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Study of the swelling dynamics with overshooting effect of hydrogels based on sodium alginate-*g*-acrylic acid

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Abstract

A series of hydrogels were synthesized by graft cross-link copolymerization of sodium alginate (SA) and acrylic acid (AA) using N, *N*-methylene-bis-(acrylamide) as a cross-linker. By study of the swelling kinetics of the hydrogels in different buffer solutions, the overshooting effect was observed in acidic medium, namely the gels firstly *swelled* to a maximum value *following* by a gradual deswelling until the equilibrium. The phenomenon is interpreted *as* a cooperative physical cross-linking caused by the hydrogen bond formation between the carboxyl groups of the hydrogels in a hydrophobic environment. The hydrogen bond formation was further confirmed by FT-IR spectra. The dependence of overshooting effect on the pH of buffer solution *was* more noticeable in comparison with the composition of hydrogels, demonstrating that the cooperative physical cross-linking caused by the hydrogen bond formation is dominant. Whether or not the overshooting effect appears is not only *relative* to the pH of *buffer* solution, but also depends on the pK_a of carboxyl groups on the network. The overshoot processes of the hydrogels under acidic medium at pH below the pK_a follow a quantitative model proposed by Díez-Peña et al., and the theoretical curves are in very good agreement with the experimental data. While in pH > pK_a buffer solutions, the overshoot phenomenon does not appear arising from the repulsive interaction between the ionized carboxyl groups, the swelling processes follow Schott second-order rate equation.

Keywords: Hydrogel; Hydrogen bond; Cooperative physical cross-link; Overshoot effect; Swelling kinetics

1. Introduction

Stimuli-responsive hydrogels, which change their structure and physical properties in response to external stimuli, are very attractive materials for application in biomaterial science and technology. Especially, the utilization of a stimuli-responsive hydrogel system would be important to drug delivery systems. An important parameter to consider in the design of these systems is the degree of swelling. Not only is the delivery of drugs accomplished by the swelling characteristics of hydrogels (i.e., pH-sensitive hydrogels) (Yin, Yang, & Xu, 2001), but the release of *drugs is also relative* to the swelling behavior of hydrogels (Yin, Yang, & Xu, 2002). So much attention has been paid to studies on the swelling behavior of hydrogels.

It is well known that PAA has carboxylic acid groups which could develop different intermolecular interaction like electrostatic interaction, hydrogen bonds, and dipole-ion with other polymers. Many investigations have shown that these interactions exert strong influence on the swelling behavior of hydrogels and there is a great potential for their application in pharmaceutical preparations, particularly in drug delivery systems. For example, the structure and swelling behavior of hydrogels based on MAA and *N*-iPAAm have been recently studied by Díez-Peña, Quijada-Garrido, and Barrales-Rienda (2002, 2003). The obtained results have revealed that the hydrogen bonds between carboxyl and amide lead to some anomalous features. A swelling–deswelling process under acidic pH, which is actually known as overshooting effect, may be

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attributed to the dynamic hydrogen bond formation (Díez-Peña et al., 2003).

The utilization of natural polysaccharides in drug delivery continues to be a subject of intense investigation because of their biodegradability and biocompatibility. Many polymeric networks based on polysaccharides (e.g: Chitosan, Dextran, Guar gum and Konjac glucomannan et al.) and acrylic acid (de la Torre, Enobakhare, Torrado, & Torrado, 2003; Kim & Oh, 2005; Huang, Yu, & Xiao, 2007; Liu, Hu, & Zhuo, 2004) have been prepared. Their swelling properties have also been studied. However, these studies are mostly concerned with the equilibrium swelling values and their changes with composition, temperature and pH, fewer investigations were dedicated to the study on the influence of the weak interaction such as hydrogen-bonding degree and electrostatic interaction on *swelling kinetics of gels*. In this paper, a series of hydrogels were synthesized by graft cross-link copolymerization of sodium alginate (SA) and acrylic acid (AA) using *N*,*N*′-methylene-bis-(acrylamide) as a cross-linker. The swelling kinetics of the hydrogels in different buffer solutions has been studied, a remarkable overshooting effect was observed in acidic medium. The effect was given *an* interpretation on the network structure and a cooperative physical cross-linking caused by the hydrogen bond formation between the carboxyl groups of the hydrogels in a hydrophobic environment. The influence of composition and pH of *buffer* solution was also investigated. The swelling data are analyzed by means of rigorous quantitative kinetics models.

