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*Article*

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# The Effect of Liquid Active Media on the Character of Equilibrium Swelling of Copolymers Based on Polypropylene Fumarate Phthalate with Acrylic Acid

The article is devoted to the study of the influence of external factors on copolymers based on poly(propylene fumarate phthalate) with acrylic acid. In the present work, the effect of low-molecular salts on the swelling rate of the synthesized copolymers was studied. The surface morphology was examined using SEM. The swelling rate of the studied polymers depends on many factors, including the nature of the polymer and the solvent, the presence of electrolytes, changes in pH and ambient temperature, the molecular weight of the polymer, etc. It is assumed that the polymer network of copolymers mainly consists of links of unsaturated polyester resin. The results show that the ratio of monomer units in the copolymer significantly affects the susceptibility of the polymer gel to the presence of low-molecular salts. Changing the properties of the comonomer has been shown to produce hydrogels that can swell or collapse due to changes in ionic strength or the thermodynamic quality of the solution. By varying the ratio of the comonomeric units, the intervals of swelling and contraction of polymer meshes inherent in polyelectrolyte bodies with the same charges were adjusted. It was also found that the polymers under consideration belong to anionic meshes.

*Keywords:* polypropylene fumarate phthalate, low-molecular weight salts, discreteness, anionic meshes, acrylic acid, radical copolymerization, polar organic solvents, swelling, collapse, unsaturated polyester resin.

## *Introduction*

Nowadays significant effort is made to study and synthesize copolymeric materials sensitive to ambient environment changes. Distinguishable compounds of this kind are “smart” polymers which are negatively sensitive to environment changes (pH, solution ionic strength, temperature, light, electromagnetic impact etc.) and are characterized by first stepped phase shift with rapid change of macromolecule volume fraction. Multiple researches have been dedicated to studying “smart” polymers; however, there is no information on unsaturated polyester resins-based copolymers study and synthesis prior to our research. That being said, unsaturated polyester resins-based copolymers study is of theoretical and practical interest because of their simplicity and efficiency as well as the presence of unsaturated ethylene bonds allows obtaining cross-linked polymers by reacting with ionogenic monomers. Such materials can keep their properties in high temperatures, aggressive environments, humidity and other destructive factors [1–4]. It is stated in [5] that the presence of a low-molecular salts component in the solution can cause either swelling or collapsing of the polymer network.

According to data [6–13], adding low-molecular salt has a significant influence on polyelectrolyte gels which leads to shielding of effects related to the charge state of the network. This suggests that the nature of the cross-linked polymer interaction with mono- and polyvalent salt ions depends on its chemical composition. This makes further work in this area promising.

The purpose of the research was to study the swelling process of p-PFPh:AA polymers depending on various aqueous solutions and properties of technological medium, to study the water-binding properties of p-PFPh:AA components during swelling at different temperatures.

## *Experimental*

Synthesis of poly(propylene fumarate phtalate) and copolymers based on it was described in authors’ previous works [14–15].

Aqueous solutions of low-molecular weight salts (LMS) were prepared in calculated amounts to determine the swelling rate of copolymers in solutions.

$CuSO_4$, $FeCl_3$, and $Pb(NO_3)_2$ were used as low-molecular weight salts.

Table 1

**Concentration of low-molecular weight salts solutions (per 100 ml)**

| Concentration, mol/l (100 ml) | | | | |
|---|---|---|---|---|
| $CuSO_4$, g | $1.60 \cdot 10^{-3}$ | $1.60 \cdot 10^{-2}$ | $1.60 \cdot 10^{-1}$ | 1.60 |
| $FeCl_3$, g | $1.62 \cdot 10^{-3}$ | $1.62 \cdot 10^{-2}$ | $1.62 \cdot 10^{-1}$ | 1.62 |
| $Pb(NO_3)_2$ | $3.31 \cdot 10^{-3}$ | $3.31 \cdot 10^{-2}$ | $3.31 \cdot 10^{-1}$ | 3.31 |

The equilibrium swelling rate of p-PFPh based copolymers with acrylic acid in the low-molecular salts solution was also determined gravimetrically [16].

