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The Effect of Primary Structural Parameters of Poly(methacrylic acid) Xerogels on the Kinetics of Swelling

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ABSTRACT: Xerogels of poly(methacrylic acid) (MAXG) with different primary structural parameters (PSP) [number average molar mass between the network crosslinks (M_c), the crosslink degree (ρ_c), and the distance between the macromolecular chains (d)] are successfully synthesized by crosslinking free-radical polymerization. The isothermal swelling curves of synthesized MAXG are measured in distilled water in the temperature range of 25–40°C. The swelling conversion curves of all the MAXG may be described with kinetics model of phase boundary controlled reaction, i.e., contracting area (R2). The values of swelling kinetics parameters (E_a and ln$A$) linearly increase with the increase in M_c. This work presented a novel and quantum model of the mechanism of xerogel's swelling activation process based on resonant coupling of vibration oscillation of water molecules and vibration modes of xerogel. A quantum nature of E_a of swelling process is proved and explained the effects of PSP on the values of swelling kinetics parameters.

KEYWORDS: activation energy; kinetics of swelling; kinetics model; poly(methacrylic acid); structural parameters; xerogels

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INTRODUCTION

Hydrogels are three-dimensional networks of hydrophilic polymers capable of absorbing significant amounts of water, water solutions, and biological liquids without dissolving or losing their structural integrity. They are also called "smart," "intelligent," "stimuli-responsive," or "environmental-sensitive" hydrogels and attracted great attention in recent years.[1,2]

The application of hydrogels in drug delivery, agriculture, horticulture, heavy metals, or toxic substances removal, could be affected significantly by their swelling properties. For "smart" hydrogels their fast response to the external stimuli is of exceptional importance. Bearing in mind the possible application of hydrogels, the equilibrium swelling degree (SD) and parameters controlling swelling kinetics (swelling rate and activation energy) appear to be the most important properties.

Because of that, the evaluation of the correlation between the structural parameters of the xerogels and the swelling kinetics parameters would be of the enormous importance, both fundamental and practical.

Numerous mathematical models have been proposed for describing the kinetics of hydrogels swelling: diffusion, diffusion-relaxations, viscoelastic, and kinetics of the first and second order chemical reaction.

The Fickian diffusion model applies Fick's law for distribution of solvent in a gel sample during swelling.[3] In accordance with that model, kinetics of hydrogel swelling may be mathematically described by the eq. (1):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} exp\left[\frac{-D(2n+1)^2\pi^2 t}{\delta^2}\right] \quad (1)$$

where M_t and M_∞ represent the amounts of absorbed solvent in time t and in equilibrium state, respectively, n is diffusion constant, D is constant of solvent diffusion, and δ is thickness of the xerogel. If we make an approximation of eq. (1) for early stage of diffusion, we get to the following mathematical expression for the kinetic of swelling of diffusion model:

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi\delta^2}\right)^{1/2} = kt^{n1/2} \quad (2)$$

The collective diffusion model is based on Li-Tanaka theory of hydrogel swelling developed for hydrogels with defined shapes.[4] On the basis of that theory, process of hydrogel swelling may be decomposed on two imaginary processes. The first one is a pure network diffusion process described by a collective diffusion equation with zero solvent velocity. This process increases the shear

energy of the hydrogels. In the second process, the solvent move together with the network so that the solvent velocity is the same as the network velocity.[5] In accordance with that theory, characteristic xerogel's swelling time (τ) is dependent on xerogel's particle size and cooperative diffusion coefficient, as is given in eq (3):

$$\tau \approx \frac{R^2}{D} \tag{3}$$

where R is a radius of xerogel's particle and D is cooperative diffusion coefficient. Therefore, the hydrogels swelling kinetics is determined with their nature, shape, and particle size.

Significant deviation of hydrogels swelling kinetics from Fick's law of diffusion are most commonly interconnected with: the variable surface concentration, history-dependant diffusion coefficients, stresses between parts of the gel swollen to different extents, polymer relaxation.[6–8]

Bearing that in mind, kinetics of hydrogel swelling is most frequently mathematically described by the well-known power-law Peppas' equation[9]:

$$\frac{M_t}{M_\infty} = k \cdot t^n \tag{4}$$

where k is swelling constant rate while n is diffusion exponent indicative for the swelling mechanism.

Alfrey et al.[10] suggested three models for describing solvent diffusion in polymer network: (1) Fick's diffusion (Case I, $n = 0.5$), which is kinetically limiting stage of swelling, when the rate of solvent diffusion is lower than the rate of polymers chains relaxations; (2) second law of diffusion (Case II, $n = 1$) when the rate of solvent diffusion is higher than the rate of polymers chains relaxations, and (3) abnormal or non-Fickian diffusion ($0.5 < n > 1$), which happens when the rates of solvent diffusion and polymer chains relaxation are similar.

Considering that the swelling is linear superposition of independent contribution from Fickian diffusion and polymer relaxation (diffusion–relaxation model), Berens and Hopfenberg[7] gave the following expression (5), which describes swelling of kinetic:

$$\frac{M_t}{M_\infty} = x_F\left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} exp\left[\frac{D(2n+1)^2\pi^2 t}{\delta^2}\right]\right] + x_R[1 - exp(-k_R t)] \tag{5}$$

where the x_F is the fraction of swelling contributed by Fickian diffusion, x_R is the fraction of swelling contributed by relaxation of chains, k_R is constant rate of relaxation of chains.

