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The effects of the synthesis parameters on the xerogels structures and on the swelling parameters of the poly(methacrylic acid) hydrogels

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ABSTRACT

Poly(methacrylic acid) hydrogels were synthesized. The effects of the synthesis parameters: the neutralization degree of methacrylic acid and the concentrations of monomer, crosslinker and initiator on the xerogels structural properties: the xerogel density (ρ_{xg}), the number average molar mass between the network crosslinks (M_c), the crosslink degree (ρ_c), the number of elastically effective chains totally induced in a perfect network per unit volume (V_e), the distance between the macromolecular chains (ξ) and the equilibrium swelling degree (SD_{eq}) and the swelling kinetics was investigated. As the concentrations of crosslinker, monomer and initiator increase, the value of ρ_{xg}, ρ_c and V_e increases and decreases the value of M_c, ξ and SD_{eq}. With the increase in the neutralization degree of methacrylic acid, the values of ρ_{xg}, M_c, ξ, SD_{eq} increase, while the ρ_c and V_e decrease. The xerogels structural properties, SD_{eq} and swelling kinetic parameters are mainly in power law form functional relationships with the synthesis parameters as well as with the xerogels crosslinking degree.

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1. Introduction

Hydrogels are three-dimensional crosslinked polymeric structures that are able to swell in an aqueous environment and which have attracted great attention in recent years. They are also called “smart”, “intelligent”, “stimuli-responsive” or “environmental-sensitive” hydrogels. Because of their characteristic properties like swellability in water, hydrophilicity, biocompatibility and intoxicity, and of their abilities to respond to a variety of changes in the surrounding medium, such as change in pH, temperature, ionic strength, light intensity, electric and magnetic field, presence and concentration of some chemicals, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical and environmental applications [1–3].

Up to date experiences in the field of new materials give emphasis to the necessity of establishing the correlations between both the structure and properties of material from one point of view and between the parameters of synthesis and material properties, from the other point of view. The real meaning is that the main prerequisite to develop the synthesis of materials with predetermined properties, the so-called conducted synthesis, is knowing the functional or corelational relationships between synthesis parameters, structure of materials and desired material properties.

Bearing in mind the possible application of hydrogels, the equilibrium swelling degree and parameters controlling swelling kinetics (kinetic swelling parameters) appear to be the most important properties. Functional relations between basic structural parameters of xerogels (xerogel density, the number average molar mass between the network crosslinks, the crosslink degree, the distance between the macromolecular chains) and the equilibrium swelling degree are defined by Flory–Rehner theory [4].

In the field of hydrogels, research on the functional relationships between the synthesis parameters (neutralization degree, concentrations of monomer, initiator and crosslinker, temperature, pH, stirring rate, etc.) and the properties of the synthesized xerogel, although important are sparse.

Chen and Zhao investigated the effects of synthesis of polyacrylate superabsorbents and found that there was decreasing power law dependence between the equilibrium swelling degree and the crosslinker concentration [5].

Pourjavadi et al. [6,7] made similar conclusions for the investigation of synthesis of polysaccharide-based superabsorbent hydrogel through the graft copolymerization of acrylic acid onto kappa-carrageenan and alginate-g-poly(sodium acrylate)/kaolin superabsorbent hydrogel composites as well as Mahdevinia et al. for superabsorbent hydrogel of poly(acrylic acid-co-acrylamide)grafted chitosan [8].

Having that in mind, the main goal of this work was to investigate the possibility of establishing functional or corelational relations between parameters of synthesis of poly(methacrylic

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acid) (PMAA) hydrogels (neutralization degree of monomer, concentrations of monomer, initiator and crosslinker), the basic structural parameters of xerogel (xerogel density, the number average molar mass between the network crosslinks, the crosslink degree, the distance between the macromolecular chains and the number of elastically effective chains totally induced in a perfect network per unit volume) and the equilibrium swelling degree and kinetic swelling parameters, in order to achieve conducted synthesis of PMAA xerogels and create preconditions for further development of swelling theory.

2. Experimental

2.1. Materials

Methacrylic acid (99.5%) was purchased from Merck KGaA, Darmstadt Germany, stored in a refrigerator and melted at room temperature before use. N,N′-methylene bisacrylamide (p.a.) was supplied by Aldrich Chemical Co., Milwaukee, USA. The initiator, 2,2′-azobis-[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) (99.8%) was supplied by Wako Pure Chemical Industries, Ltd. Sodium hydroxide (p.a.) was obtained from Aldrich Chemical Co., Milwaukee, USA. Toluene (p.a.) was purchased from Carlo Erba Reagenti SpA, Rodano, Italy. All chemicals were used as received. Distilled water was used in all experiments.

2.2. PMAA hydrogels synthesis

The poly(methacrylic acid) hydrogels with different neutralization degree of methacrylic acid (MAA), and different concentrations of monomer, crosslinker and initiator were synthesized via free-radical polymerization of MAA and crosslinking of the formed PMAA in aqueous media using the modified procedure for poly(acrylic acid) hydrogel synthesis [9,10]. The general procedure is as follows.

Firstly, 15 ml of MAA was dissolved in adequate amount of distilled water and then neutralized with 25 wt% sodium hydroxide solution under the nitrogen atmosphere and with constant stirring. After neutralization of MAA to the required neutralization degree was completed, the crosslinker (MBA), solved in distilled water, was added. After stirring well to ensure homogeneity of the reaction mixture and nitrogen bubbling through the mixture for half an hour, the initiator solution was added and the reaction mixture was once again rapidly stirred and bubbled with nitrogen for a further 20 min. Immediately, the prepared reaction mixture was poured into glass moulds (plates separated by a rubber gasket 2 mm thick), and placed in an oven at 80 °C, for 3 h. Then, the obtained hydrogel was stamped into approximately equally sized disks (10 mm in diameter) and immersed in excess distilled water. The water was changed every 2–3 h except overnights for 7 days in order to remove the sol fraction of polymer and unreacted monomer. Subsequently, the washed-out hydrogel was dried in air oven at 50 °C until constant mass was attained. The obtained products were stored in a vacuum exicator until use.

The PMAA hydrogels with different neutralization degree (*ND*) of methacrylic acid (0%, 20%, 40%, 60%, 80% and 100%) were prepared keeping constant concentration of monomer (C_{MAA} (20 wt%) as well as initiator and crosslinker (C_{in} (0.06 mol%) and C_{MBA} (0.4 mol%) (both respective to monomer)).

The PMAA hydrogels with four crosslinker concentrations were prepared through variations in nominal molar ratio of MBA and MAA (*X*, mol MBA/mol MAA: 0.003, 0.004, 0.005, 0.006) and keeping all the other parameters constant (C_{MAA} (20 wt%), *ND* (40%), C_{in} (0.06 mol%)).