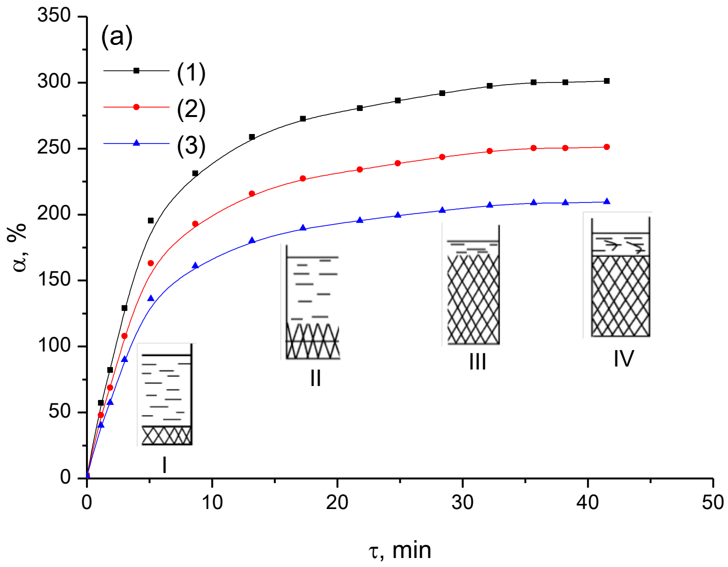
The degree of polymer swelling was measured gravimetrically [17]. The dry polymers ($m_0$) were incubated in salt solution, and their swollen masses (m) were recorded after 24 h. All samples were taken in samples to reduce errors. The swelling ratio (α) of polymers was calculated by:

$$SR(\%) = \alpha = \frac{m_s - m_d}{m_d}.$$

The morphology of the polymers was observed using a scanning electron microscope (SEM, Auriga Crossbeam 540, Carl Zeiss).

### *Results and Discussion*

The swelling rate of polymers (p-PFPh:AA) is important for studying the swelling processes. Knowing its value will allow predicting the behavior of polymers in various liquid media.



*1* — 6.77:93.23; *2* — 44.17:55.17; *3* — 86.67:13.33

Figure 1. Dependence of the degree of swelling on the contact time of p-PFPh:AA copolymers with tap water (pH 7.1) at reference ratios $M_1$:$M_2$, mol. %

As can be seen from the data presented in Figure 1, the kinetic curves of the degree of swelling dependence on the contact time of p-PFP:AA copolymers with tap water (pH 7.1) corresponded to the process of limited swelling. The curves showed a linear increase in swelling during the first 5 minutes, which was characteristic of the hydration stage and formation of the bound water layer, further gradual increase in the degree of swelling up to the maximum value corresponded to the osmotic stage, when free water diffused into the polymer matrix until reaching equilibrium and the swelling limit.

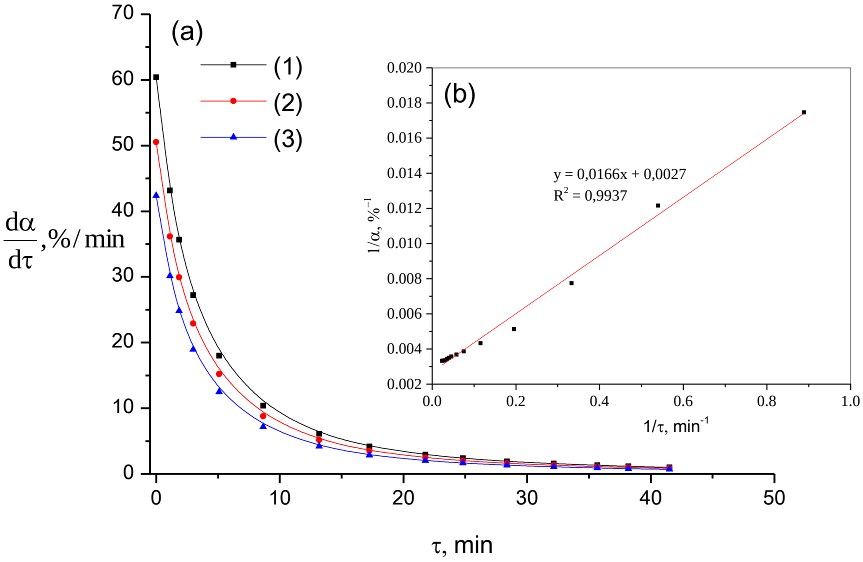
The kinetic curves (Fig. 1) in the coordinates of the degree of swelling versus contact time of p-PFP:AA copolymers with tap water (pH 7.1) are described by the equation:

$$\alpha = \alpha_{\max} \cdot \frac{i \cdot \tau}{1+(i \cdot \tau)}, \tag{1}$$

where $\alpha_{\max}$ is the maximum degree of swelling (%); $\tau$ is the time (min); $i$ is the empirical constant.

