Polymer Bulletin 58, 243–252 (2007)
DOI 10.1007/s00289-006-0591-6

Polymer Bulletin

Influence of poly(acrylic acid) xerogel structure on swelling kinetics in distilled water

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Received: 15 July 2005 / Revised version: 5 January 2006 / Accepted: 20 January 2006

Summary

The basic structural properties of xerogels of crosslinked poly(acrylic acid) were defined and determined: xerogel density (ρ_{xg}), xerogel volume fraction in the equilibrium-swollen state (v_2), the number average molar mass between network crosslinks ($\bar{M}_c$), the crosslink density (ρ_c) and the distance between macromolecular chains (d). A crosslinking ratio (X) increase leads to a linear increase in the values for ρ_{xg} and ρ_c, while the values $\bar{M}_c$ and d decrease. The isothermal swelling kinetic curves of four samples of structurally different poly(acrylic acid) xerogels in bidistilled water at different temperatures ranging from 25 to 45 °C were determined. It is shown that isothermal kinetic swelling curves could not be described with the model of first-order reaction kinetics in entire. It was found that these curves could be described by the Johanson-Mampel-Avrami (JMA) equation. For all of the investigated xerogel samples, the initial swelling rate (v_{in}), effective reaction rate constant (k) and equilibrium swelling degree increased with swelling temperature increase. Based on the determined values of the v_{in} and k, the activation energy (E_a) and pre-exponential factor ($\ln A$) were determined. It was concluded that the activation energy linearly increased with increasing distance between macromolecular chains (d) and molar mass between the network crosslinks ($\bar{M}_c$). The relationship between the activation energy changes with pre-exponential factor (compensation effect) caused by xerogel structural properties was established. Isothermal swelling kinetics could be completely described by the kinetics of phase transition of the xerogel transformation from glassy to rubbery state, i.e. with the JMA kinetic equation.

Introduction

Hydrogels are three-dimensional, water-swollen structures composed mainly of hydrophilic homopolymers or copolymers [1]. They are rendered insoluble by chemical or physical crosslinks. Crosslinks provide the network structure and physical integrity.

Presented at 44th P.M.M. Microsymposium "Polymer Gels and Networks",
Prague, 10–14 July 2005

Due to characteristic properties such as swellability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical and environmental applications [1, 2]. Among the most important properties of hydrogels are their swelling capacity and swelling behavior, [3, 4, 5, 6], their mechanical properties [7, 8] and also dehydration behavior [9, 10]. These properties affect hydrogel usability in various applications. Hydrogels of acrylic polymers and their copolymers have been reported as hydrogels with adjustable swelling kinetics, which display special properties [11]. The presence of polyacrylic segments in hydrogels significantly increases their ability of water uptake [12]. Regardless of the fundamental and practical importance, there are relatively few publications, either patents or scientific papers, concerning the establishment and investigation of xerogel and hydrogel structures. L. Gudeman and N. Peppas [13] defined the basic structural properties (xerogel density (ρ_{xg}), number average molar mass between the network crosslinks ($\bar{M}_c$), the crosslink density (ρ_c) and the distance between the macromolecular chains (d) of interpenetrating networks of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) and postulated experimental methods for their determination. Several samples of structurally different PAA xerogels were synthesized and their influence on the hydrogel isothermal swelling kinetics in bidistilled water at various temperatures was investigated in this study.

Experimental

Materials

Acrylic acid (AA) was obtained from Merck, Darmstadt, Germany, and was stored in a refrigerator before use. Sodium persulfate and sodium thiosulfate both of p.a. purity were also supplied by Merck and were used as a redox initiator pair with 30 % hydrogen peroxide, obtained from Zorka-Šabac, Serbia and Montenegro. *N,N′*–Methylenebisacrylamide (NMBA), purchased from Merck Darmstadt, Germany was used as the crosslinking agent. Ethylenediaminetetraacetic acid (EDTA), p.a., was purchased from Merck. Sodium carbonate (Na_2CO_3) p.a. Zorka-Šabac, Serbia and Montenegro, was used for neutralization. All chemicals were used as received. Bidistilled water was used in the polymerization and swelling experiments.