The PMAA hydrogels with three different monomer concentrations (20 wt%, 30 wt% and 40 wt%), and 40% *ND*, 0.4 mol% MBA and 0.06 mol% VA-044, were synthesized.

The PMAA hydrogels with different concentrations of initiator VA-044 (from 0.06 mol% to 0.10 mol%) were prepared. Other synthesis parameters were kept constant (C_{MAA} (20 wt%), *ND* (40%), C_{MBA} (0.4 mol%)).

2.3. Structural characterization of the xerogels

The following structural properties of the synthesized poly(methacrylic acid) hydrogels were determined and calculated: xerogel density (ρ_{xg}), average molar mass between the network crosslinks (M_{c}), crosslinking degree (ρ_{c}), the number of elastically effective chains totally induced in a perfect network per unit volume (V_{e}) and the distance between the macromolecular chains (ξ).

The xerogel densities of the synthesized samples were determined by the picnometer method, using the equation:

$$\rho_{\mathrm{xg}} = \frac{m_{\mathrm{xg}}\rho_{\mathrm{T}}}{m_1 + m_{\mathrm{xg}} - m_2} \tag{1}$$

where m_{xg} is the weight of the xerogel sample, m_1 is the weight of picnometer filled with toluene, used as the non-solvent, m_2 is the weight of picnometer filled with toluene with the xerogel sample in it and ρ_{T} is the density of toluene ($\rho_{\mathrm{T}} = 0.87\ \mathrm{g/cm^3}$).

The value of the M_{c} was determined by Eq. (2) proposed by Flory and Rehner [4]:

$$M_{\mathrm{c}} = \frac{-\rho_{\mathrm{xg}} V_{\mathrm{H_2O}} \upsilon_{2,\mathrm{s}}^{1/3}}{\ln(1-\upsilon_{2,\mathrm{s}}) + \upsilon_{2,\mathrm{s}} + \chi\upsilon_{2,\mathrm{s}}^2} \tag{2}$$

where $V_{\mathrm{H_2O}}$ is the molar volume of H_2O, $\upsilon_{2,\mathrm{s}}$ is the polymer volume fraction in the equilibrium swollen state and χ is the Flory–Huggins interaction parameter between a solvent (H_2O) and a polymer (PMAA). The values of $\upsilon_{2,\mathrm{s}}$ and χ were calculated using the following expressions:

$$\upsilon_{2,\mathrm{s}} = \frac{1}{1 + \rho_{\mathrm{xg}} SD_{\mathrm{eq}}} \tag{3}$$

$$\chi = \frac{\ln(1-\upsilon_{2,\mathrm{s}}) + \upsilon_{2,\mathrm{s}}}{\upsilon_{2,\mathrm{s}}^2} \tag{4}$$

The degree of crosslinking was calculated as [11]:

$$\rho_{\mathrm{c}} = \frac{M_0}{M_{\mathrm{c}}} \tag{5}$$

where M_0 is the molar mass of the repeating unit.

The number of elastically effective chains totally induced in a perfect network per unit volume (V_{e}) was calculated as:

$$V_{\mathrm{e}} = \frac{\rho_{\mathrm{xg}} N_{\mathrm{A}}}{M_{\mathrm{c}}} \tag{6}$$

where N_{A} is Avogadro number.

The distance between the macromolecular chains was calculated as:

$$\xi = l\upsilon_{2,\mathrm{s}}^{-1/3}\left(2C_n \frac{M_{\mathrm{c}}}{M_0}\right)^{1/2} \tag{7}$$

where C_n is the Flory characteristic ratio ($C_n(\mathrm{MAA}) = 14.6$) and l is the carbon–carbon bond length (1.54 Å) [12].

2.4. Swelling experiments

Dry hydrogel (xerogel) disks with an average weight of 0.050 g ± 10% were left to swell in distilled water at 25 ± 0.2 °C. At the beginning of each experiment, the xerogel disks were weighted

(m_0) and then entirely immersed in excess distilled water. At predetermined time intervals, the swollen hydrogels samples were taken out from water, wiped to remove excess surface water and weighted (m_t). This was done until the hydrogels attained constant mass, i.e. until equilibrium was reached. The measurements were performed using the grid boat technique [9,13].

2.4.1. Determination of the swelling degree and swelling kinetics parameters

The isothermal swelling degree (SD) defined as the difference between the weights of the swollen hydrogel sample at the time t (m_t) and the weight of the xerogel (dry hydrogel) (m_0) divided by the weight of the xerogel sample (m_0), was determined as a function of time at constant temperature and calculated using Eq. (8):

$$SD = \frac{m_t - m_0}{m_0} \tag{8}$$

The equilibrium swelling degree (SD_{eq}) is the swelling degree of the hydrogel at equilibrium, i.e. when the hydrogel sample attained constant mass (m_{eq}):

$$SD_{eq} = \frac{m_{eq} - m_0}{m_0} \tag{9}$$

For each sample at least three swelling measurements were performed and the mean values were used.

The normalized swelling degree (α) was calculated as:

$$\alpha = \frac{SD}{SD_{eq}} \tag{10}$$

The swelling kinetic of the PMAA hydrogel was investigated by applying the well-known semi-empirical Peppas equation [14]:

$$\alpha = kt^n \tag{11}$$

where n and k are the swelling kinetics parameters and t is the swelling time. The parameters k and n were determined from the slopes and intercepts of the straight lines of the plots $\ln\alpha$ *vs.* $\ln t$.

3. Results and discussion

3.1. Effect of neutralization degree of methacrylic acid

In order to establish the effect of the neutralization degree of MAA both on the basic structural properties and on the swelling kinetic parameters of poly(methacrylic acid) hydrogels, PMAA hydrogels were synthesized through the variation of the neutralization degree from 0% *ND* to 100% *ND*, while maintaining concentrations of monomer, crosslinker and initiator constant (C_{MAA} = 20 wt%, X = 0.004 and C_{in} = 0.06 mol%). The effect of the neutralization degree of monomer on the basic structural properties of the PMAA hydrogel is presented in Table 1.

Table 1
The basic structural properties of PMAA xerogels prepared with different neutralization degree of monomer.

