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## MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

# Effect of External Factors on the Swelling of Hydrogels Based on Poly(ethylene glycol) Maleate with Some Vinyl Monomers

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**Abstract**—Effect of the pH of the medium, temperature, and nature of solvents and inorganic salt on the behavior of hydrogels based on copolymers of poly(ethylene glycol) maleate with acrylic and methacrylic acids and acrylamide was studied. It was shown experimentally that the susceptibility of the hydrogels to changes in the factors mentioned above, depending on the nature of a comonomer.

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Recent years have been characterized by a clearly pronounced tendency toward wider use of special-purpose polymeric materials in chemistry of macromolecular compounds. That is why the attention of researchers developing new effective compounds with specific properties has been attracted by the so-called "intellectual" polymers.

To "intellectual" polymers with network structure are attributed materials that can change in a preprogrammed way their size under the action of external factors, such as temperature, pH of the medium, ionic strength and nature of a solvent, etc. Materials of this kind can be used in biochemical and biotechnological research and modeling of regulation processes in living cell, associated with phase transitions in membranes [1].

Network polymers provide unlimited opportunities for control over their properties by inclusion of functional groups adequately responding to changes in external conditions into their macroscopic networks. Presence of particular functional groups in the networks predetermines their susceptibility to certain external treatments [1–4].

In this context, a search for new monomers with appropriate functional groups in order to obtain polymers with high water-swellability is a topical task.

Of considerable interest as potential moisture sorbents are copolymers based on unsaturated polyester resins curable at low temperatures [5]. There is published evidence about copolymerization of styrene with a number of polymaleates and polyfumarates to give products having various physicomechanical properties [6]. At the same time, no data are available for copolymerization of unsaturated polyester resins and, in particular, those based on maleic acid and ethylene glycol with a number ionogenic monomers, which can serve as moisture sorbents owing to the favorable hydrophilic-hydrophobic balance.

The goal of this study was to examine the effect of external factors on the behavior of new hydrogels based on copolymers of poly(ethylene glycol) maleate (*p*-EGM) with acrylic (AA) and methacrylic (MAA) acids and acrylamide (AAm) and to search for practical areas of their application.

## EXPERIMENTAL

Poly(ethylene glycol)maleate was produced by polycondensation of maleic acid and ethylene glycol at a temperature of 393–403 K [7], with the reaction course monitored by determining the acid number.

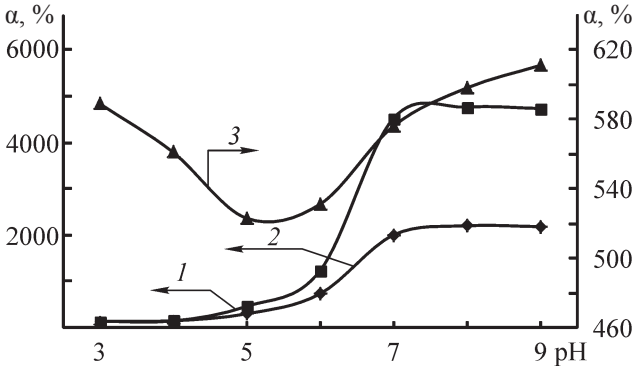


**Fig. 1.** Effect of the pH of the medium on the behavior of hydrogels based on copolymer of p-EGM with (*1*) AA, (*2*) MAA, and (*3*) AAm. (α) Degree of swelling.

The molecular masses of p-EGM, found from the volume of released water and determined by the light-scattering method [8, 9] on a 2100 NACH nephelometer, well converge: 8420 a.m.u.

The copolymers of p-EGM with AA and MAA were synthesized by radical copolymerization in mass in the presence of an initiator [DAA] = 8 mol $m^{-3}$ at an initial *p*-EGM : vinyl monomer ratio of 15 : 85 (wt %) and temperature of 333 K. Light yellow powder copolymers were obtained with the AA and MAA contents of 70.8 and 62.7 wt %, respectively.

The copolymers of p-EGN with AAm were synthesized by copolymerization in a dioxane solution in the presence of an initiator, [DAA] = 8 mol $m^{-3}$, at a starting component ratio of 15 : 85 (wt %) and a temperature of 333 K. The thus synthesized copolymer is a white powder substance with 88.6 wt % AAm units [11].

Gel samples were washed with distilled water during 10 days, transferred to a Petri dish, and kept at 313 K in a drying box under reduced pressure to constant mass.