For $M_t/M_\infty \geq 0.4$, effect of diffusion component on swelling kinetic is negligible and eq. (5) is transformed into following form:

$$ln\left(1 - \frac{M_t}{M_\infty}\right) = ln\, x_R - k_R t \tag{6}$$

On the basis of eq. (6) it is possible to calculate x_R and k_R, and thus entirely describe swelling kinetics in accordance with the diffusion-relaxation model.

Assuming hydrogel swelling as a viscoelastic system, by applying Kelvin–Voight model Omidian et al.[11] developed mathematical expression for describing deformational changes of hydrogel (ε) during swelling under constant stress (σ_o).

$$\varepsilon = \frac{\sigma_o}{E}\left[1 - exp\left(\frac{t_o - t}{\tau_o}\right)\right] \tag{7}$$

where E is Young model of elastic component of the system and τ_o is time of relaxation.

Because, the $t_o - t \leq \tau_o$ is an exponential term close to 1 (one) eq. (7) can be easily transformed to the following form:

$$ln\left(1 - \frac{\varepsilon}{\varepsilon_\infty}\right) = \frac{t_o}{\tau_o} - \frac{t}{\tau_o} \tag{8}$$

The eq. (8) is suitable to describe kinetics of swelling and to calculate the value of relaxation time.

Mathematically similar expression for describing swelling kinetics was given by Katime et al.[12] assuming that the rate of swelling at any given time is directly proportional to the available swelling capacity ($M_\infty - M_t$):

$$ln\left(1 - \frac{M_\infty}{M_t}\right) = k \cdot t \tag{9}$$

On contrary to this, Schott[13] assumed that the swelling rate is proportional to the square of the swelling capacity and obtained the expression that describes swelling kinetics:

$$M_t = \frac{kM_t^2 t}{1 + kM_\infty t} \tag{10}$$

Adnadevic and Jovanovic developed a novel method for determining kinetics model for hydrogel swelling.[14] By applying this model in evaluation kinetics the swelling of the poly(acrylic acid) (PAA) hydrogels in water, they proved that kinetics of swelling of the PAA hydrogels is phase-boundary controlled process (contracting interface area), which is described by the equation:

$$\alpha = \left[1 - (1 - kt)^2\right] \tag{11}$$

The literature information about the influence of the primary structural parameters (PSP) of the xerogel [xerogel density (ρ_{xg}), number average molar mass between the network crosslinks (M_c), the crosslink degree (ρ_c), the distance between the macromolecular chains (d)] on swelling kinetics are sparse. In the works of Lowman,[15] Lin and Metters,[16] Omidian et al.,[17] Chen and Park,[18] the effect of molecular pore size of xerogel on the mechanism and swelling kinetics is discussed. In the case of nonporous xerogel ($d \leq 1.0$ nm) major swelling mechanism is diffusion of solvent molecules through free-volume of the xerogel network. Because of that, swelling rate is very slow and size dependent. For the micro-porous xerogel (10 nm $\leq d \leq$ 100 nm) swelling, the dominant mechanism is the combination of diffusion of solvent molecules and their convection in solvent

filled pores. Here, again swelling is slow and dependent on sample size. In the case of macro-porous xerogel (0.1 μm $\leq d \leq$ 1 μm) dominant swelling mechanism is diffusion in the water filed pores. Swelling rate is high but dependent on particle size.

For super-porous xerogels (high porosity with interconnected open-cell structure) dominate swelling mechanism of capillary rising of solvent and because of that swelling kinetics is very fast and independent on sample size. Investigating effect of crosslinking degree of acrylic hydrogels, Omidian et al., found that the increase in crosslinking degree leads to the increase in the swelling rate.[11]

With consideration of everything presented above, in this work the xerogels of poly(methacrylic acid) (MAXG) with different PSP: [number average molar mass between the network crosslinks (M_c), the crosslink degree (ρ_c), the distance between the macromolecular chains (d)], were synthesized with an intention to examine the existence of correlation and functional relationship between the primarily structural parameters of the MAXG and their kinetics parameters of swelling (kinetics model, E_a and ln$A$).

EXPERIMENTAL

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 (MBA) (p.a) was supplied by Aldrich Chemical, Milwaukee, WI. The initiator, 2,2′-Azobis-[2-(2-imidazolin-2-yl)propane] Dihydrochloride (VA-044) (99.8%) was supplied by Wako Pure Chemical Industries. Sodium hydroxide (p.a) was obtained from Aldrich Chemical, Milwaukee, WI. 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.

Synthesis

The poly(methacrylic acid) hydrogels were synthesized via crosslinking free-radical polymerization of MAA in aqueous media using the procedure, which was described in details previously.[19] The general procedure is as follows. Firstly, the 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 after this, the prepared reaction mixture was poured into glass molds (plates separated by a rubber gasket 2 mm thick), and placed in an oven at 80°C, for 3 h. 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, MAXG, were stored in a vacuum exicator until use.

With intention to obtain MAXG with different structural properties, the reaction parameters were varied. Sample A was synthesized using 40% wt MAA in reaction feed, which was neutralized to 40%, while the samples C, D, and E were synthesized using 20% wt MAA neutralized to 10%, 40%, and 80%.

Structural Characterization of the Synthesized Xerogel

The following PSP of the synthesized poly(methacrylic acid) xerogels were determined and calculated: xerogel density (ρ_{xg}), average molar mass between the network crosslinks (M_c), crosslinking degree (ρ_c), and the distance between the macromolecular chains (d).

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

$$\rho_{xg} = \frac{m_{xg}\rho_T}{m_1 + m_{xg} - m_2} \tag{12}$$

where m_{xg} is the weight of the xerogel sample, m_1 is the weight of pycnometer filled with toluene, used as the nonsolvent, m_2 is the weight of pycnometer filled with toluene with the xerogel sample in it and ρ_T is the density of toluene ($\rho_T = 0.864$ g/cm^3).

