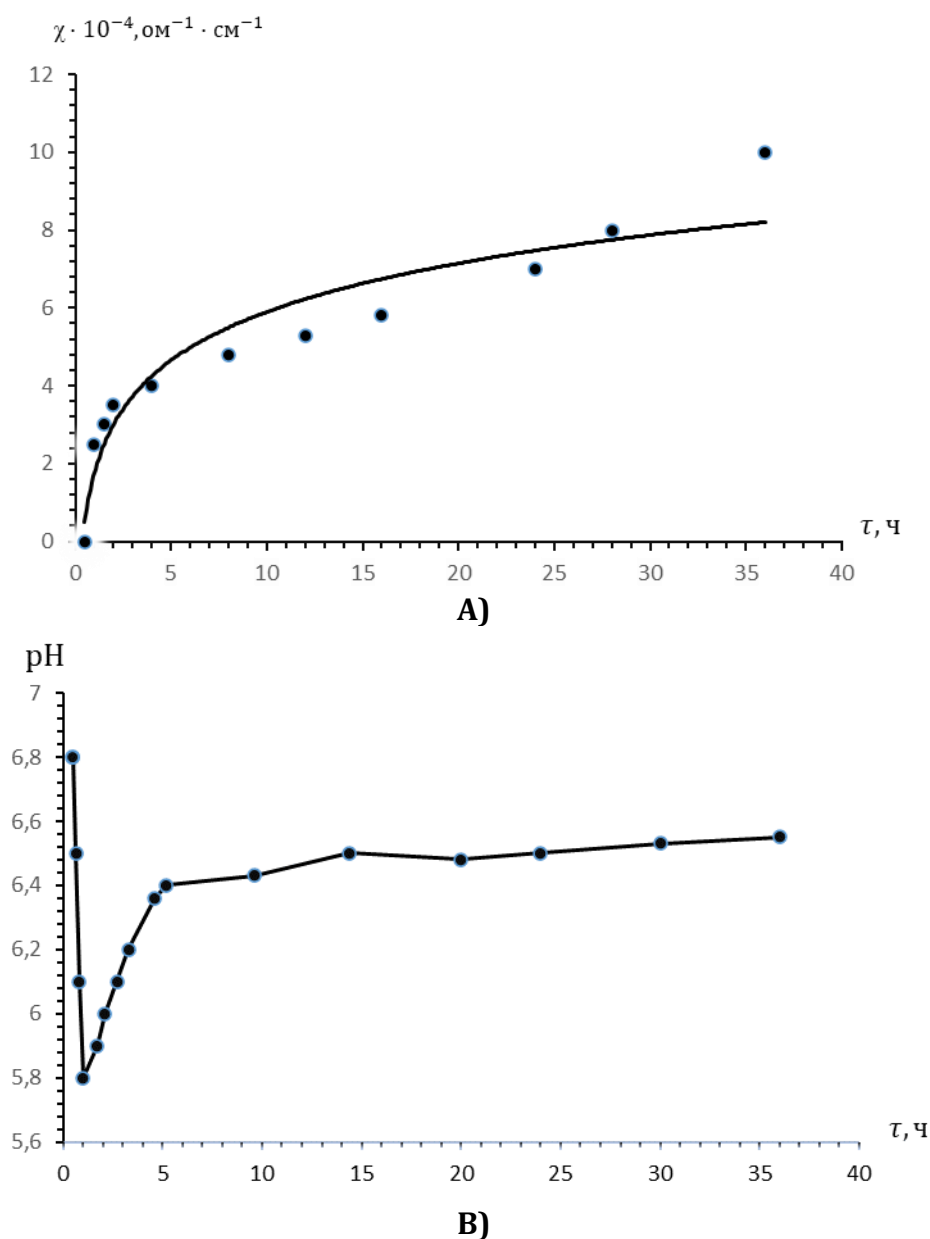


Fig1. Changes in specific electrical conductivity (a) and pH-medium (b) in the presence of GPEA hydrogel in aqueous solution as a function of time.