The pH values were adjusted with buffer solutions and measured with an I-160 MI ion meter with an ESK-10601/7 combined electrode.

The equilibrium degree of swelling was determined gravimetrically with an LV-210 electronic balance [12].

The susceptibility of ionogenic polymers to changes in the pH of the medium is one of their most important properties used in practice [13]. It is known from the literature that hydrogels containing residual amounts of a weak acid commonly swell in an alkaline medium [14].

Figure 1 shows how the degree of swelling of the hydrogels based on copolymers of *p*-EGM with AA and MAA depends on the pH of the medium.

For example, hydrogels of copolymers of p-EGM

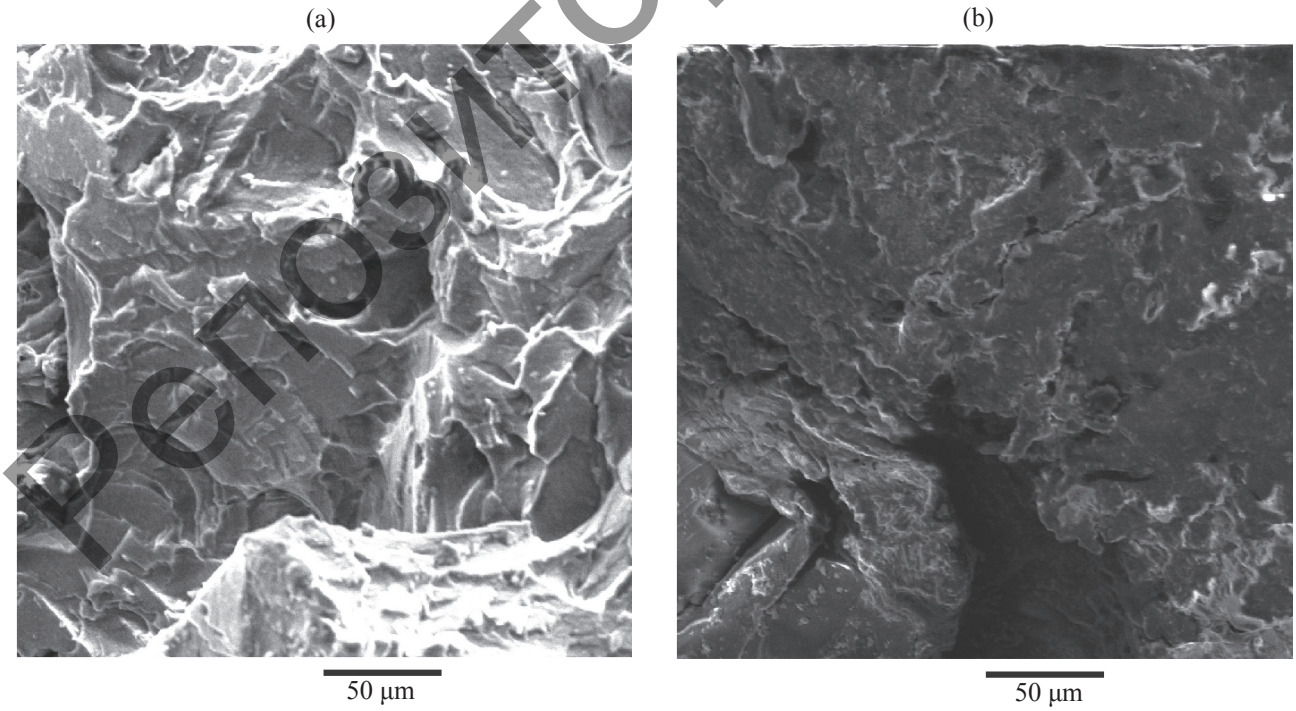


**Fig. 2.** SEM images of cross-linked polymers. (a) *p*-EGM–MAA, 37.3 : 62.7 (wt %). (b) *p*-EGM–AA, 29.2 : 70.8 (wt %).

with acrylic and methacrylic acids are collapsed to the greatest extent at low pH values. Raising the solution pH substantially enhances the capacity of a copolymer for moisture absorption' as a result, the overall size of the hydrogels sharply increase. The curve describing the dependence shows in the pH range 5–7 a stepwise increase in the degree of swelling of the copolymers, which has the form of a bulk phase transition. Further shift of the pH into the alkaline region has no significant effect on the conformation of molecules of the water-swollen network polymer. It is also noteworthy that the moisture-absorption capacity of the *p*-EGM–MAA copolymer is twice that of the copolymer with AA. Scanning electron microscopic images of these copolymers (Fig. 2) demonstrate that the *p*-EGM–MAA copolymers have a more porous structure than the p-EGM–AA copolymers.