Synthesis of poly(acrylic acid) xerogels

The samples of poly(acrylic acid) (PAA) hydrogel used for this investigation were synthesized using a procedure based on the simultaneous radical polymerization of acrylic acid and crosslinking of the formed poly(acrylic acid) according to a procedure described in our previous investigations [9, 10]. The resulting hydrogels were cut to approximately same discs and placed in an excess of distilled water. The water was changed seven-times every 5 h (or 12 h during night), in order to remove the unreacted monomers and the sol fraction of polymer. The reaction was carried out in nitrogen atmosphere, by varying crosslinker (NMBA) concentration keeping all the other reaction parameters constant, with the intention to prepare xerogels with different crosslink densities and to investigate the influence on swelling behavior. The values of the nominal crosslinking ratio (X), mol NMBA / mol acrylic acid, in the reaction mixture are presented in Table 1.

Table 1. Variation of nominal crosslinking ratio (X) in the reaction mixtures

Sample	1	2	3	4
X	0.003	0.005	0.008	0.010

Xerogel physicochemical characterization

The xerogel was characterized by determining and calculating the following structural properties: xerogel density (denoted ρ_{xg}), the crosslink density (ρ_{c}) the molar mass between the network crosslinks (denoted $\bar{M}_{\mathrm{c}}$) and the distance between the macromolecular chains (d).

Xerogel density (ρ_{xg}) determination. The apparent density of the synthesized sample was determined according to a procedure described in the literature, using *n*-hexane as the non-solvent [14].

Determination of the molar mass between the network crosslinks ($\bar{M}_{\mathrm{c}}$), crosslink density (ρ_{c}) and the distance between the macromolecular chains (d) was performed according to methods proposed by Gudeman and Peppas [13], using the following equations:

$$\bar{M}_{\mathrm{c}} = \frac{72}{2X} \qquad (\mathbf{1})$$

$$\rho_{\mathrm{c}} = \frac{\rho_{\mathrm{xg}}}{\bar{M}_{\mathrm{c}}} \qquad (\mathbf{2})$$

$$d = 0.154 \times v_2^{1/3} \left[0.19 \times \bar{M}_{\mathrm{c}} \right]^{1/2} \qquad (\mathbf{3})$$

where v_2 is the polymer gel volume fraction in the equilibrium swollen state at 25 °C, and was determined as follows (Eq.4):

$$v_2 = \frac{V_{\mathrm{p}}}{V_{\mathrm{g,s}}} \qquad (\mathbf{4})$$

where V_{p} is the volume of the dry polymer sample, and $V_{\mathrm{g,s}}$ is the gel sample volume after equilibrium swelling

$$V_{\mathrm{g,s}} = \frac{W_{\mathrm{a,s}} - W_{\mathrm{h,s}}}{\rho_{\mathrm{h}}} \qquad (\mathbf{5})$$

Where $W_{\mathrm{a,s}}$ is the weight of polymer after swelling in air, $W_{\mathrm{h,s}}$ the weight of polymer after swelling in n-heptane, and ρ_{h} is the density of n-heptane.

Swelling experiments

Dried hydrogels (xerogels), with average weight 0.1 g (±5 %), were left to swell in distilled water at temperatures ranging from 25 to 45 °C. At the beginning of each experiment, a piece of xerogel was weighed and then immersed in an excess of water for swelling. At predetermined time intervals the swollen gel was removed from the water and weighed until a constant mass was reached. Since the swollen gels appeared to be fragile, they were put on a grid boat with a mesh size of 1 mm. This technique allowed placement of the polymer in water and weighing of the sample without breaking. Each time the grid boat with the polymer was removed from water, it was gently dried by paper tissue in order to remove adhering water.