ND (%)	ρ_{xg} (g/cm^3)	M_c (g/mol)	ρ_c ($\times10^4$ mol/cm^3)	ξ (nm)	V_e ($\times10^{-19}$ cm^{-3})
0	1.33	9,700	88	29	8.20
20	1.29	78,000	12	124	0.99
40	1.35	220,000	4.2	250	0.36
60	1.38	350,000	2.8	340	0.23
80	1.42	1.1E6	1.0	710	0.08
100	1.45	2.1E6	0.5	1100	0.04

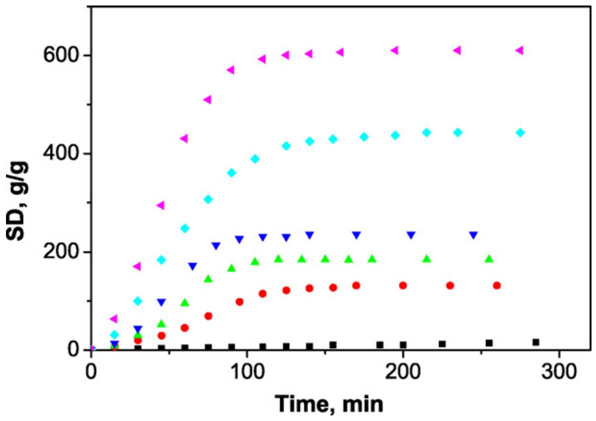

Fig. 1. The isothermal swelling kinetic curves of PMMA hydrogels synthesized with: (■) 0% *ND*, (●) 20% *ND*, (▲) 40% *ND*, (▼) 60% *ND*, (♦) 80% *ND* and (◄) 100% *ND*.

Based on the results presented in Table 1, the PMAA xerogels with different structural properties were synthesized. The increase in the neutralization degree of MAA leads to the increase in the values of the xerogel density, the average molar mass between crosslinks and the distance between the macromolecular chains, while to the decrease in the values of the crosslinking degree of the PMAA hydrogels and the number of elastically effective chains. The changes of the structural properties of xerogels that follow the change of the neutralization degree of MAA can be described by the following equations:

$$\rho_{xg} = 1.03\left[\frac{\mathrm{g}}{\mathrm{cm}^3}(\%)^{-0.07}\right] ND^{0.07} \quad R^2 = 0.99 \tag{12}$$

$$\rho_c = 0.104[(\%)^{1.5}]ND^{-1.50} \quad R^2 = 0.99 \tag{13}$$

$$M_c = 1.56\left[\frac{\mathrm{g}}{\mathrm{mol}}(\%)^{-3.06}\right] ND^{3.06} \quad R^2 = 0.99 \tag{14}$$

$$\xi = 0.18[\mathrm{nm}(\%)^{-1.89}]ND^{1.89} \quad R^2 = 0.98 \tag{15}$$

$$V_e = 9.34[\mathrm{cm}^{-3}(\%)^{1.51}]ND^{-1.51} \quad R^2 = 0.99 \tag{16}$$

The data were analyzed using the commercial program Origin Microcal 8.0 and relations with the best correlation coefficient (R) are presented.

The investigation of the swelling behaviour of the PMAA hydrogels was carried out in distilled water at 25 °C. Fig. 1 shows the obtained swelling isotherms of the PMAA hydrogels synthesized with different neutralization degrees of MAA.

The results, as depicted in Fig. 1, clearly revealed that all of the swelling isotherms of the PMAA hydrogels were similar in shape. Three particular shapes of the changes of the swelling degree with swelling time can be distinguished in all of the swelling curves, a linear, non-linear and the saturation part or plateau. Increasing the neutralization degree of MAA resulted in an increase of the slope of the linear part of the dependence of the swelling degree *vs.* time and the equilibrium swelling degree for each sample.

The possibility of applying the well-known semi-empirical Peppas Eq. (11) to describe the kinetic of the isothermal swelling of PMAA hydrogels was investigated. The plots of $\ln\alpha$ *vs.* $\ln t$ for PMAA hydrogels synthesized with 0% *ND*, 40% *ND* and 80% *ND*, as the characteristic samples, are shown in Fig. 2.

According to the results shown in Fig. 2, the plots of $\ln\alpha$ *vs.* $\ln t$ give straights lines in the limited ranges of investigated swelling process, the so-called range of applicability ($\Delta\alpha$). Within the range of applicability these dependences are linear and it is possible to model the kinetics of swelling with the above mentioned Eq. (11) and to determine the values of the swelling kinetics parameters, n and k, from the slopes and intercepts of these straight lines. The obtained values for the equilibrium swelling degree, swelling kinetics parameters and the range of applicability, for the PMAA xerogels

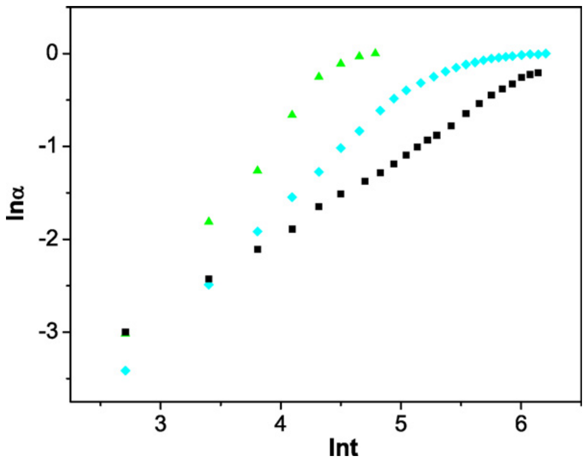

Fig. 2. The plots of ln *α* *vs.* ln *t* for swelling of PMMA hydrogels synthesized with: (■) 0% *ND*, (▲) 40% *ND* and (♦) 80% *ND*.

synthesized with different neutralization degree of the MAA are presented in Table 2.

The increase in the neutralization degree of the MAA significantly increases the equilibrium swelling degree of the PMAA hydrogel from 27 g/g (0% *ND*) to even 602 g/g (100% *ND*), while the swelling kinetics parameters change complexly. With the increasing the neutralization degree up to 60% the swelling kinetic parameter *k* decreases while at the same time the parameter *n* increases. The values of parameter *n* are higher then one ($n > 1$) which is indicative for the super-case II diffusion, which means that the swelling kinetics is controlled by the rate of the network expanding (i.e. relaxation of the elastic polymer network) [14]. One exception is the obtained value of the $n = 0.8$ for the PMAA hydrogel which was synthesized without neutralization of the monomer. It is also remarkable that the range of applicability of the applied kinetic model is very high (up to 0.9) and slightly decreases with the increase in the neutralization degree. The effect of the neutralization degree of monomer on the equilibrium swelling degree can be described by Eq. (17):

$$SD_{\mathrm{eq}} = 0.66[(\%)^{-1.47}]ND^{1.47} \quad R^2 = 0.96 \tag{17}$$

Functional relationships between the swelling kinetic parameters and the change of the neutralization degree of monomer, from 0% *ND* up to 60% *ND*, can be described by the following expressions:

$$n = 0.79[(\%)^{-0.2}]ND^{0.2} \quad R^2 = 0.98 \tag{18}$$

$$k = 0.013[\mathrm{min}^{-n}(\%)^{0.83}]ND^{-0.83} \quad R^2 = 0.97 \tag{19}$$

Table 2
The equilibrium swelling degree, swelling kinetic parameters and the range of applicability for PMAA xerogels prepared with different neutralization degree of monomer.