The value of the M_c was determined by the equation proposed by Flory and Rehner[20]:

$$M_c = \frac{-\rho_{xg} V_{H_2O} \upsilon_{2,s}^{1/3}}{ln(1-\upsilon_{2,s}) + \upsilon_{2,s} + \chi\upsilon_{2,s}^2} \tag{13}$$

where V_{H2O} is the molar volume of H_2O, $\upsilon_{2,s}$ 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 $\upsilon_{2,s}$ and χ were calculated using the following expressions:

$$\upsilon_{2,s} = \frac{1}{1 + \rho_{xg} SD_{eq}} \tag{14}$$

$$\chi = \frac{ln(1-\upsilon_{2,s}) + \upsilon_{2,s}}{\upsilon_{2,s}^2} \tag{15}$$

The degree of crosslinking was calculated as[21]:

$$\rho_c = \frac{M_0}{M_c} \tag{16}$$

where M_o is the molar mass of the repeating unit.

The distance between the macromolecular chains was calculated as:

$$d = l\upsilon_{2,s}^{-1/3}\left(2C_n\frac{M_c}{M_0}\right)^{1/2} \tag{17}$$

where C_n is the Flory characteristic ratio (C_n(MAA) = 14.6) and l is the carbon–carbon bond length (1.54 Å).[22]

Swelling Experiments

Dry hydrogel (xerogel) disks with an average weight of 0.10 g (±10%) were left to swell in distilled water at the temperatures 25, 35, and 40°C (±2°C). At the beginning of each experiment,

the xerogel disks were weighted (m_o) 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 weighed (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. For each sample and temperature, at least three swelling measurements were performed and the mean values were used.

Determination of the Swelling Degree and the Normalized Swelling Degree

The isothermal SD defined as the difference between the weight of the swollen hydrogel sample at the time t (m_t) and the weight of the xerogel (dry hydrogel) (m_o) divided by the weight of the xerogel sample (m_o), was determined as a function of time at constant temperature and calculated using the equation:

$$SD = \frac{m_t - m_0}{m_0} \tag{18}$$

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

The normalized SD (α), defined as the ratio between the SD at time (t), and the equilibrium SD for certain temperature was calculated as:

$$\alpha = \frac{SD}{SD_{eq}} \tag{19}$$

METHODS USED TO EVALUATE THE PARAMETERS OF SWELLING KINETICS

Stationary Point Method

In isothermal heterogeneous chemical reaction kinetics, the function $d\alpha/dt = f(t)$ (where $d\alpha/dt$ is the rate of the process and t is the reaction time), can be observed as a function with a local maximum. This maximum appears at the so-called stationary point, where the reaction system under the given conditions has the maximal reaction rate $[(d\alpha/dt)_{\max}]$, which can be expressed by the following equation[23]:

$$\left(\frac{d\alpha}{dt}\right)_{max} = k(T, p_j) f(\alpha_{max}) \tag{20}$$

In eq. (20), $\alpha_{\max}$ represents the degree of conversion at $t = t_{\max}$, $f(\alpha_{\max})$ is a function of the reaction mechanism at the value of $\alpha_{\max}$ $[f(\alpha_{\max}) = f(\alpha = \alpha_{\max})]$, and $k(T, p_j)$ is the rate constant at temperature T, where p_j denotes the partial pressure of the gaseous species. Commonly, if the Arrhenius dependence of $k(T, p_j)$ on temperature is assumed, eq. (20) can be transformed into the following form:

$$\left(\frac{d\alpha}{dt}\right)_{max} = A\, exp\left(-\frac{E_a}{RT}\right) f(\alpha_{max}) \tag{21}$$

where E_a is the apparent activation energy of the overall process, whereas A and R are the preexponential factor and gas constant, respectively. The logarithmic form of eq. (21) is:

$$ln\left(\frac{d\alpha}{dt}\right)_{max} = ln[Af(\alpha_{max})] - \frac{E_a}{RT} \tag{22}$$

The apparent activation energy (E_a) of the investigated process was determined from the slope of the dependence of ln $(d\alpha/dt)_{\max}$ *vs.* $1/T$.

Model-Fitting Method

The kinetics model for the PMAA hydrogel swelling was examined by the so-called model-fitting method. The model-fitting method is widely used to determine the suitability of various kinetic reaction models for solid state reactions.[24] According to the model-fitting method, the kinetic reaction models for any solid phase-reaction are classified into five groups depending on the reaction mechanism: (1) a power law reaction, (2) a phase boundary controlled reaction, (3) reaction order reaction, (4) a reaction described by the Avrami Equation, and (5) diffusion controlled reactions.

The model-fitting method is based on the following. The experimentally determined conversion curve $\alpha = f(t)_T$ has to be transformed into the so called normalized conversion curve $\alpha = f(t_N)_T$, where t_N is the so-called normalized time. The normalized time, t_N, is defined by the Equation:

$$t_N = \frac{t}{t_{0.9}} \tag{23}$$

where $t_{0.9}$ is the time at which $\alpha = 0.9$.

The kinetics model of the investigated process was determined by analytically comparing the $\alpha = f(t_N)_T$ curves with the normalized conversion curve for different theoretical models for reaction in solid state $\alpha_{te} = f(t_N)_T$ (given in Table I). A measure of deviation of the $\alpha = f(t_N)_T$ from the $\alpha_{te} = f(t_N)_T$ is the value of the sum of squares of the residual. The model for which the sum of squares of the residual is minimal is accepted as the kinetics model of the investigated process.