Determination of the swelling degree. The isothermal swelling degree (SD), defined as the difference between the weight of the swollen hydrogel sample at time (*t*) (m_t) and the weight of dry hydrogel (xerogel) sample (m_o) divided by the weight of the dry sample (m_o), was calculated according to Eq.(6) and determined as a function of time:

$$\mathrm{SD}\ [\%] = \frac{m_t - m_o}{m_o} \cdot 100 \qquad (\mathbf{6})$$

The equilibrium swelling degree ($\mathrm{SD_{eq}}$) is the swelling degree for the equilibrium-swollen hydrogel, i.e. the hydrogel sample which attained a constant mass (m_{eq}). At least three swelling measurements were performed for each sample and the mean values were reported.

Normalized swelling degree. The normalized swelling degree (α) was defined as the ratio between the swelling degree (SD) at time *t* and the equilibrium swelling degree ($\mathrm{SD_{eq}}$):

$$\alpha = \frac{\mathrm{SD}}{\mathrm{SD_{eq}}} \qquad (\mathbf{7})$$

Results and Discussion

Table 2 presents the influence of nominal crosslinking ratio (*X*) on the basic structural properties of the synthesized PAA xerogels.

Table 2. Influence of nominal crosslinking ratio (*X*) on basic structural properties of the synthesized PAA xerogels

Xerogel sample	X (mol/mol)	ρ_{xg} (kg/m^3)	$\bar{M}_c$ (g/mol)	$\rho_c.10^4$ (mol/cm^3)	v_2	d (nm)
1	0.003	688	12000	0.57	0.3	1.06
2	0.005	994	7200	1.4	0.6	1.02
3	0.008	1146	4000	2.9	0.9	0.90
4	0.010	1704	3200	4.7	1.2	0.88

The increase in the nominal molar crosslinking ratio in the reaction mixture leads to considerable changes in the basic structural properties of the synthesized xerogels. A crosslinking ratio (*X*) increase leads to an increase in the values of ρ_{xg} and ρ_c, while the values $\bar{M}_c$ and *d* decrease. A linear relationship (correlation coefficient > 0.98) between the nominal crosslinking ratio and changes of ρ_c and *d* was established as presented by the following equations:

$$\rho_c = (576\,X - 1.35)\times 10^{-4} \qquad (\mathbf{8})$$

$$d = -27.9\,X + 1.146 \qquad (\mathbf{9})$$

Also, a linear increase in xerogel density (ρ_{xg}) with the crosslink density (ρ_c) is observable, which can be presented by Eq (10):

$$\rho_{xg} = 2.298 \times 10^6 . \rho_c + 583 \qquad \textbf{(10)}$$

Figure 1 shows the swelling isotherms of the synthesized xerogels of crosslinked poly(acrylic acid) (PAA) in sodium form, in distilled water at 25 °C.

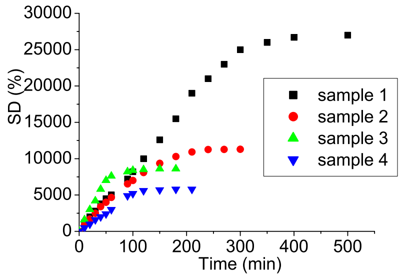

Figure 1. Swelling isotherms of PAA hydrogels in bidistilled water at 25 °C.

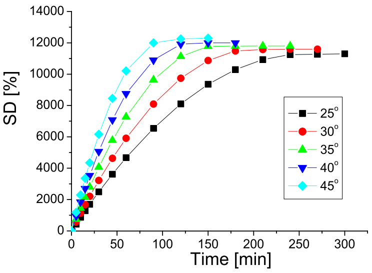

Figure 2. Swelling isotherms of PAA hydrogel, sample 2 in bidistilled water at different temperatures.

As can be seen from the presented results, Fig. 1 and Fig. 2, the swelling isotherm curves are similar in shape for all samples and at all of the investigated temperatures. Three characteristic shapes of the swelling degree changes with swelling time may be distinguished in all the swelling curves presented in Fig. 1 and Fig. 2: a linear part, a non-linear part and a saturation range or plateau.