ND (%)	SD_{eq} (g/g)	k ($\times 10^3$ min^{-n})	n	$\Delta\alpha$
0	27	5.2	0.8	0–0.9
20	101	1.1	1.4	0–0.9
40	176	0.56	1.7	0–0.9
60	225	0.50	1.8	0–0.8
80	420	1.0	1.3	0–0.7
100	602	2.5	1.4	0–0.7

Table 3
The structural properties of PMAA xerogels synthesized with different concentrations of crosslinker.

X (mol/mol)	ρ_{xg} (g/cm^3)	M_{c} (g/mol)	ρ_{c} ($\times 10^4$ mol/cm^3)	ξ (nm)	V_{e} ($\times 10^{-19}$ cm^{-3})
0.003	1.26	270,000	3.5	290	0.28
0.004	1.35	220,000	4.2	250	0.36
0.005	1.40	140,000	6.7	180	0.60
0.006	1.46	91,000	10.4	132	0.97

Making an assumption that all of the hydrogel structural parameters are in functional relationship with the crosslinking degree, by analyzing the obtained results, the correlations between the crosslinking degree and M_{c}, ξ and V_{e}, for the hydrogels samples synthesized with different degrees of neutralization of the monomer, are achieved. The changes of the structural properties of xerogels synthesized at different degrees of neutralization of MAA are found to be in power law correlation with the crosslinking degree of xerogels:

$$M_{\mathrm{c}} = 60.07\left[\frac{\mathrm{g}}{\mathrm{mol}}\right]\rho_{\mathrm{c}}^{-1.06} \quad R^2 = 0.99 \tag{20}$$

$$\xi = 1.06[\mathrm{nm}]\rho_{\mathrm{c}}^{-0.70} \quad R^2 = 0.99 \tag{21}$$

$$V_{\mathrm{e}} = 1.10 \times 10^{22}[\mathrm{cm}^{-3}]\rho_{\mathrm{c}}^{-1.03} \quad R^2 = 0.99 \tag{22}$$

By analyzing the effects of the crosslinking degree on the swelling behaviour of investigated hydrogels it is found that the increasing the ρ_{c} of the xerogel leads to the decreasing the SD_{eq}, which can be described as follows:

$$SD_{\mathrm{eq}} = 1.92\rho_{\mathrm{c}}^{-0.58} \quad R^2 = 0.99 \tag{23}$$

The swelling kinetics parameters change complexly with the changes of the degree of crosslinking. With the decrease in the ρ_{c} of the PMAA hydrogel sample synthesized with up to 60% *ND* of the MAA, the swelling kinetic parameter *k* also decreases while the *n* increases. The changes of the parameters, *n* and *k*, with the ρ_{c} can be descried by the following equations:

$$n = 0.33\rho_{\mathrm{c}}^{-0.21} \quad R^2 = 0.99 \tag{24}$$

$$k = 0.17[\mathrm{min}^{-n}]\rho_{\mathrm{c}}^{0.73} \quad R^2 = 0.99 \tag{25}$$

Bearing in mind the established relationships between the degree of crosslinking and the average molar mass between the network crosslinks, the distance between the macromolecular chains, the number of elastically effective chains (Eqs. (20)–(22)), by replacing the crosslinking degree in Eqs. (23)–(25) it is possible to get the functional relationship between the SD_{eq}, *n*, *k* and the average molar mass between the network crosslinks, the distance between the macromolecular chains and the number of elastically effective chains.

The observed changes of the structural parameters of the xerogels as a function of the neutralization degree of MAA can be explained by interactions between ionized and non-ionized reaction species present in the system. The monomer can exist in two forms, as methacrylic acid or as a methacrylate anion. The increase in the neutralization degree increases the concentration of the methacrylate anion and therefore reduces the polymerization rate and reaction yields. Because of that, the average molar mass between crosslinks increases, i.e. the crosslinking degree decreases and that, as presented above, leads to the change in all the others structural parameters. That in turn, reflects on the swelling behaviour, what can be seen from the changes of the SD_{eq} and the swelling kinetic parameters.

3.2. *Effect of crosslinker concentration*

The effect of the crosslinker concentration in the reaction feed was studied by varying the nominal molar ratio of MBA and MAA (X) from 0.003 to 0.006 and keeping all the other synthesis parameters constant ($ND = 40\%$, $C_{\mathrm{MAA}} = 20$ wt%, $C_{\mathrm{in}} = 0.06$ mol%). Table 3 presents the basic structural properties of the PMAA hydrogels synthesized with different concentration of crosslinker.

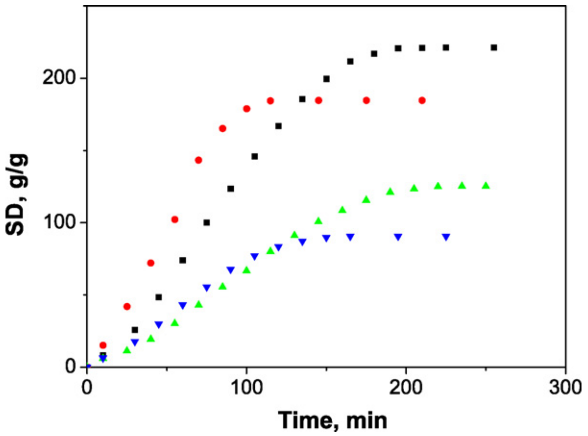

Fig. 3. The isothermal swelling kinetic curves of PMAA hydrogels synthesized with X: (■) 0.003, (●) 0.004, (▲) 0.005 and (▼) 0.006.

From the data presented in Table 3 it is clear that the values of the basic structural parameters of the xerogels change with the increase in the crosslinker concentration: crosslinking degree, xerogel density and the number of elastically effective chains, while the values of the average molar mass between the crosslinks and the distance between macromolecular chains decrease. The changes of these parameters, within the investigated range of X, can be fitted with the following power form equations:

$$\rho_{xg} = 4.35\left[\frac{g}{cm^3}\right]X^{0.21} \quad R^2 = 0.99 \tag{26}$$

$$\rho_c = 14.63X^{1.87} \quad R^2 = 0.96 \tag{27}$$

$$\xi = 458[\mathrm{nm}] - 54,000[\mathrm{nm}]X \quad R^2 = 0.99 \tag{28}$$

$$V_e = 4.93 \times 10^{23}[\mathrm{cm}^{-3}]X^{2.12} \quad R^2 = 0.97 \tag{29}$$

The dependence between the M_c values and the crosslinker concentration is found to be linear:

$$M_c = 460,000\left[\frac{g}{mol}\right] - 6.17 \times 10^7\left[\frac{g}{mol}\right]X \quad R^2 = 0.99 \tag{30}$$

The swelling behaviour of the PMAA hydrogels synthesized with different concentrations of crosslinker is presented in Fig. 3.