As follows from Fig. 1, the initial points of the graph show the concentration of the hydrogel, at which the properties of the electrolyte are rarely manifested. However, over the next 8 hours, there is a sharp increase in electrical conductivity due to the beginning of the interaction of the macromolecule with water. An increase in electrical conductivity indicates an increase in carboxylate anions in solution due to the dissociation of functional groups, which leads to an increase in the size of the crosslinked macromolecule.

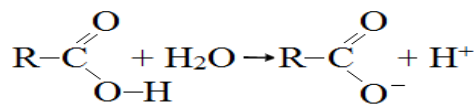
A slight increase in electrical conductivity in the time interval from 24 to 36 hours is due to the fact that GPEA is a weak acid and, as a result, its degree of dissociation is not high.

The smoothed nature of the curve of electrical conductivity versus time (Fig. 1) can be interpreted by the prevailing role of electrostatic repulsion between carboxylate anions, which prevents the polymer coil from folding.

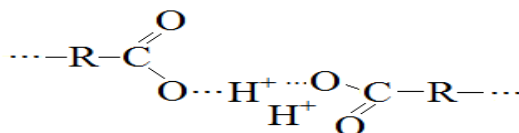
During the ionization of the GPEA hydrogel, the concentration of protons in the aqueous

medium sharply increases with the further formation of intramolecular associates, with the participation of the proton and carboxylate anions stabilized by the hydrophobic

interactions of the network structure of the crosslinked polymer. This process proceeds in two stages, which can be schematically displayed as follows:



(1)



(2)

This process is also affected by differences in the pH values of the aqueous medium in the presence of the hydrogel. The established regularity in electrical conductivity is confirmed by the nature of the change in the concentration of hydrogen ions in an aqueous hydrogel solution depending on time (Fig. 1b). The result obtained in Fig. 1 can be divided into two stages: the first stage—a sharp transition of a weak acid macromolecule from a folded conformation to an unfolded macromolecular coil; in this case, a sharp increase in acidity is observed due to the dissociation of carboxyl groups, as a result of which the concentration of protons in the aqueous medium increases sharply. The second stage begins with an increase in the pH of the medium, due to a decrease in the concentration of H^+ ions, associated with the destruction of previously formed intramolecular associates with the participation of two carboxylate anions and a proton.

It should be noted that carboxyl groups are located on a three-dimensional intertwined

polymer chain, and for the detachment of each next proton, additional work must be expended to overcome the forces of the electrostatic field created by neighbouring, previously dissociated groups. This means that the dissociation process will depend on the number of previously dissociated groups, so the increase in pH values after 24 hours is insignificant.

Thus, the nature of the conformational transformation of cross-linked GPEA macromolecules in water, which we assumed, is confirmed by a rather noticeable change in the hydrodynamic dimensions of the GPEA polyelectrolyte network. Due to the increase in electrostatic repulsion of like-charged chain links, the volume of cross-linked macromolecular coils increases.

The swelling of GPEA hydrogel in an aqueous medium was studied as a function of time. Figure 2 shows the swelling coefficient curve of GPEA hydrogel in an aqueous medium as a function of time.