In order to analyze the influence of xerogel structure on the swelling isotherm shape, specific parameters of the swelling isotherms are defined: period of linearity (denoted *P*), initial swelling rate (denoted v_{in}) and swelling equilibrium degree (SD_{eq}). The period of linearity (*P*) presents the region of the normalized swelling degree, within which the kinetic swelling curves are linear. The initial swelling rate (v_{in}) is defined as the ratio of the swelling degree in the final point of the linear part of the swelling curve (SD_{i}) to the swelling time that corresponds to the linear part of the swelling curve (t_{i}) (Eq 11).

$$v_{in} = \frac{\text{SD}_{\text{in}}}{t_{\text{in}}} \qquad \textbf{(11)}$$

Table 3 presents the temperature changes of the equilibrium swelling degree (SD_{eq}), the initial swelling rate (v_{in}) and period of linearity (*P*) for the hydrogel sample 2.

Table 3. Temperature influence on the equilibrium swelling degree (SD_{eq}), initial swelling rate (v_{in}), and period of linearity (*P*) for the hydrogel sample 2

Temperature [°C]	SD_{eq} [%]	v_{in} [% /min]	*P* [%]
25	11300	75	0-33
30	11600	107	0-27.7
35	11800	135	0-34.5
40	12000	156	0-32.5
45	12300	193	0-42.3

As the swelling temperature increases, the swelling equilibrium degree (SD_{eq}) increases as well as the initial swelling rate, while the period of linearity varies with temperature, as can be seen from the results presented in Figure 2 and Table 3.

Swelling kinetics are most frequently described using either the Fick's diffusion law or kinetic curve that corresponds to the kinetics of chemical reaction of the first order [14, 15].

If one assumes that the swelling kinetics of this hydrogel are controlled by water diffusion and that Fick's law is valid, it is easy to show that the experimental curve must behave according to the relationship $\mathrm{SB} = k\sqrt{t}$.

Figure 3 presents a plot of the swelling degree (SD) as a function of the square root of time ($t^{½}$) for different swelling temperatures, for hydrogel sample 2.

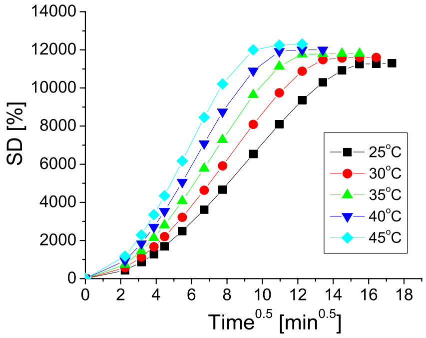

Figure 3. The plots of swelling degree as a function of the square root of time ($t^{1/2}$) for hydrogel sample 2.

The results obtained as plots of the swelling degree (SD [%]) as a function of the square root of time ($t^{1/2}$), at all of the investigated temperatures, for hydrogel sample 2 (Fig 3.), significantly deviate from straight lines.

This result implies that the so called Fickian type of solvent diffusion into the hydrogel is not the factor which dominantly influences the hydrogel swelling kinetics and the changes of swelling kinetics with temperature over the investigated temperature range.

In the case when the isotherms of swelling kinetics could be described by the first-order kinetics, the following equation (Eq. 12) can be applied:

$$\ln \frac{\mathrm{SD}_{\mathrm{eq}}}{\mathrm{SD}_{\mathrm{eq}} - \mathrm{SD}} = k \cdot t \qquad \textbf{(12)}$$

i.e., the plots of $\ln \frac{\mathrm{SD}_{\mathrm{eq}}}{\mathrm{SD}_{\mathrm{eq}} - \mathrm{SD}}$ versus time (t) give straight lines. Figure 4 presents these dependences for the investigated hydrogel sample 2 swelling at the investigated temperatures.