The isothermal swelling kinetic curves of PMAA hydrogels prepared with different crosslinker concentrations are similar in shape to the curves of the PMAA samples of the hydrogels synthesized with different neutralization degree of MAA. The increasing value of the X leads to the decreasing equilibrium swelling degree while the slope of the linear part of the SD dependence with time change complexly, showing the highest value at $X = 0.004$. In order to get the values of the swelling kinetic parameters, the swelling data were analyzed by Eq. (11), as described previously. Fig. 4 presents the plots of $\ln t$ *vs.* $\ln \alpha$, for PMAA hydrogels synthesized with different concentrations of crosslinker.

The effect of the crosslinker concentration on the equilibrium swelling degree and the values of the swelling kinetics parameters (n and k) is shown in Table 4.

Table 4
The equilibrium swelling degree, swelling kinetic parameters and the range of applicability for PMAA xerogels prepared with different crosslinker concentrations.

X (mol/mol)	SD_{eq} (g/g)	k ($\times 10^3$ min^{-n})	n	$\Delta\alpha$
0.003	221	0.58	1.5	0–0.6
0.004	176	0.56	1.7	0–0.9
0.005	125	1.0	1.3	0–0.7
0.006	91	1.7	1.3	0–0.7

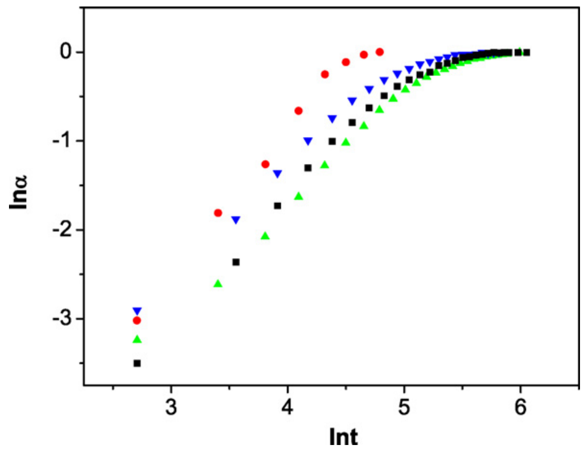

Fig. 4. The plot of $\ln \alpha$ *vs.* $\ln t$ for swelling of PMMA hydrogels synthesized with X: (■) 0.003, (●) 0.004, (▲) 0.005 and (▼) 0.006.

As the crosslinker concentration in the initial feed composition increases, the values of the SD_{eq} significantly decrease in a power form manner, which is fitted by the following equation:

$$SD_{eq} = 0.14X^{-1.28} \quad R^2 = 0.97 \tag{31}$$

Tendency of decreasing SD_{eq} with increasing the crosslinker concentration is in agreement with the Flory theory and with the results of other authors [5,15,16].

The increase in the crosslinker concentration leads to complex change of the values of the characteristic constant of the hydrogel k, the swelling exponent n and the $\Delta\alpha$. The maximum values of the swelling exponent n and the range of applicability is found at $X = 0.004$, while at the same crosslinker concentration parameter k reaches its minimum. The range of applicability of the semi-empirical Peppas equation (11) for PMAA xerogels prepared with different crosslinker concentrations are lower then for samples prepared with varying the neutralization degree of MAA.

As in the case the investigation the effect of the degree of neutralization, the values of the swelling parameter n are higher then one ($n > 1$). That implies that the PMAA xerogels synthesized in reaction feed with different crosslinker concentrations undergoes swelling mechanism the super-case II diffusion.

The changes of the structural parameters can be related to the change of the crosslinking degree in the following manner:

$$\rho_{xg} = 3.4\left[\frac{g}{cm^3}\right]\rho_c^{0.12} \quad R^2 = 0.91 \tag{32}$$

$$\xi = 0.89[\mathrm{nm}]\rho_c^{-0.73} \quad R^2 = 1 \tag{33}$$

$$V_e = 1.98 \times 10^{22}[\mathrm{cm}^{-3}]\rho_c^{1.11} \quad R^2 = 1 \tag{34}$$

The changes of the equilibrium swelling degree and the swelling kinetics parameters, n and k, can also be described as a function of the ρ_c:

$$SD_{eq} = 0.29\rho_c^{-0.83} \quad R^2 = 0.99 \tag{35}$$

$$n = 0.14\rho_c^{-0.32} \quad R^2 = 0.82 \tag{36}$$

$$k = 2.13[\mathrm{min}^{-n}]\rho_c^{1.04} \quad R^2 = 0.99 \tag{37}$$

As shown, the crosslinking degree and the xerogel density increase with the increase in crosslinker concentration, while the distance between the macromolecular chains and the average molar mass between the network crosslinks decrease. The changes of the structural properties of hydrogels, SD_{eq} and swelling kinetic parameters which are caused by the variation of the crosslinker concentration could be explained by the changed number of formed

Table 5
The basic structural properties of PMAA xerogels synthesized with different concentrations of monomer.

C_{MAA} (wt%)	ρ_{xg} (g/cm^3)	M_c (g/mol)	ρ_c ($\times 10^4$ mol/cm^3)	ξ (nm)	V_e ($\times 10^{-19}$ cm^{-3})
20	1.35	220,000	4.2	250	0.36
30	1.40	51,000	19	88	1.7
40	1.44	6,400	149	21	13.5

crosslinking points in the hydrogel network which in turn determined the crosslinking degree. The polymer sample with the higher crosslinker concentration has the stronger and rigider crosslinked network which is less capable of absorbing water and therefore it has the lower value for the equilibrium swelling degree.

3.3. Effect of monomer concentration

With intend to investigate the effect of monomer concentration on the PMAA hydrogel properties, the weight percentage of MAA in the reaction mixture was varied from 20 wt% to 40 wt%, whereas the other synthesis parameters were kept constant ($ND = 40\%$, $X = 0.004$, $C_{in} = 0.06$ mol%). The basic structural properties of poly(methacrylic acid) hydrogels prepared with different concentrations of monomer are shown in Table 5.