A set of the reaction models used to determine the model, which describes the swelling kinetic of PMAA hydrogels is given in Table I, where $f(\alpha)$ is the analytical expression describing the kinetic model and $g(\alpha)$ is the integral form of the kinetics model.

RESULTS AND DISCUSSION

The structural parameters of the MAXG used in this investigation as well as their equilibrium SDs determined in distilled water at 25°C are presented in Table II.

As can be seen from Table II, based on the values of structural parameters of the MAXG, it is obvious that the MAXG with significantly different structural parameters were successfully synthesized.

The values of the average molar masses between crosslinks were in wide range (range of 6400–1,100,000 g/mol), as well as the values of the crosslinking degrees (range of 1.5–225 $\times$ 10^{-4} mol/cm^3) and the distances between the macromolecular chains (range of 21–790 nm), while the values of the Flory's polymer-solvent interaction parameter (χ) are very similar.

Table I. Set of the Kinetics Reaction Models Used to Determine the Kinetics Model of MAXG Swelling

Symbol	Kinetics models	$f(\alpha)$	$G(\alpha)$
P1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
P2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
R1	Zero-order (Polany–Winger equation)	1	α
R2	Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
R3	Phase-boundary controlled reaction (contracting volume, i.e., tridimensional shape)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
F1	First-order (Mampel)	$(1-\alpha)$	$-\ln(1-\alpha)$
F2	Second-order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
F3	Third-order	$(1-\alpha)^3$	$0.5[(1-\alpha)^{-2}-1]$
A2	Avrami–Erofe′ ev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3	Avrami–Erofe′ ev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A4	Avrami–Erofe′ ev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
D1	One-dimensional diffusion	$1/2\alpha$	α^2
D2	Two-dimensional diffusion (bidimensional particle shape)	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3	Three-dimensional diffusion (tridimensional particle shape), Jander equation	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
D4	Three-dimensional diffusion (tridimensional particle shape), Ginstling–Brounshtein	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

To investigate nature of the xerogels structure, we tried to find mathematical relationship between the SDeq and the structural parameters of the MAXG. The variations of the SDeq with the structural parameters of xerogels (M_c, ρ_c, and d) can be expressed by the following equations:

$$SD_{eq} = 0.1\left[\frac{mol}{g}\right] M_c^{0.605} \; R^2 = 0.998 \tag{24}$$

$$SD_{eq} = 0.1\left[\frac{cm^3}{mol}\right] \rho_c^{-0.62} \; R^2 = 0.999 \tag{25}$$

$$SD_{eq} = 1.52\left[\frac{1}{nm}\right] d^{0.87} \; R^2 = 0.999 \tag{26}$$

where and R^2 is the correlation coefficient. The data were analyzed using the commercial program Origin Microcal 8.0.

The found power law dependence of SDeq on the PSP implies on fractal nature of the xerogels network and fractal nature of network expanding.

Assuming that basic structural parameter of the xerogel network is the Mc, by using the scaling functional relationships given with eqs. (24)–(26), we can get to the functional relationships between the values of the crosslinking degrees (ρ_c) and the distances between the macromolecular chains (d) with and the M_c as is presented by the following equations:

$$\rho_c = 131.63 \cdot M_c^{-0.96} \; R^2 = 0.999 \tag{27}$$

$$d = 0.085 \cdot M_c^{-0.63} \; R^2 = 0.998 \tag{28}$$

The eqs. (27) and (28) and completely confirms that the proposed fractal nature of xerogel network structure and the possibility of scaling the other properties of the xerogel with the M_c.

The swelling isotherms of the PMAA hydrogel for selected sample A, in distilled water at different temperatures, are presented in Figure 1.

From Figure 1 it can be observed that the isothermal swelling curves were similar in shape for all the investigated MAXG samples. Three characteristic shapes of the changes of the SD with swelling time can be distinguished in all of the swelling curves, a linear, nonlinear, and the saturation part or plateau. Increasing the swelling temperature resulted in an increase in the equilibrium SD and the slope of the linear part of the dependence of the SD vs. time.

Table II. The Structural Paramaters and Equilibrium Swelling Degrees in Distilled Water at 25°C of the MAXG

Samples	ρ_{xg} (kg/m^3)	M_c (g/mol)	$\rho_c \times 10^4$ (mol/cm^3)	d (nm)	χ	SD_{eq}, (g/g)
A	1440	6400	225	21	−0.54	21
C	1310	105,000	13	154	−0.51	120
D	1350	220,000	6	176	−0.50	176
E	1420	1,100,000	1.5	790	−0.50	420

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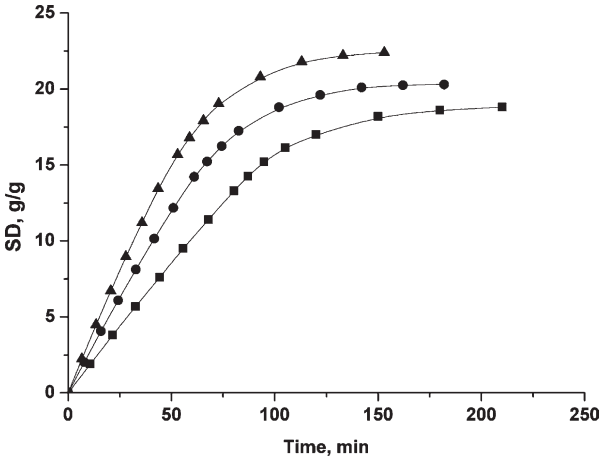

Figure 1. The isothermal swelling curves of the MAXG, sample A, in distilled water at: (■) 25°C, (●) 35°C, and (▲) 40°C.