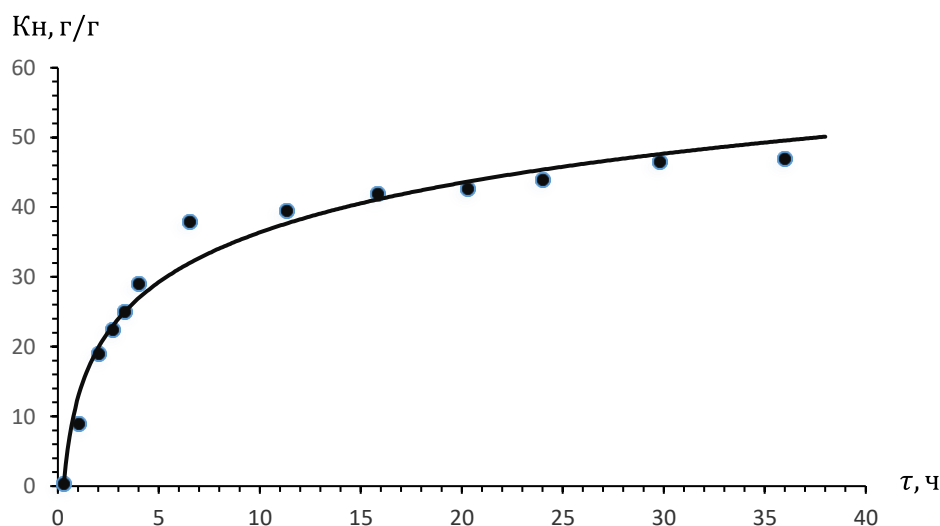
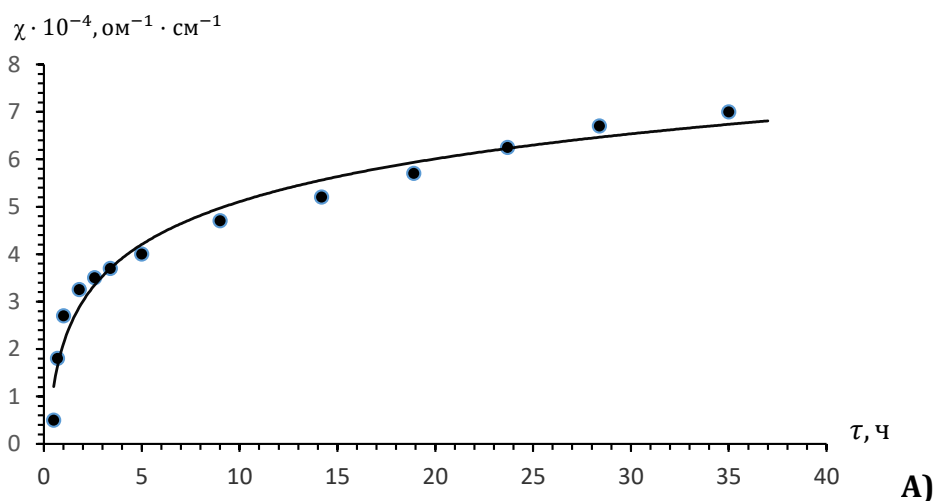


Fig. 2. Swelling coefficient of GPEA hydrogel in an aqueous medium depending on time

As can be seen from Fig. 2, the results obtained reflect two processes that are different in nature, which can be divided into two sections, complementing the results obtained by measuring the specific electrical conductivity and pH medium. As follows from Fig. 2, the initial part of the curve up to 6 hours shows the concentration areas of the aqueous solution in the presence of GPEA, in which the polyelectrolyte properties are still weakly manifested. From Fig. 2, it can be seen that the polyelectrolyte properties of GPEA increase within 6 hours. In the time interval from 6 to 24 hours, the curve shows the state of ionized cross-linked GPEA macromolecules. At the

maximum points of the obtained curve, the processes of dissociation and polyelectrolyte swelling of GPEA are balanced. The maximum value of the swelling coefficient of GPEA hydrogel (K_n) equal to 46 is reached after 36 hours.

The specific electrical conductivity and pH media in the presence of a hydrogel were studied GPGA in an aqueous solution as a function of time. The obtained results of changes in the specific electrical conductivity and pH-medium in the presence of a hydrogel GPGA in an aqueous solution depending on time are presented in Figure 3 a, b.



A)