It is found that the increase in monomer concentration significantly influence all of the investigated structural parameters of the PMAA xerogels. The values of the xerogel density, the crosslinking degree and the number of elastically effective chains increase, while the average molar mass between the network crosslinks and the distance between the macromolecular chains decrease. The results presented in Table 5 were further analyzed and the correlations between C_{MAA} and the characteristic structural parameters of PMAA xerogels were found to be best fitted by the following power form equations:

$$\rho_{xg} = 1.03\left[\frac{g}{cm^3}(\%)^{-0.09}\right]C_{MAA}^{0.09} \quad R^2 = 1 \tag{38}$$

$$\rho_c = 5.66 \times 10^{-14}[(\%)^{-7.13}]C_{MAA}^{7.13} \quad R^2 = 1 \tag{39}$$

$$M_c = 2.63 \times 10^{10}\left[\frac{g}{mol}(\%)^{3.90}\right]C_{MAA}^{-3.90} \quad R^2 = 0.99 \tag{40}$$

$$\xi = 1.415 \times 10^{6}[nm(\%)^{2.88}]C_{MAA}^{-2.88} \quad R^2 = 0.99 \tag{41}$$

$$V_e = 3.66 \times 10^{8}[cm^{-3}(\%)^{-7.22}]C_{MAA}^{7.22} \quad R^2 = 0.99 \tag{42}$$

The swelling isotherms of poly(methacrylic acid) hydrogels synthesized using different concentrations of monomer in the reaction mixtures are given in Fig. 5.

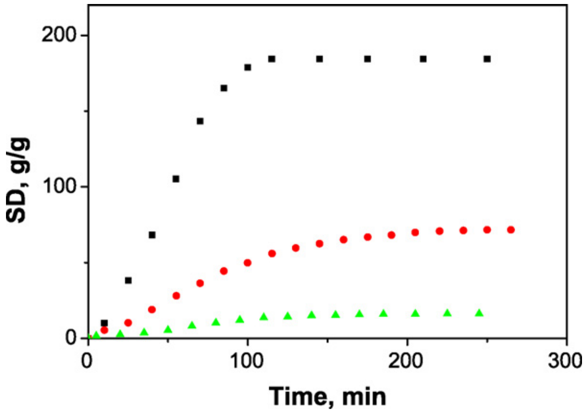

Fig. 5. The isothermal swelling kinetic curves of PMMA hydrogels synthesized with MAA concentration of: (■) 20 wt%, (●) 30 wt% and (▲) 40 wt%.

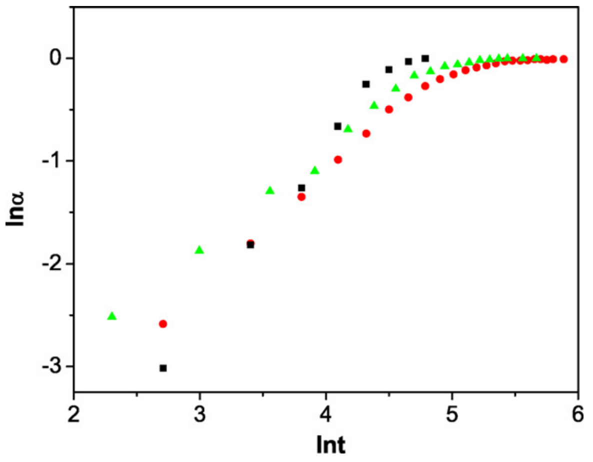

Fig. 6. The plot of ln α *vs.* ln t for swelling of PMMA hydrogels synthesized with (■) 20 wt%, (●) 30 wt% and (▲) 40 wt% of MAA.

The swelling kinetic curves of the PMAA hydrogels synthesized with different monomer concentration are similar to the previously presented curves for the PMAA hydrogel samples prepared with different neutralization degree of monomer and different concentration of crosslinker. With increasing monomer concentration the SD_{eq} values of the synthesized PMAA hydrogels decrease, as well as the slope of the linear part of the dependence SD *vs.* time. The swelling kinetics of these PMAA hydrogels was investigated by analyzing the swelling results using the same method as in previous parts of this work. The plots of ln α *vs.* ln t values for the isothermal swelling of PMAA hydrogels synthesized with different concentrations of monomer are given in Fig. 6.

Once again, as depicted in Fig. 6, the plots of ln α *vs.* ln t did not give straight lines thought the whole ranges of the investigated swelling process. The swelling kinetics parameters, n and k, are calculated for the corresponding range of applicability. The obtained results for the equilibrium swelling degree, swelling kinetic parameters and the range of applicability for PMAA hydrogels synthesized with different concentrations of MAA are presented in Table 6.

With the increasing concentration of monomer in the reaction feed, the equilibrium swelling degree, as well as the swelling parameter n and corresponding $\Delta\alpha$ decreases, while the parameter k increases. The n for the PMAA sample synthesized with 40 wt% of the MAA is lower then 1 ($n < 1$) in opposite to the samples synthesized with 20 wt% and 30 wt% of the MAA for which the n values are higher then 1 ($n > 1$). That implies that there is a change in swelling kinetic mechanism for the PMAA hydrogel which was synthesized with 40% of MAA in reaction feed. The relationships between the C_{MAA} and the swelling kinetic parameters of the poly(methacrylic acid) hydrogels were analyzed and the best fitted correlations are the follows:

$$SD_{eq} = 506797[(\%)^{2.65}]C_{MAA}^{-2.65} \quad R^2 = 0.99 \tag{43}$$

$$n = 19.84[(\%)^{0.83}]C_{MAA}^{-0.83} \quad R^2 = 1 \tag{44}$$

$$k = 9.71 \times 10^{-10}[min^{-n}(\%)^{-4.37}]C_{MAA}^{4.37} \quad R^2 = 1 \tag{45}$$

Table 6
The equilibrium swelling degree, swelling kinetic parameters and corresponding range of applicability for PMAA hydrogels prepared with different concentrations of monomer.

C_{MAA} (wt%)	SD_{eq} (g/g)	k ($\times 10^3$ min^{-n})	n	$\Delta\alpha$
20	176	0.56	1.7	0–0.9
30	68	2.8	1.2	0–0.8
40	19	9.9	0.9	0–0.7

The similar observation for the decrease in the values of the SD_{eq} with the increase in monomer concentrations in initial reaction feed composition is reported by others [7,17].