To determine the kinetic parameters of the MAXG swelling by free-models methods, the stationary point method was applied. The dependences of the rate of swelling ($d\alpha/dt$) with the normalized degree of swelling at the investigated temperatures are shown in Figure 2 for sample A.

For each of the investigated MAXG, in spite of their different structural properties, the curves of the dependences of $d\alpha/dt$ on the normalized degree swelling were similar by a shape, which implies the identical kinetics model.

The found shape of the change of $d\alpha/dt$ with α, implies that it was not possible to describe swelling kinetics by the models of diffusion, diffusion-relaxation visco-elastic, which were described in the Introduction section.[25]

From the presented curves, it is noticeable that increasing value of α resulted in a characteristic decrease of the rate of swelling and that the maximal rates of swelling (v_{max}) were achieved at the beginning of the process, i.e., when $\alpha \rightarrow 0$. Table III presents the dependence of the maximal rate of swelling on temperature for the investigated samples of PMAA hydrogels.

Table III. The Changes of the Maximal Rate of Swelling for the MAXG with Temperature and Kinetics Parameters

	$v_{max,}$ min^{-1}				
Samples	298 K	303 K	313 K	$E_{a,s}$ (kJ/mol)	$ln[Af(\alpha_{max})]$
A	0.009	0.013	0.015	24.9	5.31
C	0.005	0.008	0.009	28.2	6.20
D	0.0075	0.012	0.017	39.7	11.14
E	0.0049	0.0060	0.091	30.7	7.08

The values of the swelling kinetic parameters obtained by the method of stationary point are presented in Table III, columns 5 and 6. For swelling temperatures 298 and 308 K, sample A of the investigated MAXG, which had the minimal values of the M_c and the d achieve the maximal rate of swelling with the minimal value of $E_{a,s} = 24.9$ kJ/mol. In contrast to this, at $T =$ 313 K, sample E had the maximal value of the swelling rate of with the $E_{a,s} = 30.79$ kJ/mol.

To determine the kinetic model of PMAA hydrogels swelling by applying model-fitting method, the normalized conversion curves of the isothermal swelling for all of the used MAXG samples at all the investigated temperatures were determined. The normalized conversion curves, of the isothermal swelling of the PMAA for sample A as an example, at the investigated temperatures are shown in Figure 3.

For each sample, all of the obtained curves at all the investigated temperatures were identical in shape, which implies an existence of a same kinetic model. In fact, this means that the swelling kinetic model is independent on the primarily structural parameters of the studied MAXG.

By means of the applied model-fitting method, it was recognized that the isothermal swelling kinetics of the structurally different MAXG can be modeled by the kinetic model of a

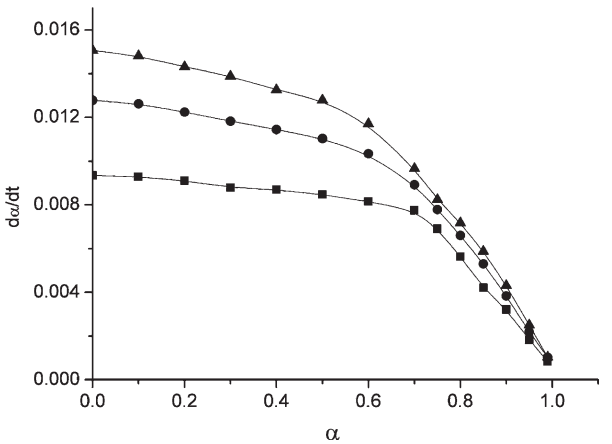

Figure 2. The plot of the ($d\alpha/dt$) with the normalized degree of swelling at: (■) 25°C, (●) 35°C, and (▲) 40°C, for MAXG, sample A.

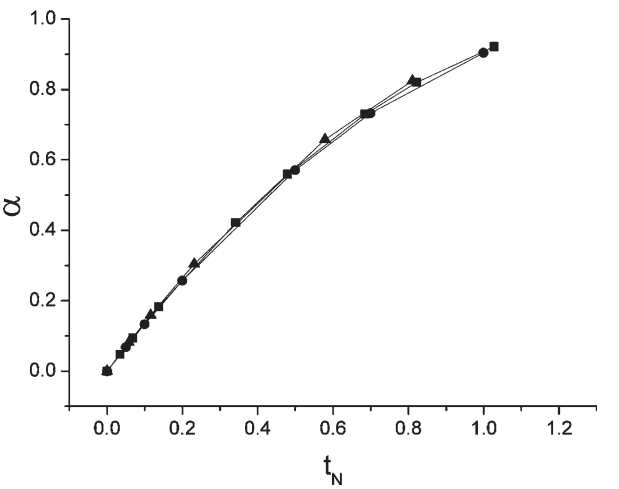

Figure 3. The normalized conversion curves of the isothermal swelling of MAXG, sample A at: (■) 25°C, (●) 35°C, and (▲) 40°C.