2. Experimental

2.1. Materials and methods

Sodium alginate (SA) (Analar grade). Ceric ammonium nitrate (CAN), *N*, *N*′-methylene- bis-(acrylamide) (MBAA) was used without any further purification. Acrylic acid (AA) was vacuum distilled.

The chemical compositions of the dried gels were determined using a CHN EA1106- Elemental Analyzer (Carlo Erba Instruments, Italy).

2.2. Synthesis of graft copolymers

Sodium alginate-*graft*-poly(acrylic acid) (SA-*g*-PAA) hydrogels cross-linked with *N*,*N*′-methylene-bis-(acrylamide) (MBAA) were prepared by radical graft copolymerization with CAN as an initiator as previously described (Shah, Patel, & Trivedi, 1995). The compositions of the materials used for the synthesis of hydrogels *were* listed in Table 1. As a general procedure, SA and MBAA dissolved in moderate deionized water and AA neutralized with 6.0 mol/l NaOH solution were mixed with stirring and bubbling of a slow stream of nitrogen gas for about 30 min. A freshly prepared solution of 60 mg CAN dissolved in moderate deionized water was slowly added into the mixture to initiate the graft copolymerization. After polymerization at 50 °C for 5 h, the solid copolymer slab was taken out, and cut into 9.5-mm diameter circular disks *by punches*. These disks were divided into two parts. One part was directly used for the determination of grafting percentage; the other part was immersed in deionized water for 4 days to remove the unreacted chemicals, during this time the water was changed once every 8 h, then this part was dried under vacuum at 40 °C until constant weight was obtained and used for *swelling* kinetics.

2.3. FT-IR analysis

The FT-IR was performed by using Nicolet fourier transform infrared spectroscopy (made by Thermo Nicolet), over the *range* 500–2500 cm^{-1}. Sample B_2 was soaked in *buffer* solution of pH 2.2 till the swelling equilibrium, and then dried in vacuum at 60 °C for 24 h. Each sample B_2 before and after soaked was ground with 2 mg of KBr and then pressed to form transparent discs.

2.4. Determination of grafting percentage

The samples of the crude copolymers were weighed about 2.0 g, and extracted with *acetone* as solvent for 10 h. After complete removal of the homopolymers the residues were dried under vacuum at 60 °C for 12 h. The extractors were weighed. The grafting parameters were calculated as:

$$\text{Grafting percentage (G\%)} = [(W_2 - W_1)/W_1] \times 100\% \tag{1}$$

where W_1 and W_2 denote the weight of SA and the extractors, respectively.

Grafting percentage of each graft copolymer is given in Table 1.

2.5. Analysis of graft copolymer compositions

The samples purified in deionized water were weighed, the mass percentages of SA in the dried gels (W_{SA}) were calculated as:

$$\begin{aligned} W_{\text{SA}}\ (\%) &= \{[W_1 - (W_2 - W_3)]/W_3\} \times 100 \\ &= 100 - \text{G} \times W_1//W_3 \times 100 \end{aligned} \tag{2}$$

where W_3 denotes the weight of graft copolymers.

The mass percentages of nitrogen in the dried gels (W_{N}) were determined using a CHN EA1106- Elemental Analyzer (Carlo Erba Instruments, Italy). The mass percentages of AA and MBAA in the dried gels were calculated as, respectively

$$W_{\text{MBAA}}\ (\%) = (W_{\text{N}}/14) \times 154 \tag{3}$$

$$\begin{aligned} W_{\text{AA}}\ (\%) &= 100 - W_{\text{SA}} - W_{\text{MBAA}} \\ &= \text{G} \times W_1//W_3 - (W_{\text{N}}/14) \times 154 \end{aligned} \tag{4}$$

Table 1
Characterization of the SA-*g*-AA copolymeric gels

Gels	Feed composition (mol%)[a]			Actual Composition (mol%)			Grafting percentage (G%)
	SA (%)	AA (%)	NMBA (%)	SA (%)	AA (%)	NMBA (%)	
B1	5	92	3	4.58	91.90	3.52	571.75
B2	5	90	5	4.44	89.64	5.92	584.06
B3	10	85	5	7.34	86.86	5.80	383.07

[a] The molar content of SA is calculated based on monosaccharide unit.

where W_{MBAA} and W_{AA} denote the mass percentages of AA and MBAA in the dried gels, respectively.