Bearing in mind the previous assumption that all of the hydrogel structural parameters are in functional relationship with the degree of crosslinking, the obtained results are analyzed and correlations between the degree of crosslinking and the ρ_{xg}, ξ and V_e, for the PMAA hydrogel samples synthesized with different concentrations of monomer are established. The changes of the discussed structural parameters with the crosslinking degree of the xerogel are found to be best describe by the following expressions:

$$\rho_{xg} = 1.56\left[\frac{\mathrm{g}}{\mathrm{cm}^3}\right]\rho_c^{0.018} \quad R^2 = 0.97 \tag{46}$$

$$\xi = 1.1[\mathrm{nm}]\rho_c^{-0.70} \quad R^2 = 1 \tag{47}$$

$$V_e = 9.63 \times 10^{21}[\mathrm{cm}^{-3}]\rho_c^{1.01} \quad R^2 = 1 \tag{48}$$

The increasing ρ_c value results in the decrease of the SD_{eq} and n values, while the swelling parameter k increases. These dependences can be described by the following equations:

$$SD_{eq} = 1.22\rho_c^{-0.64} \quad R^2 = 1 \tag{49}$$

$$n = 0.43\rho_c^{0.17} \quad R^2 = 0.97 \tag{50}$$

$$k = 0.16[\mathrm{min}^{-n}]\rho_c^{0.66} \quad R^2 = 0.99 \tag{51}$$

The established changes of the primary structural parameters of the xerogel and the equilibrium swelling degree caused by the increase in the monomer concentration are not in agreement with the prediction based on the theory of free-radical polymerization and the swelling theory, proposed by Flory. According to the theory of free-radical polymerization the increase in the monomer concentration should result in average molar mass increase, what would, in turn (according to the swelling theory), lead to increase in the equilibrium swelling degree. Opposite to that, our experimental results imply that when concentration of monomer increase, the equilibrium swelling degree decreases. These results are in agreement with the results obtained by Baker, during the investigation of poly(acrylamide-co-acrylic acid) hydrogel [18] and Lee and Yeh, who investigated superabsorbents based on poly(acrylic acid) [19]. The most probably explanation is that the chain transfer to the polymer increases with monomer concentration especially at high extent of conversion. Because the rate of chain transfer increases with the increasing monomer concentration, the amount of branching and self-crosslinking reactions also increase and due to that the degree of crosslinking increase, the M_c decrease and the SD_{eq} decrease.

3.4. Effect of initiator concentration

In order to examine the effect of the concentration of the initiator in the reaction mixture on the synthesized PMAA hydrogel properties, the initiator concentration was varied from 0.06 mol% to 0.10 mol%, whereas the other synthesis parameters were kept constant (ND = 40%, X = 0.004, C_{MAA} = 20 wt%). The effect of the initiator concentration on the basic structural properties of the PMAA xerogel is given in Table 7.

Table 7
The basic structural properties of PMAA xerogels synthesized with different concentrations of initiator.

C_{in} (mol%)	ρ_{xg} (g/cm^3)	M_c (g/mol)	ρ_c ($\times 10^4$ mol/cm^3)	ξ (nm)	V_e ($\times 10^{-19}$ cm^{-3})
0.06	1.35	220,000	4.2	250	0.36
0.08	1.36	206,000	4.6	237	0.40
0.10	1.37	120,000	8.0	160	0.70

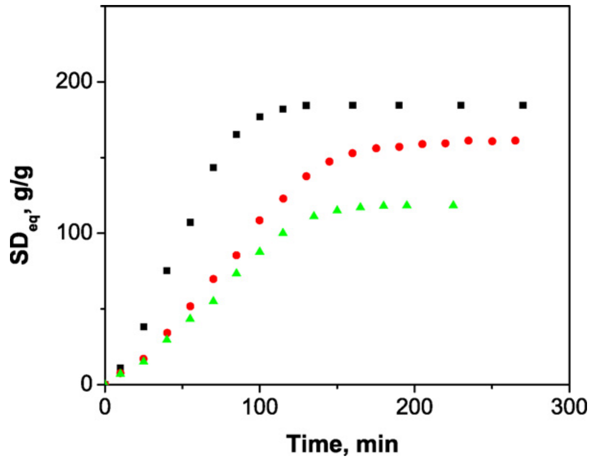

Fig. 7. The isothermal swelling kinetic curves of PMMA hydrogels synthesized with the initiator concentrations of: (■) 0.06 mol%, (●) 0.08 mol% and (▲) 0.10 mol%.

It should be emphasized that the increasing the initiator concentration (C_{in}) in the reaction feed composition, within the investigated range, leads to the decrease in the M_c and the ξ values, but to the increase in the ρ_c and the V_e values.

Functional relations that describe the discussed changes of the basic structural properties with the change of initiator concentration can be presented with the following equations:

$$\rho_{xg} = 1.32\left[\frac{\mathrm{g}}{\mathrm{cm}^3}\right] + 0.5\left[\frac{\mathrm{g}}{\%\mathrm{cm}^3}\right]C_{in} \quad R^2 = 1.0 \tag{52}$$

$$M_c = 382,000\left[\frac{\mathrm{g}}{\mathrm{mol}}\right] - 2.5 \times 10^6\left[\frac{\mathrm{g}}{\%\mathrm{mol}}\right]C_{in} \quad R^2 = 0.92 \tag{53}$$

$$V_e = -1.93 \times 10^{18}[\mathrm{cm}^{-3}] + 8.5 \times 10^{19}\left[\frac{\mathrm{cm}^{-3}}{\%}\right]C_{in} \quad R^2 = 0.93 \tag{54}$$

$$\xi = 395.7[\mathrm{nm}] - 2250\left[\frac{\mathrm{nm}}{\%}\right]C_{in} \quad R^2 = 0.92 \tag{55}$$

$$\rho_c = 25[\%^{-1.24}]C_{in}^{1.24} \quad R^2 = 0.92 \tag{56}$$

The swelling kinetic curves of the poly(methacrylic acid) hydrogels synthesized with different concentration of initiator are presented in Fig. 7.

The plot of the swelling degree as a function of swelling time for the PMAA hydrogels synthesized with different initiator concentration are similar to the previously presented swelling isotherms of the PMAA hydrogels synthesized with different concentrations of neutralization degree, crosslinker and monomer. Once again, the data from the presented swelling curves were analyzed by using Eq. (11). The plots of $\ln\alpha$ *vs.* $\ln t$ for PMAA hydrogels synthesized with different concentrations of initiator are given in Fig. 8.

As in the former parts of this work, the swelling kinetics parameters, n and k, are calculated for corresponding range of applicability. The effect of the initiator concentration on the equilibrium swelling degree, swelling kinetics parameters and the range of applicability ($\Delta\alpha$) for them, of the synthesized PMAA hydrogels are given in Table 8.

Table 8
The equilibrium swelling degree, swelling kinetic parameters and the range of applicability for synthesized PMAA hydrogels with different initiator concentrations.