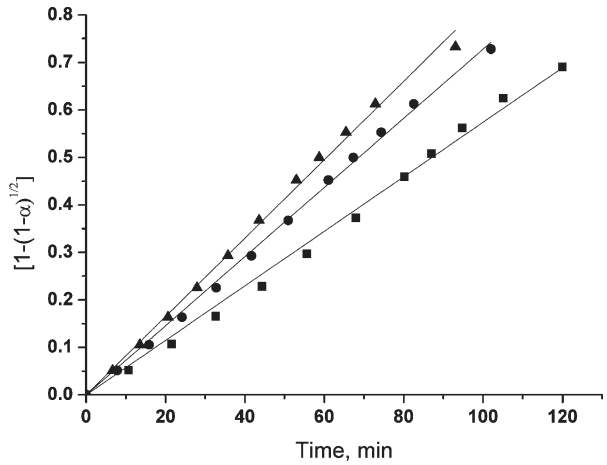

Figure 4. The dependences of $[1 - (1 - \alpha)^{1/2}]$ vs. time at: (■) 25°C, (●) 35°C, and (▲) 40°C for MAXG, sample A.

phase boundary controlled reaction, i.e., contracting area (R2), which is given by the following equation:

$$\left[1 - (1 - \alpha)^{1/2}\right] = k_M \cdot t \tag{29}$$

where k_M is the rate constant of swelling.

If eq. (29) describes the swelling kinetics of the PMAA hydrogels, then the dependence $[1 - (1 - \alpha)^{1/2}]$ on the swelling time should be a straight line. The dependences of $[1- (1 - \alpha)^{1/2}]$ vs. time at the investigated temperatures of PMAA hydrogel, for sample (A) as an example, are shown in Figure 4.

For each sample at all the investigated temperatures, the dependences $[1 - (1 - \alpha)^{1/2}]$ on the swelling time give straight lines over the whole range of the studied swelling process.

The obtained results confirm that the established kinetic model of xerogel swelling is general and independent on the PSP of the xerogel, i.e., that the swelling kinetics of hydrogel is limited with the rate of decrease in the area of interaction between the xerogel's core and the swellable layer. Therefore, the swelling kinetic is neither controlled with the process of solvent diffusion process nor the polymer network relaxation, but it is limited with the processes on the boundary phase between the xerogel core and the swelled layer of the hydrogel. That is the main reason why the kinetics model of swelling is independent of PSP.

Table IV presents the changes of the model constant of the isothermal swelling rate of the PMAA hydrogels (k_M) with temperature and the kinetic parameters of the swelling process.

The swelling rate constant exponentially increases with increasing temperature for each PMAA hydrogel sample, which enables determining the kinetics parameters of the PMAA hydrogels swelling for this model by applying the Arrhenius Equation (activation energy and preexponential factor), which are also given in Table IV.

For the MAXG samples A, C, and D, the increase in the values of the average molar mass between the network crosslinks (M_c) and the distance between the macromolecular chains (d) as well

Table IV. The Changes of the Model Constant of the Swelling Rate of the MAXG with Temperature and Their Kinetics Parameters

Samples	$k_{M,\ min}{}^{-1}$ 298 K	303 K	313 K	$E_{a,M}$ (kJ/mol)	ln (A_M/min^{-1})
A	0.0057	0.0072	0.0085	18.1	2.14
C	0.0048	0.0069	0.0083	28.5	6.17
D	0.0041	0.0067	0.0081	38.5	10.05
E	0.0044	0.0068	0.0084	33.3	8.03

the decrease in the value of crosslinking degree (ρ_c) lead to the decrease in the values of swelling rate constants and to the increase in the values of activation energy and preexponential factor.

Linear dependence of k_M on M_c can be described by the following equation:

$$k_{298} = 5.7 \cdot 10^{-3} - 7.45 \cdot 10^{-5} \cdot M_c \; R^2 = 0.993 \tag{30}$$

Bearing in mind the possibility of scaling the value of crosslinking degree (ρ_c) and the distance between the macromolecular chains (d) with the average molar mass between the network crosslinks (M_c), eqs. (31) and (32) enable us to get easy to the dependence of swelling rate constant on ρ_c and d.

$$k_{298} = 5.7 \cdot 10^{-3} + 0.010 \cdot \rho_c^{-1.01} \tag{31}$$

$$k_{298} = 5.7 \cdot 10^{-3} - 3.72 \cdot d^{1.59} \tag{32}$$

Also, the changes of activation energy calculated for this model ($E_{a,M}$) with the variation in the primarily structural parameters of the MAXG were in the following correlations:

$$E_{a,M} = 17.84 + 9.5 \cdot 10^{-5} \cdot M_c \tag{33}$$

$$E_{a,M} = 17.84 - 0.013 \cdot \rho_c^{-1.01} \tag{34}$$

$$E_{a,M} = 17.84 + 4.75 \cdot 10^{-3} \cdot d^{1.59} \tag{35}$$

Linear decrease in swelling rate constant, i.e., the increase of E_a and ln$A$ with the increase in the M_c is caused with a fractal nature of polymer network structure of the MAXG and is a consequence of the increase in energy required for initialization of the basic structural parameter of the xerogel network is the M_c, i.e., for formation "active complex" polymer network-water molecules.

The values of preexponential factor for structurally different MAXG are in functional relationship with their activation energies, which means that a compensation effect exists, which is described by the equation:

$$\ln A_M = -4.86 + 0.387 E_{a,M} \quad R = 0.995 \tag{36}$$

The existence of a compensation effect concerning to the PSP of the used hydrogels directly confirms that the changes of swelling kinetics parameters of the hydrogels are consequences of the changes in their structural parameters.[26]

Also, by comparing the $E_{a.M}$ values for one to another hydrogel, we can conclude that the differences between the $E_{a.M}$ ($\Delta E_{a.M}$)

Table V. The Values of Differences Between the $\Delta E_{a.M}$ of Structurally Different MAXG (ε_o = 5.22 kJ/mol)

Δ Samples	$\Delta E_{a.M}$ (kJ/mol K)	$\Delta E_{a.M}/\varepsilon_o$	N
A-E	15.22	2.92	3
C-A	10.44	1.99	2
D-C	10.04	1.92	2
D-E	15.22	1.0	1

are for structurally different MAXG multiplied integer number of an energetically quantity ε_o = 5.22 kJ/mol. That information implies on the assumption that activation energy of swelling process is multiplied integer number of some basic energetically quantity, i.e., that the E_a changes stepwise with the changes in the hydrogels structures and that corresponds to different levels of vibrational excitation.