The molar composition calculated from the mass compositions is presented in Table 1.

2.6. Swelling of hydrogels

Analysis of the dynamic swelling characteristics of all hydrogels was performed in a citrateborate-phosphate buffer system at 37 °C. The dried gel disks were left to swell in the different pHs of buffer solutions until the swelling equilibrium was reached. The swollen gels were withdrawn at regular time intervals from the buffer solutions, and weighted after removal of excess surface water by light blotting with a filter paper, and placed again in the same immersion bath. The normalized swelling degree Q_t at time t were calculated in grams of water per gram of dry gel using the following expression:

$$Q_t = (m_t - m_0)/m_0 \tag{5}$$

where m_0 is the initial weight of the dried disk, namely, the weight at $t = 0$, and m_t is the weight after a time t and Q_t is the weight of the water absorption at a time t. The normalized equilibrium swelling Q_∞ is given by

$$Q_\infty = (m_\infty - m_0)/m_0 \tag{6}$$

3. Results and discussion

3.1. Overshooting effect under acidic medium of hydrogels

The swelling curves at pH 2.2 for a series of Poly (SA-*g*-AA) copolymers (B_1–B_3) are shown in Fig. 1. These dynamic swelling curves corresponding to copolymers exhibit an overshooting effect, that is, the swelling curves show a maximum *following* by a gradual decrease until the swelling equilibrium. During experiment, it was observed that hydrogels were almost transparent before the maximum swelling degree was reached, and after the overshooting, the opacity increased with the gradual shrinkage of *volume*.

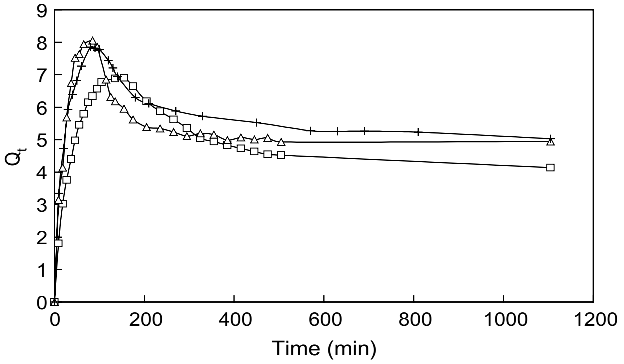
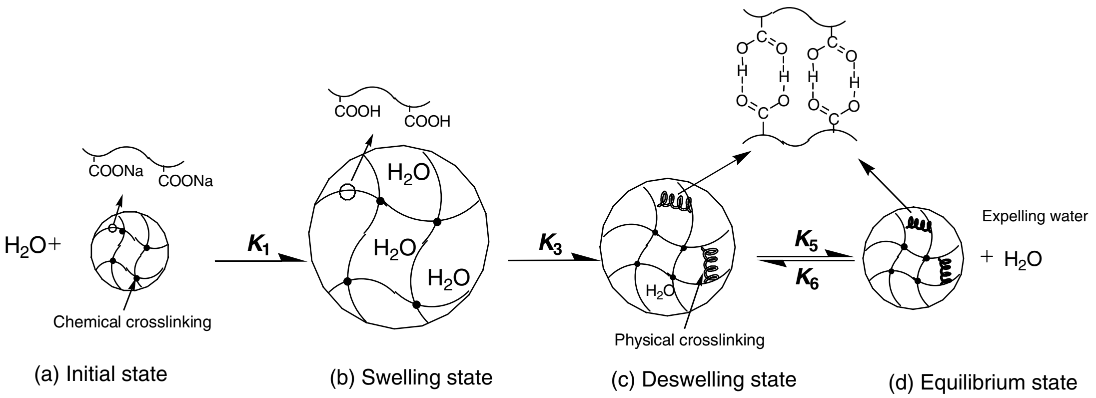


Fig. 1. Dynamic swelling curves of gel B_1–B_3 in the pH 2.2 *buffer* solution at 37 °C. +, B_1; □, B_2; △, B_3.