C_{in} (mol%)	SD_{eq} (g/g)	k ($\times 10^3$ min^{-n})	n	$\Delta\alpha$
0.06	176	0.56	1.7	0–0.9
0.08	165	0.95	1.4	0–0.75
0.10	118	0.90	1.3	0–0.75

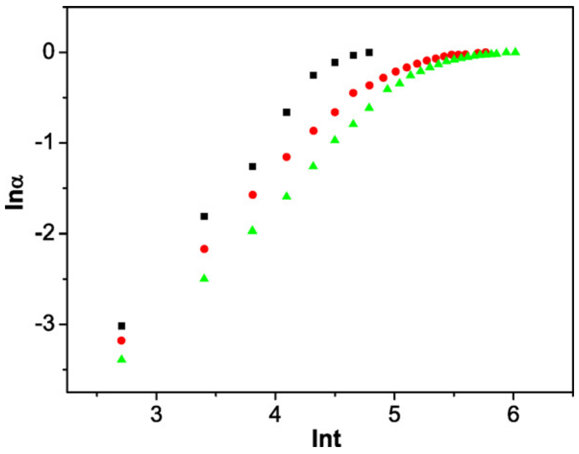

Fig. 8. The plot of $\ln \alpha$ *vs.* $\ln t$ for swelling of PMMA hydrogels with initiator concentrations of: (■) 0.06 mol%, (●) 0.08 mol% and (▲) 0.10 mol%.

The values of the SD_{eq} decrease with the increase in the initiator concentration from 118 g/g to 176 g/g. Those changes are significantly lower then the changes of SD_{eq} which were caused by the other three synthesis parameter, the *ND*, the C_{MBA} and the C_{MAA}. Regarding to the effect of the increase in the concentration the initiator on the swelling kinetics parameters, the *n* decreases from 1.7 to 1.3, while the *k* changes complexly.

The equilibrium swelling degree and the swelling parameter *n* can also be related to the initiator concentration, in the following manner:

$$SD_{eq} = 269 - 1450[\%^{-1}]C_{in} \quad R^2 = 0.95 \tag{57}$$

$$n = 0.47[(\%)^{0.44}]C_{in}^{-0.44} \quad R^2 = 0.95 \tag{58}$$

The correlations between the crosslinking degrees of synthesized PMAA hydrogels and their structural properties, i.e. the equilibrium swelling degree, are found to follow the power law dependences:

$$\xi = 1.06[\text{nm}]\rho_c^{-0.70} \quad R^2 = 1 \tag{59}$$

$$V_e = 9.63 \times 10^{21}[\text{cm}^{-3}]\rho_c^{1.01} \quad R^2 = 1 \tag{60}$$

$$SD_{eq} = 1.47\rho_c^{-0.6} \quad R^2 = 0.99 \tag{61}$$

The established changes of the primary structural parameters of xerogel and the equilibrium swelling degree with the initiator concentration are completely in agreement with the prediction based on free-radical polymerization theory and the hydrogel swelling theory. That means that the increasing initiator concentration leads to the formation of the short chain lengths and that is reason for decreasing molar mass and the most probably for the decreasing M_c value. The decreased values of the molar mass and the M_c are reasons for the decrease in the equilibrium swelling degree of hydrogel.

4. Conclusions

- Functional and corelational relationships between the reaction parameters of the synthetic parameters and the basic structural parameters of the xerogel and the equilibrium swelling degree and swelling kinetic parameters were established.
- The xerogel density, the equilibrium swelling degree and swelling parameter *n* are increasing function of neutralization degree, while the crosslinking degree and the number of elastically effective chains are decreasing function of neutralization degree.
- The increasing concentration of crosslinker leads to the increase in the xerogel density, the crosslinking degree and the number of elastically effective chains.
- The increasing concentration of crosslinker leads to the decrease in the equilibrium swelling degree, the number average molar mass between the network crosslinks and the distance between the macromolecular chains.
- The xerogel density, the crosslink degree, the number of elastically effective chains and swelling parameter *k* are increasing functions of monomer concentration, while the number average molar mass between the network crosslinks, the distance between the macromolecular chains, the equilibrium swelling degree and swelling parameter *n* are decreasing functions of monomer concentration.
- The increase in the initiator concentration leads to the increase in the crosslinking degree and to the decrease in the value of the parameter *n* and the equilibrium swelling degree, meanwhile leads to the increase in xerogel density and the number of elastically effective chains.
- The equilibrium swelling degree and parameter *n* are decreasing functions of the crosslink degree, while parameter *k* is increasing function of the crosslink degree. The number average molar mass between the network crosslinks, the distance between the macromolecular chains and the number of elastically effective chains are decreasing functions of the crosslink degree.

List of symbols

C_{MAA}	concentration of monomer (MAA) (wt%)
C_{MBA}	concentration of crosslinker (MBA) (mol%)
C_{in}	concentration of initiator (VA-044) (mol%)
C_n	Flory's characteristic ratio (C_n(MAA) = 14.6)
$\Delta\alpha$	range of applicability of semi-empirical Peppas equation: $\alpha = kt^n$
k	characteristic constant of the hydrogel (min^{-n})
l	carbon–carbon bond length (Å)
m_0	weight of xerogel (dry hydrogel) (g)
m_1	weight of picnometer filled with toluene (g)
m_2	weight of picnometer filled with toluene and with xerogel sample in it (g)
m_{eq}	weight of the hydrogel sample swollen to equilibrium (g)
m_t	weight of the swollen hydrogel sample at the time *t* (g)
m_{xg}	weight of the xerogel sample (g)
M_c	average molar mass between the network crosslinks (g/mol)
M_0	molar mass of repeated unit (g/mol)
MAA	methacrylic acid
MBA	N,N′-methylene bisacrylamide
n	characteristic exponent indicative for the mode of the penetrant transport mechanism
N_A	Avogadro number (6×10^{23} mol^{-1})
ND	neutralization degree of monomer (%)
$\upsilon_{2,s}$	polymer volume fraction in the equilibrium swollen state
PMAA	poly(methacrylic acid)
ξ	distance between the macromolecular chains (nm)
R	correlation coefficient
ρ_c	crosslinking degree
ρ_T	density of the toluene (ρ_T = 0.87 g/cm^3)
ρ_{xg}	xerogel density (g/cm^3)
SD	isothermal swelling degree (g/g)
SD_{eq}	equilibrium swelling degree (g/g)
t	time (min)
V_e	number of elastically effective chains totally induced in a perfect network per unit volume (cm^{-3})
V_{H_2O}	molar volume of H_2O (cm^3/mol)

VA-044	2,2′-azobis-(2-(2-imidazolin-2-yl)propane) dihydrochloride
X	nominal molar ratio of MBA and MAA (mol MBA/mol MAA)
χ	Flory-Huggins interaction parameter between solvent (H_2O) and polymer (PMAA)

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