Table V presents the values of differences between the $\Delta E_{a.M}$ of structurally different MAXG (ε_o is the smallest number of the Δ values contained in the $\Delta E_{a.M}$).

The compensation effect is caused with different values of the structural parameters of the MAXG and with the fact that the activation energy of the overall process is proportional to the multiple integer of an elementary energy quantity (ε_o). This means that the activation energy is quantized and is in well accordance with the Larson's model of the formation of the transition state specific for particular physico–chemical process.[27]

In accordance with the model of selective energy transfer, the existence of a compensation effect is explained as a consequence of resonant transfer of the necessary amount of vibrational energy from an energetic reservoir onto a reacting molecule. The main idea of the model of selective energy transfer is a state of resonance between vibrational modes both of the energy reservoir (ω) and reacting molecule (v), which is most likely to carry the reactant towards formation of the "activated complex." This activation requires a transfer of resonance energy from the energy reservoir to the reactant and when the reactant has received a suitable number of vibrational quanta, the reaction proceeds. Treating this resonance system as a classical forced, damped harmonic oscillator, an empirical Arrhenius Equation can be obtained:

$$\ln k = \ln A + \frac{\omega}{v^2 - \omega^2}\left[\pm\frac{\pi}{2} - arctg\frac{v\omega}{2(v^2-\omega^2)}\right]\frac{\sum_i \Delta E_i}{hc} - \frac{E_a}{RT} \quad (37)$$

where $\Delta E_i = hcv_i$ is the energy increment between the two levers n_i and n_{i+1}, h is the Planck constant, and c is the velocity of light.

This $n\sum_i \Delta E_i = E_a$ in eq. (37) can be rewritten in the following form:

$$\ln k = \ln A + \frac{E_a}{R}\left(\frac{1}{T_{ic}} - \frac{1}{T}\right) \quad (38)$$

where:

$$T_{ic} = \frac{Nhc}{R}\frac{v^2 - \omega^2}{\omega}\frac{1}{\pm\frac{\pi}{2} - arctg\frac{v\omega}{2(v^2-\omega^2)}} \quad (39)$$

For resonance conditions, eq. (39) can be transformed to:

$$T_{ic} = \frac{Nhcv}{2R} = 0.715v \quad (40)$$

which v is given in cm^{-1} and T_{ic} is in K.

According to Linert,[28] the isokinetic temperature (T_{ic}) is in relationship with the slope of the equation of the compensation effect (b) as follows:

$$T_{ic} = \frac{1}{R \cdot b} \quad (41)$$

Therefore, by combining eqs. (40) and (41), it is possible to get the expression for wave number of resonant frequency:

$$v = \frac{1}{0.719R \cdot b} \quad (42)$$

According to the model of selective energy transfer (SET) model, the E_a of reacting molecule equals to the change of its vibration energy level, which is caused with resonant absorption of energy, which is given with the following expression:

$$E_a = G_o(n) + RT \quad (43)$$

where $G_o(n)$ is the vibration energy of the molecule in excess of the zero energy vibrational level, n is the vibrational quantum number.

Since, the values of energetic terms of an anharmonic vibrator (reacting molecule) are defined with the eq. (44) given by Herzberg[29]:

$$G_o(n) = nv + n^2vx \quad (44)$$

than:

$$E_a - RT = nv + n^2vx \quad (45)$$

where x is the anharmonicity constant.

It is easy to transform the eq. (45) to (46):

$$E_a - RT = nv(1 + nx) \quad (46)$$

Because the numeric value of x is small it can be neglected in first approximation and then, we can calculate approximate value of vibration quantum number n^* by using eq. (46) as follows:

$$n* = \frac{Ea - RT(J/mol)}{v(J/mol)} \quad (47)$$

As the value of the vibration quantum number has to be the integer number, we can round number of n^* to the integer number, where x is a negative number, we get the value of n.

Table VI. The Vibration Quantum Number and the Anharmonicity Constant

Samples	$E_a - RT$ (kJ/mol)	n	x
A	15.32	4	−0.062
C	26.02	6	−0.027
D	36.02	8	−0.016
E	30.82	7	−0.021

On the basis of knowing values of E_a, v, and n, the x is calculated according to the expression:

$$x = \frac{\left(\frac{Ea-RT}{nv}\right) - 1}{n} \quad (48)$$

On the basis of the parameters of the interactive compensation effect, the values of v, n, and x for the investigated MAXG samples were calculated and the results are presented in Table V.

Bering in mind the established relation of the compensation effect, by which is found that $b = 0.387$ (mol/kJ), by employment the eq. (42) is easy to calculate the wave number of the resonance frequency ($v = 435$ cm^{-1}). The calculated values of the wave number of the resonance frequency implies that the active state formation during the swelling process occurred due to the resonance coupling of the vibration of the polymer backbone chains C—C—C— of the MAXG network ($\omega = 435$ cm^{-1}) and to the intermolecular modes of the libration rotation of water in clusters ($v = 435$ cm^{-1}).[30,31]

The wave number of the resonance frequency (v =435 cm^{-1}) corresponds to the quantum of energy, $\varepsilon_o = 5.18$ kJ/mol. The ε_o value of is in well agreement with established differences in the values of activation energies obtained by comparison of the E_a of structurally different PMAA hydrogels (ε_o).