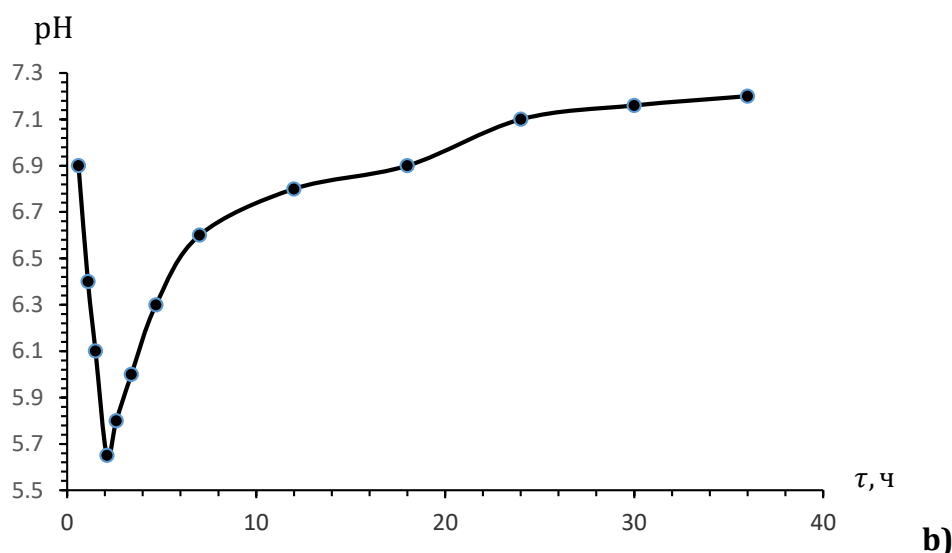


Fig. 3. Dependence of changes in specific electrical conductivity (a) and pH-medium (b) in the presence of GPHA in an aqueous solution as a function of time.

As can be seen from the results obtained in Fig. 3, the GPHA hydrogel showed lower electrical conductivity values (Fig. 3a) compared to the GPEA polyelectrolyte. Relatively low values of the electrical conductivity of GPHA (Fig. 3a) in relation to GPEA (Fig. 1a) can be justified by the presence of a bulky methyl substituent in the GPHA structure, which hinders the process of unfolding the macromolecular coil.

As can be seen from the results obtained in Fig. 3a, at the initial stage of the process, a decrease in the pH of the medium is observed due to a sharp increase in the concentration of H^+ ions in the aqueous solution. However, after the time of interaction of the GPHA hydrogel with the solution, the concentration of hydrogen ions decreases, associated with the destruction of previously formed intramolecular associates

with the participation of two carboxylate anions and a proton. For the GPGA-water system, an intensive increase in pH is observed within 10 hours. The reason for this process is the decay of associates within the macromolecule, followed by the addition of protons to the formed carboxylate anions. It should be noted that in this case, the intramolecular associates are stronger than in the GPEA hydrogel. This result is associated with a higher degree of hydrophobicity of the GPHA hydrogel.

The swelling of GPHA hydrogel in an aqueous medium was studied as a function of time. Fig. 4 shows changes in the swelling coefficient (K_n) of the GPHA hydrogel in an aqueous medium depending on time.

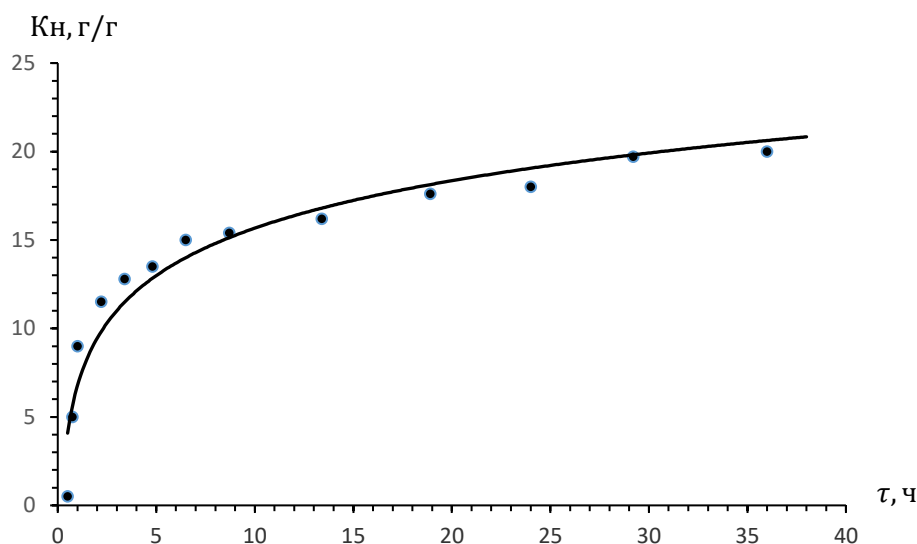


Fig. 4. Changes in the swelling coefficient (K_n) of the GPHA hydrogel in an aqueous medium depending on time.