The overshooting effect was given many interpretations. For instance, Peppaset al. (Smith & Peppas, 1985; Urdahl & Peppas, 1987; Peppas & Urdahl, 1988) observed that the swelling curves of cross-linked polystyrene in nonopolar solvent showed a maximum *following* by a gradual decrease until the swelling equilibrium. They assumed that the phenomenon is *relative* to a relaxation process of the macromolecular chains. Later the overshooting effect in the nonionic but hydrophilic solvent has also been reported (Shieh & Peppas, 1991; Lee and Shieh, 1999, 2001). The effect was also assumed to be a result from chain relaxation. The overshooting effect of hydrogel based on poly(2-hydroxy ethyl methacrylate-co-sodium *p*-styrenesulfonate) was firstly reported by Bhardwaj, Sabharwal, and Majali (2000), they assumed that the assemblage and overlap of ion-dipole hydration shells inside the hydrogel result in the effect. Valencia and Pierola (2002) attributed the overshooting effect appearing in the swelling curves of Poly(*N*-vinylimidazole-*co*-sodium styrenesulfonate) to the formation of ionic cross-linking. Recently, Díez-Peña et al. (2003) observed that the swelling curves of cross-linked Poly (*N*-iPAAm-*co*-MAA) hydrogels in acidic medium showed an overshooting effect. They assumed that the main factor responsible for the phenomenon is a cooperative physical cross-linking (i.e. chemical cross-linking and physical cross-linking coexist and are cooperative) caused by the formation of hydrogen bonds between the carboxyl groups and the amide groups of the hydrogels in a hydrophobic environment.

On the basis of that there exist pendant carboxyl groups on structural units of two components of SA and AA for hydrogels studied here, we propose that the *overshooting* effect appearing during swelling under *acidic buffer* solutions is attributed to a cooperative physical cross-link caused by the hydrogen bond formation between the neighbouring carboxyl groups (see Fig. 2). This cooperative physical cross-link or hydrogen bond cross-link was demonstrated by the IR spectra of hydrogel (see Fig. 3). Comparing the IR spectrum (curve a) before and that (curve b) after hydrogel B_2 being soaked in buffer solution of pH 2.2,



(a) Initial state (b) Swelling state (c) Deswelling state (d) Equilibrium state

Fig. 2. Schematic picture of the swelling process with overshooting effect in acidic *buffer* solutions.

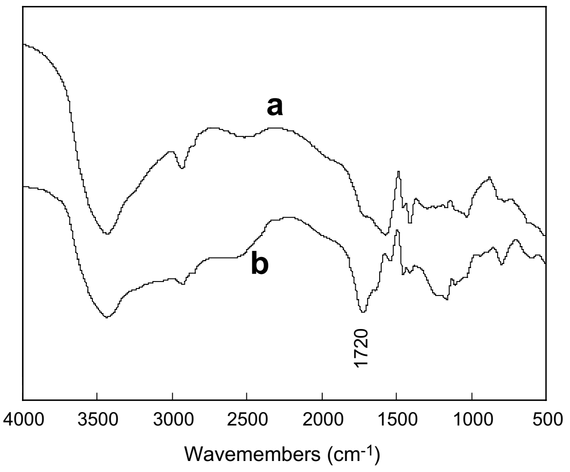


Fig. 3. FT-IR spectra of gel B_2 before and after soaked in the pH 2.2 *buffer* solution. (a) before soaked; (b) after soaked.

it was obviously seen that there existed a characteristic absorption band at $1720\,\mathrm{cm}^{-1}$ in curve b, whereas not in curve a, which indicated the formation of hydrogen bonding between carboxyl groups after soaked. The similar absorption bands in the region $1700–1720\,\mathrm{cm}^{-1}$ have also been observed in the literature Bures and Peppas (2000); Lee, Painter, and Coleman (1988); Devine and Higginbotham (2003), which were attributed to the formation of dimers between the carboxyl groups.

In *acidic* medium, before the protonization of carboxyl ions on the networks, hydrogels rapidly swell due to the repulsive forces between the carboxyl ions. With the gradual protonization of carboxyl ions, there is appearing the competition of the following two opposite processes: on the one hand the unprotonated carboxyl ions lead to the continual increase of swelling degree; on the other hand, the protonated neighbouring carboxyl groups will form hydrogen bond cross-linking as long as the space distance is allowable, and *give* rise to the contraction of network with the expelling of water. When the increased value of swelling degree caused by the former is equal to the decreased value of swelling degree led by the latter, the swelling degree reaches a maximum. Subsequently, with the continual increase in the degree of protonization of carboxylic ions, the degree of hydrogen bond cross-linking will further increase, the decreased value in the degree of swelling will exceed the increased value in the degree of swelling, the hydrogels begin to deswell till a new equilibrium is reached.