Presumably, the methyl group in the MAA molecule causes a steric hindrance, which precludes formation of compact structures.

Thus, the hydrogels of copolymers of *p*-EGM with AA and MAA behave as typical polyelectrolytes containing ionized acid groups covalently bound to the backbone. The key factor predetermining the swelling of the gels under study is the electrostatic repulsion of like charged COO– groups. In an acid medium, owing to the excess of hydrogen ions, dissociation of carboxy groups is suppressed and subchains are close to the maximum possible extent, i.e., their more compact conformation is formed, which leads to a collapse of the polymeric gel.

An increase in the pH of the medium to above a certain critical range stimulates dissociation of carboxy groups and thereby promotes repulsion of macromolecules with like-charged functional groups.

The fundamental aspects of the interaction of low-molecular compounds with cross-linked polymers are also a question of interest for researches working in the field of chemistry and physics of polymers.

Figures 3 and 4 show how mono- and divalent salts affect the swelling capacity of hydrogels based on copolymers of p-EGM with AA and MAA, respectively.

It follows from the data presented above that the samples under study of *p*-EGM–AA and *p*-EGM–MAA hydrogels behave similarly in the presence of mono- and divalent salts. With increasing molar content of low-molecular salts, contraction of samples is observed in the system. It should be noted, however, that the contraction of the gels occurs at lower concentrations upon addition of $CaCl_2$. This is due to the divalence of $CaCl_2$ ions, which causes binding of a larger number of carboxy groups and results in the formation of additional cross-links in the network.

It is known that one more factor that can strongly and reversibly affect the overall size of gels is the solvent quality [15]. A hydrogel swells in a thermodynamically good solvent and collapses in a bad solvent.

We studied how the composition of a mixed aqueous-organic solvent affects the swelling of the samples under consideration (Figs. 5–7). It can be seen from the experimental data that the curves describing the dependence of the degree of swelling on the fraction n0 of the organic solvent exhibit a behavior typical of polymer networks with charged subchains.

The network collapse observed in the study upon addition of polar solvents and, in particular, ethanol, dimethylformamide, and dimethyl sulfoxide, occurs as a first order transition. At the same time, the highest

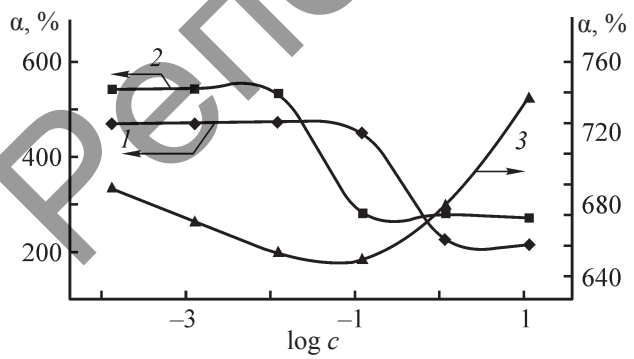


**Fig. 3.** Degree of swelling, α, of hydrogels based on copolymer of p-EGM with (*1*) AA, (*2*) MAA, and (*3*) AAm vs. the NaCl concentration *c*, M.

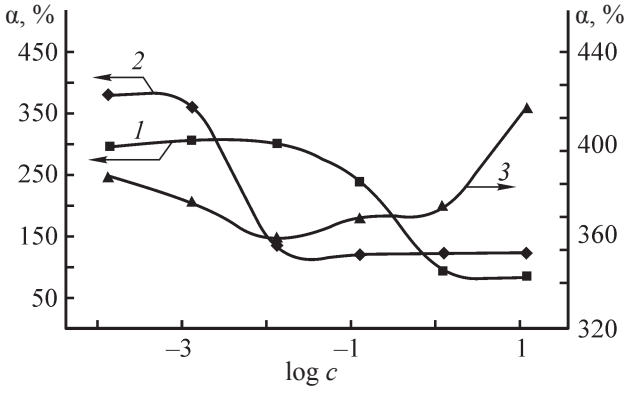


**Fig. 4.** Degree of swelling, α, of hydrogels based on copolymer of *p*-EGM with (*1*) AA, (*2*) MAA, and (*3*) AAm vs. the $CaCl_2$ concentration *c*, M.