As can be seen from the obtained results, there is an increase in the swelling coefficient of the hydrogel in an aqueous medium, which is associated with the ionization of the structured form of the GPHA hydrogel. In the next stages of the process, an increase in the swelling coefficient of the hydrogel in an aqueous medium with an increase in the charge on the chain is compensated by the unfolding of the macromolecular coil and an equilibrium state occurs in the hydrogel-water system. The obtained research results showed that the nature of the dependence curves of the studied physicochemical parameters is associated with a conformational change, which consists of the destruction of compact structures in the GPHA molecule in water. Upon ionization of the GPHA macromolecule, compact globules unfold to an expanded solvated coil. Therefore, the maximum value of the hydrogel swelling coefficient in the aquatic environment is 20. The effectiveness of the use of GPHA hydrogel in the cultivation of pistachio plantations on pebble lands was studied. The results of studies on the effectiveness of the use of GPHA hydrogel in the cultivation of pistachio plantations on pebble lands are presented in Table 1. As can be seen from the results

obtained in Table 1, the use of the GPHA preparation for pistachio cultivation in mountainous conditions makes it possible to reduce the multiplicity of care in the near-trunk circles by 5-6 times by preventing the appearance of weeds and keeping the soil in the near-trunk circles in an optimally loose state due to reduction of moisture consumption for physical evaporation in tree trunks. Also, the frequency of irrigation is reduced on average instead of 12 irrigations per growing season to 5-6 irrigations.

From the data of taxation indicators of annual plants obtained at the end of the growing season, there is a more intensive increase in their height and diameter in the variants of the experiment with the introduction of "HPHA", in comparison with the control (without the introduction of the drug). On average, their height, stem diameter and current linear growth exceeded the control ones by 14-16% (Table 1).

The observations of the intensity of pistachio transpiration in the variants of the experiment with the introduction of "HPHA" showed that in the first year after planting, young plants responded to improved moisture conditions by increasing their daily and seasonal indicators.

Table 1. Growth of one-year-old pistachio seedlings in the experimental variants with the use of the GPGA preparation.

Experience Variant	Annual seedlings		
	Height, cm	Diameter at the root collar, mm	The current linear increase in height, cm
0.2%	17.4-17.6	3.9-4.0	4.9-5.0
0.4%	21.2-21.4	4.3-4.4	8.7-8.8
Control	12.8-13.1	3.2-3.3	3.7-3.8

Transpiration intensity, compared with the control by 16-20%. Higher, compared with the control, indicators of transpiration intensity in pistachio seedlings with the introduction of "HPHA" led to an increase in the saturation of the leaves with water. On the variants of the experiment with the introduction of "HPHA", the water deficit at a concentration of a solution of 0.2% was 6.72%, at a concentration of a solution of 0.4% it was 5.5%, with the control variant it was 8.24%. According to the results of field tests of "GPGA", it can be stated that the technology of its use in growing pistachio plantations on pebble lands is promising. And GPEA and GPHA can be used to make hydro-swellable seals. For example, when mixing elastomer (natural rubber) and hydrogels GPEA or GPHA improves their mechanical properties. The resulting compositions can be used for sealing pre-cast concrete drainage pipes and precast concrete manhole rings, sealing against penetration of pipe inlets, public utilities, etc.

Conclusion

The specific electrical conductivity and pH media in the presence of a hydrogel were studied GPEA and GPGA in an aqueous solution as a function of time. Studied swelling of GPEA and GPHA hydrogels in an aqueous medium as a function of time. It has been established that the state of the cross-linked polyelectrolyte structure of the new GPEA and GPHA hydrogels is determined by the electrostatic interaction of charged groups. The presence of electrostatic repulsion forces between similarly charged groups of the studied hydrogels leads to a sharp change in the spatial arrangement of chains between the crosslinking sites and a change in the conformation of the

macromolecular coil. Mutual influences of physicochemical parameters (electrical conductivity, pH medium, and swelling coefficient) in the presence of new GPEA and GPHA hydrogels in an aqueous solution have been established. It has been shown that during the ionization of hydrogels in an aqueous medium, intramolecular associates are formed with the participation of a proton and carboxylate anions, stabilized by hydrophobic interactions of the network structure of a rare cross-linked polyelectrolyte. This process is accompanied by a sharp change in the pH values of the medium, an increase in the electrical conductivity and the swelling coefficient of the hydrogel in water. The good efficiency of using GPHA hydrogel in growing pistachio plantations on pebble lands and for sealing building materials has been established.

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