To determine the constants included in the equation data (1), the dependence $\alpha = f(\tau)$ is approximated and then plotted in coordinates $d\alpha/d\tau$ from $\tau$. The result is a dependence of the swelling rate on the swelling time (curve *a*, Fig. 2). Calculation of constants ($\alpha_{\max}$ and $i$) is performed using a graphoanalytical method. To do this, the experimental data (Fig. 2, *a*) are reconstructed into coordinates $\frac{1}{\alpha} - \frac{1}{\tau}$ (curve *b*, Fig. 2) and described by the equation:

$$\frac{1}{\alpha} = \frac{1}{\alpha_{\max}} + \frac{1}{\alpha \cdot i_{\max}} \cdot \frac{1}{\tau}. \tag{2}$$

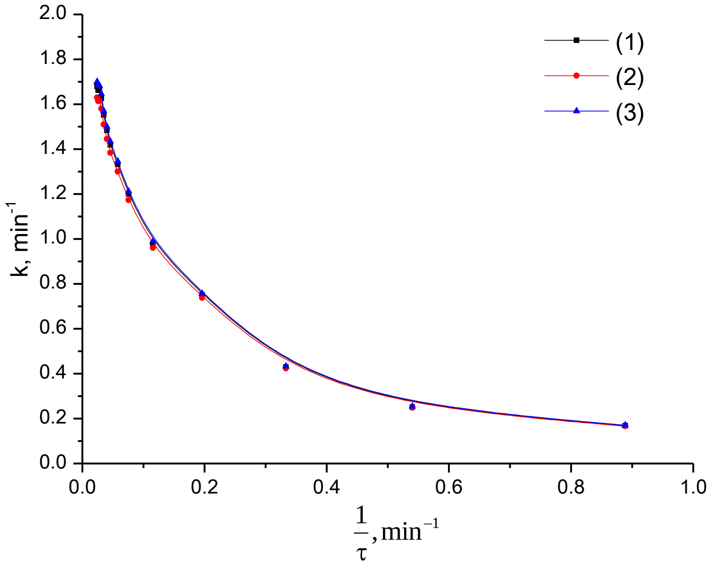


*1* — 6.77:93.23; *2* — 44.17:55.17; *3* — 86.67:13.33

Figure 2. Diagram of constants determination for graphoanalytic approximation method p-PFPh:AA copolymers at initial ratios of M1:M2, mol.%

When extrapolating (Fig. 2, *b*) $\frac{1}{\tau} = 0$ the maximum swelling of the p-PFPh:AA copolymer is determined (6.77:93.23 mol.%) $\alpha_{\max} = 370.34$ %, and the tangent of the slope angle is a straight empirical constant $i = 0.16$. From the data presented in Figure 2, (curve, *a*) it can be seen that the swelling rate is determined by the diffusion of solvent molecules in the p-PFPh:AA copolymer, then swelling can be described by first-order kinetic equations analogous to chemical reactions of type A→B, that is, the rate of swelling $\frac{d\alpha}{d\tau}$ will be directly proportional to the degree of swelling $\frac{d\alpha}{d\tau} = k(\alpha_{\max} - \alpha)$.

The average rate of the process was calculated using the formula obtained by differentiating Equation 1: $\frac{d\alpha}{d\tau} = \frac{\alpha_{\max} \cdot i}{(1+i \cdot \tau)^2}$ (Fig. 2, *a*). Analysis of the obtained data showed (Fig. 2, a) that with an increase in the contact time of the p-PFPh:AA copolymer (6.77:93.23 mol.%) with tap water (pH 7.1) the swelling rate decreased and after 17 minutes decreased significantly to 4.15 %/min. This indicated that during this time of contact $\frac{d\alpha}{d\tau}$ tends to zero and the process reaches equilibrium, and $\alpha$ becomes constant and reaches the maximum value. Analysis of kinetic calculations showed (Fig. 3) that the swelling process of p-PFPh:AA copolymers in tap water proceeded at a sufficiently high rate ($\bar{k}$ = 9.72·$10^2$ $s^{-1}$). It should be noted (Fig. 1) that the contact time of the p-PFPh:AA copolymers with tap water, during which the maximum degree of swelling is achieved, is fast enough (5–10 minutes), which indicates the hydrophilic nature of the components included in the p-PFP: A copolymer in a ratio of 6.77:93.23 mol.%.