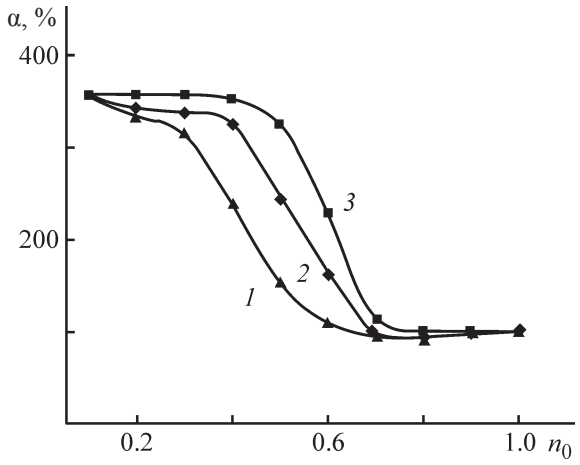


**Fig. 5.** Effect of the composition of (*1*) water–ethanol, (*2*) water–DMFA, and (*3*) water–DMSO solvents on the swelling of the hydrogel based on the *p*-EGM–AA copolymer. (α) Degree of swelling and ($n_0$) fraction of the organic solvent; the same for Figs. 6 and 7.

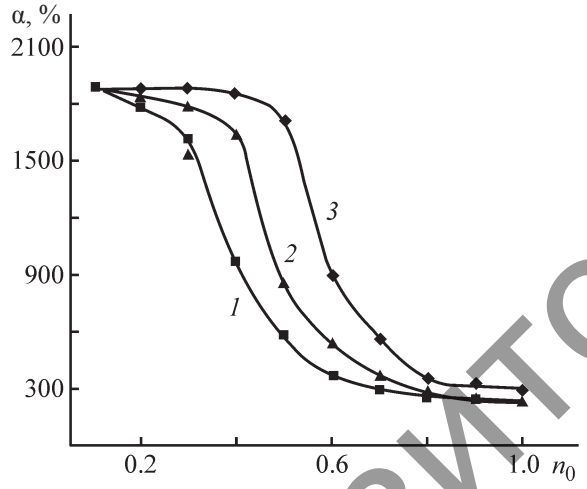


**Fig. 6.** Effect of the composition of (*1*) water–ethanol, (*2*) water–DMFA, and (*3*) water–DMSO solvents on the swelling of the hydrogel based on the *p*-EGM–MAA copolymer.

susceptibility of the samples under consideration to the quality of an organic solvent grows within the range 0.2–0.5 vol. fraction, depending on the nature of the solvent. It is known that the main characteristics of the polarity of a solvent are the dielectric constant and the dipole moment of the medium. The solvents can be arranged in order of these parameters as DMSO > DMFA > ethanol.

It should be noted that the collapse of the copolymers under study in the solvents under consideration occurs in the reverse order. The *p*-EGM–MAA copolymer can sorb a larger amount of water than the copolymer with AA, despite the stronger hydrophilicity of the latter. In all probability, this is due to the smaller number

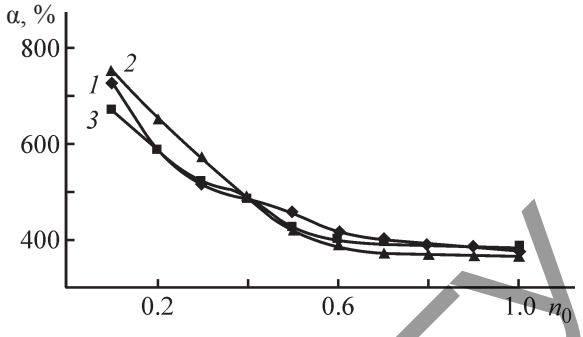


**Fig. 7.** Effect of the composition of (*1*) water–ethanol, (*2*) water–DMFA, and (*3*) water–DMSO solvents on the swelling of the hydrogel based on the p-EGM–AAm copolymer.

of hydrophobic MAA units is incorporated into the copolymer and to the higher affinity of MAA to the organic medium, compared with the acrylic acid.

In a study of the behavior of the hydrogel based on *p*-EGM–AAm copolymer with varying pH of the medium, we observed an extremal run of the curve describing this dependence, with a minimum in the acid medium.