The plots of $\ln \frac{\mathrm{SD}_{\mathrm{eq}}}{\mathrm{SD}_{\mathrm{eq}} - \mathrm{SD}}$ as a function of time (t) give straight lines only in parts of the swelling process. Because, according to the obtained results, swelling kinetics

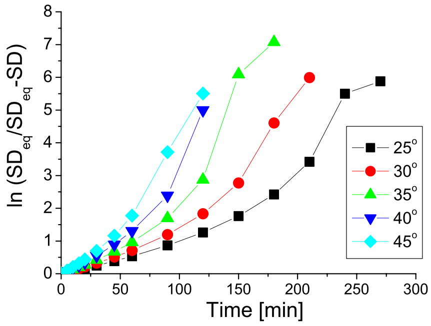

Figure 4. A plot of $\ln\frac{SD_{eq}}{SD_{eq}-SD}$ *versus* time at the investigated temperatures for hydrogel sample 2.

could not be described completely, neither with the Fick type of diffusion, or with the first-order model of reaction kinetics, the initial swelling rate was used for determination of the kinetic parameters.

Because these initial swelling rates exponentially increase with increasing temperature, using the well-known Arrhenius equation, we were able to determine the kinetic parameters of the investigated swelling process: activation energy (E_a) and pre-exponential factor (A):

$$\ln v_{in} = \ln A - E_a/RT \qquad (\mathbf{13})$$

where E_a is the activation energy and ln$A$ the pre-exponential factor. The obtained values of the kinetic parameters determined for different PAA xerogel samples are summarized in Table 4.

Table 4. Kinetic parameters for different PAA xerogel samples

Sample	E_a, kJ/mol	ln A	E_a, kJ/mol for JMA model
1	59.8	28.6	41.8
2	44.7	22.1	41.3
3	21.36	13.6	14.9
4	20.9	12.48	14.5

By comparing the results presented in Tables 2 and 4, one can conclude that the xerogel structural properties considerably influenced the swelling kinetic parameters. An increase in the molar mass between the network crosslinks ($\bar{M}_c$) and the distance between the macromolecular chains (*d)* leads to an increase in the values of the swelling kinetic parameters, while an increase in the xerogel density (ρ_{xg}) and crosslink density (ρ_c) has the opposite effect, the values of both E_a and ln$A$ decrease. The activation energy increases linearly (R > 0.98), it depends on the increase in the distance between macromolecular chains (*d*) and can be explained by Eqs (14) and (15):

$$E_a = 212\ [\text{kJ/mol nm}]\ d - 167 \qquad (\mathbf{14})$$

$$E_a = 4.7\times10^{-3}\ [\text{kJ /g}]\ \bar{M}_c + 5.9 \qquad (\mathbf{15})$$

By comparing the values of the activation energy (E_a) and pre-exponential factor (A), it can be concluded that the ln$A$ increase also coincides with the E_a increase (compensation effect) [15]. The linear relationship between ln$A$ and E_a can be expressed as:

$$\ln A = 4.539 + 0.399 E_a \qquad \textbf{(16)}$$

The established linear dependence of activation energy of the swelling process on the molar mass between the networks crosslinks ($\bar{M}_c$) and the distance between the macromolecular chains (d) implies the followings:

a) dominant influence of the kinetics of the xerogel phase transition into the viscoelastic state (rubbery state) on the swelling kinetics, and

b) possible swelling xerogel mechanism.

The first stage in the swelling mechanism is binding (adsorption) of water molecules on the macromolecular chains of the xerogel, i.e. xerogel solvation. The energy released due to xerogel solvation is a source of faster motion of chain segments, separation of the chains (highly elastic state) and chain stretching (rubbery state). The determined value of E_a corresponds to the energy of water adsorption on adsorbents which contain free OH groups on surface [16]. So, with a great degree of certainty it can be claimed that the primary water bonding occurs to the carboxyl groups of macromolecular chains. The existence of the compensation effects confirms the postulated swelling mechanism because the E_a increase is a consequence of the increase in the entropy of the solvation complex that is formed on the xerogel-water interface.