*1* — 6.77:93.23; *2* — 44.17:55.17; *3* — 86.67:13.33

Figure 3. Dependence of swelling rate constant on time for p-PFPh:AA copolymers at initial ratios of $M_1$:$M_2$, mol.%

In order to verify the correctness of the obtained data, we made an attempt to match experimental kinetic curves with calculated ones using mathematical technique. The possible form of kinetic curves, i.e. the dependence α = *f* (τ) of the p-PFPh:AA copolymers (6.77:93.23 mol.%) is shown in Figure 4.

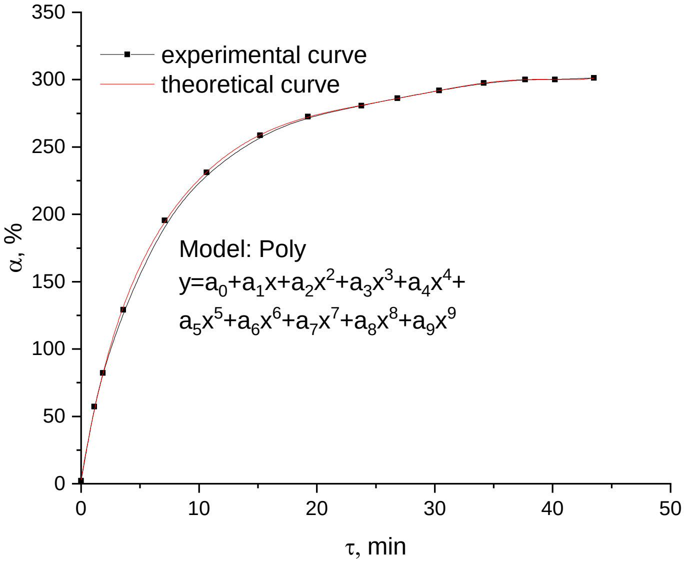


Figure 4. Experimental and calculated dependence of the degree of swelling on contact time of p-PFPh:AA copolymer with tap water (pH 7.1) at initial ratios of 6.77:93.23 mol.%

As can be seen from Figure 4, the p-PFPh:AA (6.77:93.23 mol.%) swelling degree values calculated by model function — Poly(function type: $y=a_0+a_1x+a_2x^2+a_3x^3+a_4x^4+a_5x^5+a_6x^6+a_7x^7+a_8x^8+a_9x^9$)

have satisfactory similarity with the experimental data, the same pattern is typical for other p-PFPh:AA copolymer with reference ratios of 44.17:55.17 mol.%; 86.67:13.33 mol.%.

As a further investigation of the swelling kinetics of p-PFPh:AA copolymers, we predicted swelling rates in the temperature range of 291, 295 and 303 K when exposed to salt and fresh water (Fig. 5, Table 1).

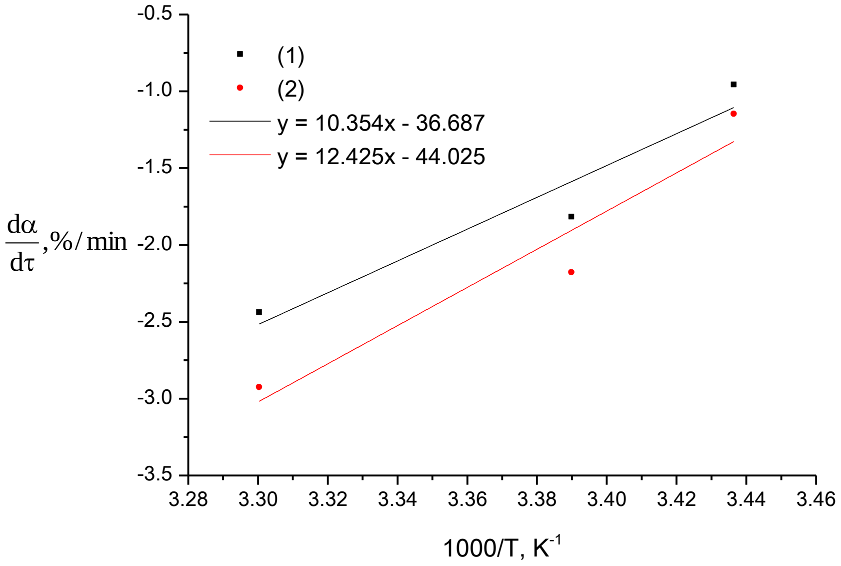


Figure 5. Dependence of swelling rate on inverse temperatures in fresh (1) and salty (2) water