3.2. Dependence of the overshooting effect on the pH of buffer solution

The dependence of the overshooting effect on the pH of *buffer* solution is shown in Fig. 4. It is seen from the figure that the maximal swelling degree of B_2 in the pH 2.2–5.0 of *buffer* solutions increases with pH, but the overshooting effect is gradually weakened with the increase of pH. This result obviously comes from the decrease of degree of hydrogen bond cross-linking or the increase of degree of ionization of the carboxyl groups on the network: on the one hand, the increase of pH lowers the degree of protonization of the carboxyl groups, and the degree of hydrogen bond cross-linking weakens with the decrease of the capacity of expelling water out of hydrogels, and the overshooting effect being gradually weakened; on the other hand, the increase of pH increases the degree of ionization of the carboxyl groups, and the repulsive force between macromolecular chains being increased, and the maximum network

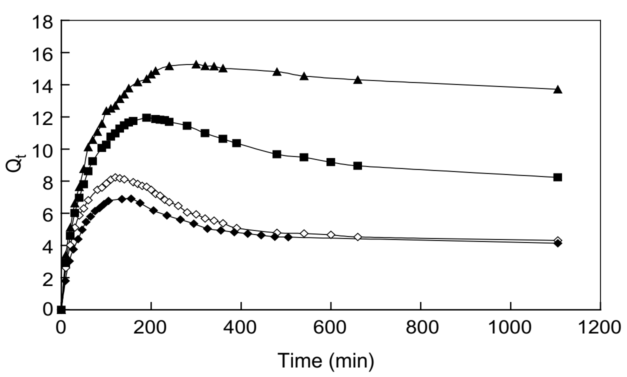


Fig. 4. Dynamic swelling curves of gels B_2 in the pH 2.2–5.0 *buffer* solutions at 37 °C. ◆, pH 2.2 ; ◇, pH 3.0; ■, pH 4.0; ▲, pH 5.0.

space which hold water becoming large, and the maximum swelling degree being gradually increased, and the time to reach the maximum swelling degree being delayed.

It is still seen from the figures that the overshooting effect of hydrogel hardly *appears* at the pH 5.0 of *buffer* solution. This is obviously *relative* to the pK_a of carboxyl groups containing in the polymer (p$K_a \approx 4.6$, (Li, Wu, Wang, & Duan, 2006)). When pH > pK_a, the degree of ionization of the carboxyl groups comes into prominence, and leading to disappearance of the overshooting effect.

3.3. Influence of composition of hydrogels on overshooting effect

The effect of composition of hydrogels B_1–B_3 on the overshooting effect is also shown in Fig. 1. An unremarkable change for the swelling curves of these hydrogels is observed. This result is different from the result reported by Díez-Peña et al. (2003) in the case of P(*N*-iPAAm-*co*-MAA) hydrogels. Because there exits a pendant carbonyl group on per structural unit of component SA and AA for hydrogels studied in the paper, the total molar percentage of carboxyl groups does not change with the molar ratio of SA and AA in the case of the same molar percentage of cross-linkers, the degree of cooperative physical cross-linking caused by the carboxyl groups little or not changes. While in the case of P(*N*-iPAAm-*co*-MAA) hydrogels, the cooperative physical cross-link comes from the hydrogen bond formation between the carboxyl groups and the amide groups in a hydrophobic environment. The degree of cooperative physical cross-linking obviously changes with the molar ratio of *N*-iPAAm and MAA. So the influence of their composition on overshooting effect is more remarkable than that for the tested hydrogels.

The little influence of composition of hydrogels B_1–B_3 on the overshooting effect may be attributed to the difference in their degree of chemical cross-linking. *Meanwhile*, this also indicates that the degree of physical cross-linking is dominant over the overshooting effect in some cases.

3.4. Kinetics model for interpretation of overshooting effect

Although the overshooting effect has been reported early in the 1980s, much attention is paid to the qualitative explanation of this phenomenon. Up to recent years, a quantitative kinetics model *given* by Díez-Peña et al. (2003) for the overshooting effect *appeared* in the swelling processes of poly(*N*-iPAAm-*co*-MAA).