Bearing in mind the dominant influence of the kinetics of xerogel phase transition on the swelling kinetics and the widely used fact that kinetics of phase transition may be described using the Johanson-Mampel-Avrami (JMA) Equation [17], we try to express and explain the swelling kinetics with same Eq. (17):

$$\ln[-\ln(1-\alpha)] = \ln k + n \ln t \qquad \textbf{(17)}$$

where α is the normalized swelling degree, k is the overall isothermal swelling rate constant, and n is the parameter indicating the extent of swelling.

Figure 5 presents an example of isothermal dependence of ln[-ln(1-α)] on time for the hydrogel sample 2 at the investigated temperatures.

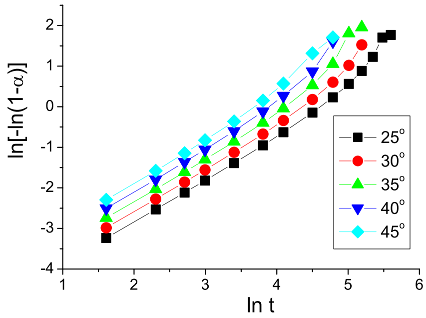

Figure 5. A plot of ln[-ln(1- α)] *versus* time for PAA hydrogel at the investigated temperatures.

If the linearity in the related coordinates, is accepted as a criterion of the applicability of any kinetic relation, then, on the basis of the results shown in Fig. 5, we can claim with a great degree of certainty that Eq. (17) describes the isothermal swelling kinetics of PAA hydrogel in bidistiled water very well. Table 5 presents the temperature changes of the linearity for the proposed kinetic model, the correlation coefficient (*R*) and the determined kinetic parameters (*k* and *n*).

Table 5. Temperature changes of the linearity (*L*), the correlation coefficient (*R*) and the kinetic parameters (*k* and n)

Temperature [^{o}C]	L [%]	R	k [n/min]	n
25	0-97	0.996	0.0050	1.16
30	0-94	0.9970	0.0070	1.15
35	0-94	0.9960	0.0087	1.16
40	0-100	0.9920	0.0092	1.24
45	0-94	0.9960	0.0123	1.22

With increasing swelling temperature the overall swelling rate constants increase exponentially. At temperatures higher than 40 ^{o}C, the values of parameter *n* slightly increased. Because the values of the kinetic parameter *n* are higher than unity (n=1.15-1.24), one can state that the swelling process took place under kinetically controlled conditions of the xerogel phase transition.

In Table 4, column 4, activation energy (E_a) for PAA xerogel samples, obtained using the JMA equation is presented. The values of the activation energy for the investigated swelling process determined on the basis of the initial velocities and the JMA model are different, but show the same tendency with the structural parameters changes of xerogels.

Different values obtained for the kinetic parameters (E_a, A) of the hydrogel swelling process using different kinetic models are a logical consequence of the limitation of applicability of a specific model to a specific stage (region) of the swelling kinetics. The values of the kinetic parameters for hydrogel swelling using phase transition kinetics, i.e. the JMA model, are realistic, which additionally confirms the validity of proposed model for the investigation of PAA hydrogel swelling kinetics.

Conclusions

The crosslinked poly(acrylic acid) xerogel structure has an important influence on the kinetics of swelling in bidistilled water. An increase in the molar mass between network crosslinks ($\bar{M}_c$) and the distance between the macromolecular chains (*d)* leads to an increase in the values of swelling kinetic parameters, the activation energy and pre-exponential factor, while an increase in the xerogel density (ρ_{xg}) and crosslink density *(*ρ_c) has the opposite effect, causing decrease in both E_a and ln$A$. Isothermal swelling kinetics may be completely described by the kinetics of the xerogel phase transition from glassy to rubbery state, using the JMA kinetic model.

Acknowledgements. This investigation was partly supported by the Ministry of Science and Environmental Protection of Serbia (projects 1948 and 1448).

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