Table 2

**Values of physical constants of p-PFPh: AA copolymers**

| Ratio $M_1$:$M_2$, mol. % | Liquid medium | Type of impact | $E$, kJ mol$^{-1}$ | $A$, min$^{-1}$ |
|---|---|---|---|---|
| 6.77:93.23 | Fresh water | swelling | 86.08 | $8.57 \cdot 10^{15}$ |
| | Salt water | | 103.30 | $1.32 \cdot 10^{19}$ |
| 44.17:55.17 | Fresh water | | 61.49 | $6.12 \cdot 10^{15}$ |
| | Salt water | | 77.67 | $9.91 \cdot 10^{18}$ |
| 86.67:13.33 | Fresh water | | 40.61 | $4.04 \cdot 10^{15}$ |
| | Salt water | | 44.34 | $5.91\ 10^{18}$ |

Table 2 shows that the swelling characteristics of the p-PFPh:AA copolymers depend on the polymer mesh density and water composition. As shown in Table 2, when the p-PFPh:AA copolymer (at a ratio of 6.77:93.23 mol.%) swells in salt water, the invariant kinetic parameters have high values of $E = 103.30$ kJ·mol$^{-1}$ and $A = 8.57 \cdot 10^{15}$, which indicates a greater rate of their swelling. For the p-PFPh:AA copolymer (at a ratio of 86.67:13.33 mol.%) the swelling activation energy is low.

For comparative analysis, the surface morphologies of the p-PFPh AA copolymers were investigated before (Fig. 6, (*a* and *b*)) and after swelling (Fig. 6, (*c* and *d*)) (Fig. 6).

The study of the surface morphology of the copolymer showed that the latter is a rather complex structurally morphological organization. During cryostructuring, copolymers with a characteristic openwork structure with a large pore content were formed (Fig. 6, *a* and *b*), and systems in a different phase of circulation — after swelling (Fig. 6, *c* and *d*), in the structure of which the main field of the pattern was occupied by a large number of smaller macropores.

Considering that the existing types of superabsorbents cannot be used effectively enough in the climatic conditions of arid zones, since they do not have sufficient thermal stability required for their use at temperatures above 35 °C, and at the same time, these products are highly sensitive to changes in ionic composition and soil pH, therefore, there has been a need to study the effect of inorganic salts on the swelling of p-PFPh:AA polymers.

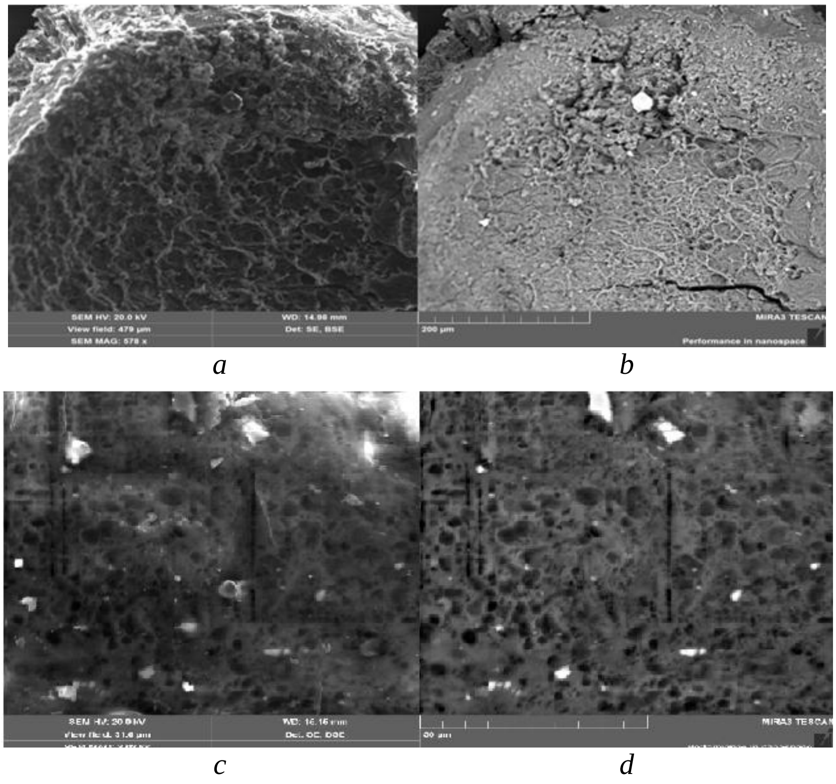


Figure 6. Micrographs of p-PFPh: AA copolymer structure at initial ratios of 6.77:93.23 mol % before (*a*, *b*) and after (*c*, *d*) swelling

Figure 7 shows the dependence of the external dimensions of the lattice on the concentration of the added low-molecular weight electrolyte, namely $Pb(NO_3)_2$, $CuSO_4$ and $FeCl_3$ for gels based on p-PFPh with AA of different molar composition. According to the presented experimental data, an increase in the ionic strength of the solution in the region from 0.001 to 1.0 mol/l has a significant effect on the external dimensions of the samples under consideration.