According to the model, the topology of the hydrogels during swelling is divided into four states (see Fig. 2): (1) the initial state, with coil *macromolecular* chains and a collapsed network; (2) the swelling state, gradual transition of the network segments from the compact coiled state to the extended state; (3) the deswelling state, the hydrogen bonds between the functional groups being gradually forming and leading to the gradual contraction of network with the expelling water; (4) the deswelling equilibrium state.

The four states decide the existence of four different *species of water in hydrogel*, at the beginning of the swelling process, the hydrogen bonds between the functional groups of copolymer hydrogel are not formed and possess a capability of water uptake that is called A_1; the absorbed water at each time for this hydrogel is called A_2. The formation of hydrogen bonds promoted by the low pH of the medium leads to a more compact structure with a lower water absorption capability. The water content of this second structure is called A_3. Because the water content of this structure is higher than its equilibrium value, a water release occurs. The deswelled water is called A_4. The concentrations of these four species of water are regulated by the six rate constants as shown in Eq. (5).

If the concentrations of the four species of water are A_1, A_2, A_3, and A_4 and the six rate constants may be denoted by k_1, k_2, k_3, k_4, k_5, and k_6, the process may be expressed as

$$A_1 \underset{k_2}{\overset{k_1}{\rightleftarrows}} A_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} A_3 \underset{k_6}{\overset{k_5}{\rightleftarrows}} A_4 \tag{7}$$

that is, three consecutive reversible first-order reactions.

If the first and second stages of the reactions are nonreversible, i.e., $k_2 = k_4 = 0$. Then the rate may be expressed by the following series of fundamental equations

$$\begin{aligned}
\frac{dA_1}{dt} &= -k_1A_1 \\
\frac{dA_2}{dt} &= k_1A_1 - k_3A_2 \\
\frac{dA_3}{dt} &= k_3A_2 - k_5A_3 + k_6A_4 \\
\frac{dA_4}{dt} &= k_5A_3 - k_6A_4
\end{aligned} \tag{8}$$

The solution of this equation then gives the dependence of each water concentration on time. The overall content of water imbibed by the gel at time t is then given by Q_t

$$\begin{aligned}
Q_t &= A_2 + A_3 \\
&= \left(\frac{k_1}{k_1 - k_3}\left(e^{-k_3t} - e^{-k_1t}\right) + \frac{k_3}{k_1 - k_3}\frac{k_1 - k_6}{k_1 - k_5 - k_6}e^{-k_1t}\right. \\
&\quad - \frac{k_1}{k_1 - k_3}\frac{k_3 - k_6}{k_3 - k_5 - k_6}e^{-k_3t} + \frac{k_1}{k_1 - k_5 - k_6}\frac{k_5}{k_5 + k_6} \\
&\quad \left.\times \frac{k_3}{k_3 - k_5 - k_6}e^{-(k_5+k_6)t} + \frac{k_6}{k_5 + k_6}\right)a
\end{aligned} \tag{9}$$

where a represents a capability of water uptake of dried gel at $t = 0$, i.e., $A_1 = a$; $A_2 = A_3 = A_4 = 0$ when the equilibrium is reached, $t \to \infty$, Eq. (7) may be written as

$$Q_\infty = A_{3\infty} = \frac{k_6}{k_6 + k_5}a \tag{10}$$

The overall content of water absorbed by the gel at equilibrium state Q_∞ is the concentration of A_3 species in the equilibrium. It is a function of the rate constants k_5 and k_6.

Although the structure for hydrogels studied here is different from that for hydrogels reported in the literature

Díez-Peña et al. (2003), we assume that the swelling processes of the hydrogels in *acidic* medium also go through the above-mentioned four states. What is different from them is the interaction of intermolecular chains in the deswelling state. This interaction is ascribed to the hydrogen bond cross-linking between the carboxyl moieties (see Fig. 2). The swelling kinetics of the hydrogels should follow the quantitative model proposed by Díez-Peña et al. (2003).

The values of the four rate constants calculated by the fitting of the experimental data for samples B_1–B_3 to Eq. (9) are gathered in Table 2. As it can be seen, the values of the determination coefficients are quite good, in most of the cases $R^2 > 0.97$.

From Fig. 4, it is known that the overshoot process depends on the two rate constants k_1 and k_3, the two constants are *relative* to the two characteristic times, respectively, namely the time of the water to penetrate into the gel and the time to form hydrogen bonding between the carboxyl groups or the time at which the overshoot maximum appears. Only when k_3 is lower than k_1, the overshoot appears. So are the results from theoretical calculation (see Table 2).