On the basis of the experimentally determined values of activation energies of structurally different samples of MAXG, by employment of eq. (46), it is possible to determine vibration quantum number and the anharmonicity constant. The n and the x values for the investigated swelling process are given in Table VI.

Therefore, the activation of the swelling process occurs due to the resonant interaction of polymer backbone vibrations of the MAXG network and due to the intermolecular modes of water molecules in the clusters. Because of that, selective quanta transfer of necessary quantum of energy from water molecules to the polymer network takes place and that energy is enough to provoke network movement and consequently occurs network shrinking and transport of water molecules into the network.

CONCLUSIONS

Polymer network of the investigated MAXG is of fractal nature with basic structural parameter M_c.

The equilibrium SD is power function of the structural parameters of the MAXG.

The swelling conversion curves of all the MAXG may be described with kinetics model of phase boundary controlled reaction, i.e., contracting area (R2).

The kinetic swelling parameters (k_M, $E_{a,M}$, lnA_M) are linear function of their structural parameters M_c.

The changes in the lnA_M for the structurally different MAXG are in functional relationship with the changes in the $E_{a,M}$, which means that compensation effect exists concerning to the structural parameters of the investigated xerogels.

The activation of the swelling process takes place due to the resonant coupling of normal intermolecular modes of water cluster and backbone skeleton vibration of polymer network [($v = \omega = 435$ cm^{-1}), which leads to the selective transfer of energy from water molecules to the polymer network and causes movement of the network.

Activation energy of the investigated swelling process is quantized.

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REFERENCES

1. Peppas, N. A.; Mikos, A. G. In Hydrogels in Medicine and Pharmacy; Peppas, N. A., Ed.; CRC Press: Boca Raton, **1986**; Vol.*1*, pp 1–27.
2. Park, K.; Shalaby, W. C. W.; Park, H. In Biodegradable Hydrogels for Drug Delivery; Park, K., Shalaby, W. C. W., Park, H., Eds.; Technomic Pub.: Lancaster, **1993**; pp 1–252.
3. Buckley, D. J.; Berger, M. *J. Polym. Sci.* **1962,** *56*, 175.
4. Li, Y.; Tanaka, T. *J. Chem. Phys.* **1990,** *92*, 1365.
5. Hirose, H.; Shibayama, M. *Macromolecules* **1998,** *31*, 5336.
6. Crank, J.; Park, G. S. *Trans. Faraday Soc.* **1951,** *47*, 1072.
7. Berens, A. R.; Hopfenberg, H. B. *Polymer,* **1978,** *19*, 489.
8. Josh, S.; Astarita, G. *Polymer,* **1979,** *20*, 455.
9. Ritger, P. L.; Peppas, N. A. *J. Controlled Release* **1987,** *5*, 37.
10. Alfrey, T.; Gurnee, E. F.; Lloyd, W. G. *J. Polym. Sci. Polym. Symp.* **1966,** *12*, 249.
11. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Maldrun, I. *Polymer* **1998,** *39*, 6697.
12. Katime, I.; Velada, J. L.; Novoa, R.; Diaz de Apodeca, E. *Polym. Int.* **1996,** *40*, 281.
13. Schott, H. *J. Macromol. Sci. B. Phys.* **1992,** *31*, 1.
14. Adnađevic, B.; Jovanovic, J. *J. Appl. Polym. Sci.* **2008,** *107*, 3579.
15. Lowman, A. M. Smart pharmaceuticals. www.gatewaycaolition.org/files/NewEH/ htmls/Owman.don (accessed 2008).
16. Lin, C. C.; Metters, A. T. *Adv.Drug. Delivery. Rev.* **2006,** *58*, 1379.
17. Omidian, H.; Roccaa, J. G.; Park, K. *J. Controlled. Release* **2005,** *102*, 3.

18. Chen, J.; Park, K. *J. Biomed. Mater. Res. A* **1999,** *44*, 53.
19. Panic, V.; Adnadjevic, B.; Velickovic, S.; Jovanovic, J. *Chem. Eng. J.* **2010,** *156*, 206.
20. Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943,** *11*, 521.
21. Vlad, C. D.; Poinescu, I. G.; Costea, E. *Eur. Polym. J.* **1996,** *32*, 1067.
22. Brandrup, J.; Immergut, E. H. Polymer Handbook, 2nd ed.; Wiley: New York, **1975**; pp 38, 39.
23. Klarić, I.; Roje, U.; Kovačić, T. *J. Therm. Anal. Calorim.* **1995,** *45*, 1373.
24. Brown, M. E.; Dollimore, D.; Galway, A. K., Eds. In Comprehensive Chemical Kinetics; Elsevier: Amsterdam, **1980**; pp 87–91.
25. Khawan, A.; Flanagan, D. R. *J. Phys. Chem., B.,* **2006,** *110*, 17315.
26. Vyazovkin, S.; Wight, C. *Annu. Rev. Phys. Chem.* **1997,** *48*, 125.
27. Larsson, R. *J. Mol. Catal.* **1989,** *55*, 70.
28. Linert, W. J. *Chem. Inf. Comp. Sci.* **1992,** *32*, 221.
29. Herzberg, G. In Molecular Spectra and Molecular Structure, 2nd ed.; Van Nostrand Reinhold: New York, **1950**; Vol.*1*, pp 15–85.
30. Rufino, E. S.; Monteiro, E. E. C. *Polymer* **2003,** *44*, 7189.
31. Eisenberg, D.; Kauzmann, W. The Structure and Properties of Water; Clarendon Press: New York, **2005**; pp 222–226.