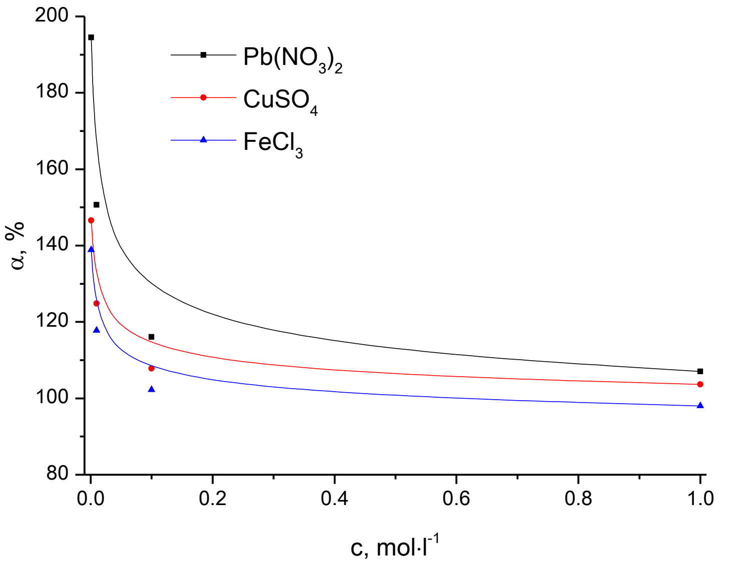


Figure 7. Effect of low molecular electrolyte ($Pb(NO_3)_2$, $CuSO_4$ and $FeCl_3$) on p-PFPh:AA copolymer swelling at initial ratios of 6.77:93.23 mol. %

The graphical dependencies (Fig. 7) show that at the lowest concentrations of added salt, the size of the gels varies slightly, a smooth contraction is observed. Further, at a certain critical concentration of the p-

PFPh used, a sharp collapse of the meshes is observed. A further increase in salt concentration does not affect the course of the curves. Based on the nature of the curves inherent in polyelectrolyte gels with the same charges, it can be concluded that the polymers we are considering should be attributed to anionic meshes. The shrinkage of the samples with increasing p-PFPh content in the mesh can be due to several reasons: first, the thermodynamic quality of the solvent — water, in which the samples are most swollen, deteriorates with increasing salt concentration; second, as low-molecular weight substrates are added to the surrounding solution, the polyelectrolyte effect may be suppressed as a result of shielding of charged ions by low-molecular weight ions.

As the proportion of p-PFPh units in the polymers increases, the sorption capacity of the gels decreases. The increase in the number of carboxyl groups in this series increases the sensitivity to additives of the low-molecular weight salt, while the concentration of the latter increases. The transition of hydrogels from the swollen state to the most contracted state is characterized by discreteness. It should be noted that for copolymers containing AA units, this phenomenon is observed at lower p-PFPh concentrations.

## *Conclusions*

The results obtained demonstrate the possibilities of controlling the physicochemical properties of copolymers based on poly(propylene fumarate phthalate) and acrylic acid induced by the polymer composition, which allows creating new materials with a predetermined program of behavior. The swelling rate of the polymers we studied depends on many factors, including the nature of the polymer and solvent, the presence of electrolytes, ambient temperature, the molecular weight of the polymer, etc. It is assumed that the polymer network of copolymers mainly consists of links of unsaturated polyester resin.

The results show that the ratio of monomer units in the copolymer significantly affects the susceptibility of the polymer gel to the presence of low-molecular weight salts. It has been proved that changing the properties of the comonomer allows obtaining hydrogels capable of swelling or collapsing under the influence of changes in the ionic strength or thermodynamic quality of the solution. By varying the ratio of the comonomeric units, the swelling and contraction intervals of the polymer meshes inherent in polyelectrolyte bodies with the same charges were adjusted. It was also found that the polymers in question belonged to the anionic meshes.

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