Because k_3 is *relative* to the characteristic time at which the overshoot maximum appears, the increase of k_3 in the following order: $B_1 > B_2 > B_3$ (see Table 2) leads to a decrease of the characteristic time to reach the maximum in the following order: $B_1 < B_2 < B_3$ (see Fig. 1).

The comparison of the experimental swelling values of samples B_1–B_3 with the theoretical curves extracted from the fitting to Eq. (9) is shown in Fig. 5. In the figure, a good agreement between the values obtained experimentally and those calculated with the Díez-Peña E's model is observed.

Table 2
Rate constants k_1, k_3, k_5, k_6 and determination coefficients R^2 calculated according to Eq. (9) for gel B_1 –B_3

Gels	10^3k_1 (min^{-1})	10^3k_3 (min^{-1})	10^3k_5 (min^{-1})	10^3k_6 (min^{-1})	R^2
B_1	0.3443	0.0801	42.8125	48.9700	0.9855
B_2	0.1773	0.0657	66.8835	46.6998	0.9928
B_3	0.3911	0.0458	13.2263	16.1990	0.9710

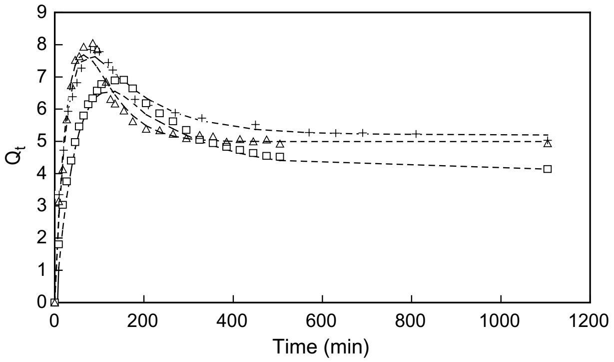


Fig. 5. Comparison of the experimental swelling curves of gels B_1–B_3 in the pH 2.2 *buffer* solution at 37 °C with the theoretical curves extracted from the fitting to Eq. (9). +, B_1; □, B_2; △, B_3; ⋯, theoretical curves.

3.5. Swelling kinetics of hydrogels in buffer solutions at pHs above 5.0

As it is seen from Fig. 4 that the overshooting effect gradually reduces with the increase of pH till its disappearance at pH = 5.0, namely the deswelling hardly *appears* after the maximum swelling degree is reached at pH = 5.0. This is ascribed to the cooperative physical cross-linking not being formed due to the complete ionization of carboxyl groups at pHs above pK_a. The swelling kinetics curves of hydrogel B_2 in the *buffer* solutions at pH 5.0–7.0 are shown in Fig. 6. Little influence of pH on the degree of swelling was observed, moreover it is inferred from the shape of the curves, the swelling kinetics of hydrogels follows either the first order swelling kinetics (Yilmaz & Pekcan, 1998) or the second order swelling kinetics (Schott, 1992). Because Fick's law considers that the diffusion coefficient D of penetrating agent (solvent or solution) and sample volume remain constant during the entire swelling process. However, for an extensive swelling system the volume obviously does not remain constant. Thereby we assume that the swelling processes of hydrogels in the *buffer* solutions at pHs above 5.0 should follow the second order swelling kinetics. This kinetics equation is expressed as

$$dQ_t/dt = K(Q_t - Q_\infty)^2 \tag{11}$$

This equation upon integration between the limits $Q_t = 0$ when $t = 0$ and Q_t for t results in

$$Q_t = \frac{KQ_\infty^2 t}{1 + KQ_\infty t} \tag{12}$$

which after rearrangement yields the well known Schott's equation.

$$\frac{t}{Q_t} = \frac{1}{KQ_\infty^2} + \frac{t}{Q_\infty} \tag{13}$$

Therefore by plotting t/Q_t against t, a straight line with a slope of $1/Q_\infty$ and an intercept of $1/KQ_\infty^2$ is obtained.