It is known that polyampholyte gels swell upon acidification or alkalization. Intermediate pH values provide an equimolar ratio between the negatively and positively charged units, which corresponds to the isoelectric point characterized by the most contracted state of the gel. The run of the curves describing the dependence of the swelling of the *p*-EGM–AAm hydrogel on the pH of the medium (Fig. 1) points to its polyampholyte state due to the partial hydrolysis of acrylamide groups to give amine groups, as shown in [16]. The sufficiently high content of AAm in the copolymer presumably leads to a pronounced hydrolysis of these groups and is responsible for the pronounced extremum in the curve of the dependence, with the minimum swelling at the nearly acidic pH of the medium. There occurs dissociation of $NH_3^+$ groups, which leads to contraction of the polymer network. This can be attributed to a decrease in the osmotic pressure of counter-ions and to a significant increase in the Coulomb attraction of oppositely charged units.

The results of the study are indicative of the strong influence exerted on the swelling of *p*-EGM–AAm copolymers by inorganic salts present in the aqueous medium (Figs. 3 and 4).

The behavior of *p*-EGM–AAm hydrogels in a salt solution can be attributed on the basis of the experimental data (Figs. 3 and 4) neither to the polyampholyte nor

polyelectrolyte mode. Introduction of an inorganic salt into the external solution leads first to a decrease in the size of the polymer network sample to a certain minimum, and then to its decrease.

The curve describing the dependence of α on the logarithm of the salt concentration can be conditionally divided into two portions. The first of these corresponds to the contraction of a sample upon addition of a comparatively small amount of the salt. The second portion reflects a certain increase in the network size upon further addition of the salt. The first portion of the curve describing the dependence of the network size on the salt concentration resembles the polyelectrolyte mode, and the second, the polyampholyte mode. This is possible when the macromolecular network contains, together with the oppositely charged groups, an excess amount of one of the charges. As shown above, the source of the oppositely charged groups is the keto-imide bond of units in AAm. Like-charged groups may appear as a result of a partial hydrolysis of acrylamide units in the macrochain, as confirmed by Tanaka [17]. Consequently, the behavior of the gel in the initial stage obeys the polyelectrolyte mode. Introduction of a low-molecular salt leads to contraction of the polymeric network, presumably because like-charged parts of the chain, due to the hydrolysis of acrylamide units, are shielded and repulsion forces between these parts become weaker. In the next stage, when most of effective chain portions determining the electrolyte behavior of the gel are shielded, the behavior of the gel in solution enters the next phase. The salt present within the gel shields the attraction of the oppositely charged $–NH_3^+$ and $–COO^–$ units and the hydrogel swells under the action of the thrusting osmotic pressure of counter-ions.

Thus, with increasing concentration of both mono- and divalent salt, the acrylamide gel undergoes a swelling–collapse–swelling reversible phase transition.

The behavior of hydrogels based on *p*-EGM–AAm was studied in mixtures of aqueous-organic solvents (DMSO, DMFA, and ethanol). The results obtained (Fig. 7) demonstrate a higher degree of swelling of *p*-EGM–AAm copolymers in an aqueous medium, compared with that of organic nature, which well accounts for the gradual contraction of the polymer network with increasing fraction of the organic solvent in the binary mixture.

It should be noted that the lower polarity of ethanol results in that the hydrogels under study are the most globular in the aqueous-ethanolic medium, with the most pronounced contraction of polymer networks observed for all the aqueous-ethanolic mixtures under study in the range 0.1–0.6 vol. fraction.

The collapse of polymer networks, observed as the content of the organic solvent in the aqueous-organic mixture is raised, occurs in the continuous mode due to the attraction of the hydrophobic fragments of macromolecules, rather than in the discrete mode.

Thus, copolymers based on poly(ethylene glycol) maleate with acrylic and methacrylic acids are susceptible to changes in the pH of the medium, ionic strength of the solvent, and its quality.

One of practical application areas of the hydrogels we synthesized is to optimize the physical state of soils. Presently, this problem has received further impetus to development due to the formation of a separate soil-ecological area of research: construction of soils with prescribed technological characteristics to provide sustainable farming, functioning of city landscapes and elements of these, as well as other objects with increased anthropogenic impact and technogenic load.

In this context, we studied the effect of *p*-EGM–MAA (SP1) and *p*-EGM–AA (SP2) copolymer as sorbents on the germinative capacity, growth, and sprouting of seeds and shoots of common pine and shoots of aster and domestic lily. A comparative analysis of seed and shoot sprouting under ordinary conditions and in the presence of a hydrogel demonstrated a positive effect of copolymer of poly(ethylene glycol) maleate with acrylic and methacrylic acids on the plant parameters being tested: a higher sprouting energy and earlier appearance of shoots were observed, which favored an increase in productivity due to the improved natural aeration of soil.

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