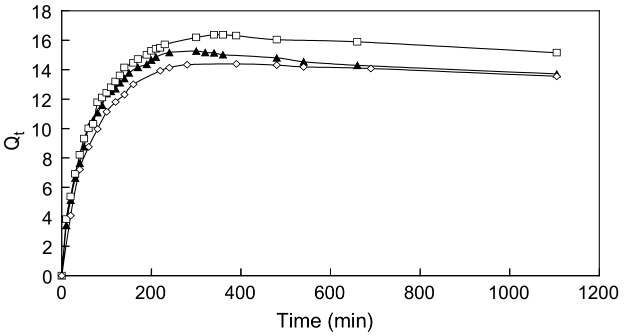


Fig. 6. Dynamic swelling curves of gel B_2 in the *buffer* solutions at pH 5.0–7.0 at 37 °C. ▲, pH 5.0; □, pH 6.0; ◇, pH 7.0.

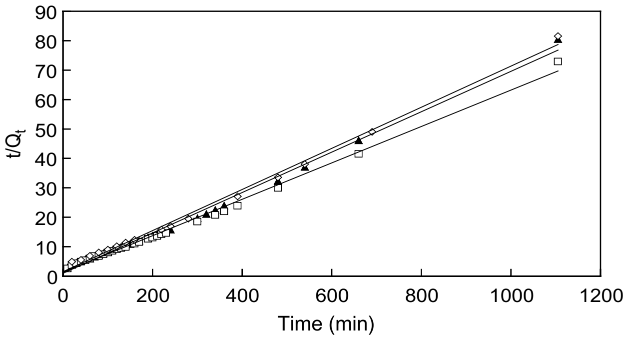


Fig. 7. Variation of the reciprocal rate of swelling t/Q_t as a function of the swelling time for gel B_2 in pH 5.0–7.0 *buffer* solutions at 37 °C. ▲, pH 5.0; □, pH 6.0; ◇, pH 7.0.

Table 3
Rate constants K and determination coefficients R^2 calculated according to Eq. (13) for gel B_2 in pH 5.0–7.0

pH	5.0	6.0	7.0
10^3K	7.3211	3.5282	4.3259
R^2	0.9947	0.9954	0.9965

By the application of the swelling data of gel B_2 to Eq. (13), a straight linear relation between the reciprocal of the average rate of swelling (t/Q_t) and the swelling time is obtained in Fig. 7. Rate constants K and determination coefficients R^2 calculated according to Eq. (13) for B_2 in pH 5.0–7.0 are gathered in Table 3. As it can be seen, the values of the determination coefficients are quite good, in most of the cases $R^2 > 0.99$. This result demonstrates that the swelling processes of hydrogels in the *buffer* solutions at pHs above 5.0 follow Schott's swelling theoretical model.

4. Conclusion

The dynamic swelling experimental results indicated that the swelling process of P(SA-*g*-AA) hydrogels exhibit a remarkable overshooting effect in the *buffer* solutions at pH $\leqslant$ 4.0. The phenomenon is attributed to a cooperative physical cross-link caused by the hydrogen bond formation between the carboxyl groups of the hydrogels in a hydrophobic environment. The hydrogen bond cross-linking reduces the swelling capacity and consequently leads to water expelling during the dynamic swelling process.

The effect of pH of buffer solution on overshooting effect is more remarkable in comparison with the composition of hydrogels. Because the pH change of buffer solution can cause the remarkable change in the extent of protonization of carboxyl groups, consequently resulting in a noticeable variation of the degree of hydrogen *bond* cross-linking; while the degree of hydrogen *bond* cross-linking is little or not changed by the composition of hydrogels because the total molar percentage of carboxyl groups does not change with the molar ratio of the units of SA and AA in the case of the same molar percentage of cross-linker.

The swelling processes of the hydrogels under acidic medium follow a quantitative model proposed by Díez-Peña E, and the theoretical curves are in very good agreement with the experimental data.

In pH $\geqslant$ 5.0 buffer solutions, the overshoot phenomenon hardly appears, the pH values have a little influence on the degree of swelling. This is ascribed to the repulsive interaction between the carboxyl groups of complete ionization in the media. The swelling processes of the hydrogels follow Schott second-order kinetics equation.

Whether or not the overshooting effect under swelling appears is not only *relative* to the pH of *buffer* solution, but also depends on the pK_a of the carboxyl groups.

Only at the pH < pK_a, the overshooting effect appears, and becomes weak with the increasing pH; while at the pH > pK_a, the overshooting effect hardly appears.

It is of important significance the dependence of the hydrogen bond *cross-linking* degree between carboxyl groups on the pH value for the design of intelligent materials such as drug controlling systems et al.

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