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Analysis of the Swelling Dynamics of Cross-Linked P(*N*-iPAAm-*co*-MAA) Copolymers and Their Homopolymers under Acidic Medium. A Kinetics Interpretation of the Overshooting Effect

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ABSTRACT: Dynamic swelling curves of copolymer hydrogels based on *N*-isopropylacrylamide (*N*-iPAAm) and methacrylic acid (MAA) under acidic medium exhibit a remarkable overshoot. This effect may be interpreted as the consequence of a swelling−deswelling process. The fundamental origin of this process is attributed to a reorganization of their own gel structures due to the hydrogen bond formation among the amide groups of *N*-iPAAm and the carboxyl groups of MAA in a hydrophobic environment. This fact, which may be considered as a *cooperative physical cross-linking*, leads to water expelling during the dynamic swelling measurements. A quantitative model of the gel swelling kinetics, coupled with the release of water from the gel, has been developed, which is in very good agreement with the experimental data. Some other overshooting phenomena from the literature may be also explained on the basis of a *cooperative physical cross-linking process* due to intermolecular forces among functional group moieties, promoted by the solvent. The influence of the previous soaking pH on the overshooting has been proved by using samples with controlled swelling history.

Introduction

Polymers in concentrated solution can interact among themselves through noncovalent forces depending on both chemical structure and solvent quality, leading to a *physical gel*. These forces typically include ionic, hydrogen-bond, hydrophobic and van der Waals interactions. On the other hand, c*hemical gels* are polymers cross-linked by covalent bonds. However, in some cases, physical and chemical bonds may coexist and be cooperative. The noncovalent interactions may depend on external stimuli such as pH,[1] ionic strength,[2] solvent composition,[3] or temperature,[4] and this induces a volume phase transition under certain environmental changes.[5] Although the driven forces governing the gel phase behavior are weak, they are very numerous, and their contribution along the whole polymer chain produces a quite complex behavior.

The dynamic swelling properties of a polymer gel may be considered from two different points of view, namely, the transport mechanism controlling the solvent sorption and the sorption rate or kinetic response. The mechanism or nature of the diffusion process may be predicted by calculating the diffusional Deborah number, *De,* which is defined as the ratio of the characteristic relaxation time of the polymer to the characteristic diffusion time of the penetrant.[6,7] Depending on the value of *De*, diffusion may be classified in Fickian or anomalous. Diffusion coefficients are estimated by solving the differential form of Fick's law[8,9] under a certain number of assumptions, considering that the diffusion coefficient *D* of the penetrating solvent and film thickness remain constant during the entire swelling process. Both approaches render information on the type of diffusion and give values for the diffusion coefficients more or less reliable. With respect to the kinetic approach, in most of cases, the analysis has been carried out by means of a first-order rate equation[10,11] which is a simplified form of the more rigorous and formal equation of Li and Tanaka[12] or by means a second-order rate equation known as the Robinson−Schott equation.[13−15] The analysis of experimental data, in some cases, may be opened to discussion.

Furthermore, in the current literature a significant number of water uptaking curves of the sigmoidal[16−19] shape and some others presenting a curvature, which is actually known, as *overshooting effect*,[20−39] can be found. Sigmoidal swelling curves were interpreted by taking into account the glassy state of the polymer, which induces a moving rigid core during swelling. When the rigid core vanishes the acceleration occurs, leading to the sigmoidal shape.[16] Very recently, a kinetic interpretation of the sigmoidal swelling by means of an *autocatalytic process* of the water penetration into the gel has been given.[19] On the contrary, at present, the overshooting effect has not been unambiguously interpreted, neither the kinetics nor the transport mechanism of the process. After a revision of the cases found in the literature, the main problem for a general interpretation is that this phenomenon has been found for systems with very different chemical structures and it seems to depend on a large number of factors. For instance, it has been found in ionic systems, in nonionic but hydrophilic systems, and even in nonpolar systems.

Thus, for instance, Bhardawaj et al.[20] in the case of poly(2-hydroxy ethyl methacrylate-*co*-sodium p-styrenesulfonate) (HEMA-*co*-SSS) hydrogels observed that the swelling curves showed a maximum followed by a decrease in the uptake and a gradual attainment of the swelling equilibrium. They assumed the interpretation given by Mauritz.[40] in the case of hydration of Nafion perfluorosulfonate films, i.e.: during cluster formation of water molecules inside the polymer matrix, the ion−

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dipole hydration shells come together and overlap with the ejection of a few water molecules owing to *thermodynamic compatibility*. In a similar way, Valencia and Pierola,[21] attributed the overshooting effect appearing in the swelling curves of poly(*N*-vinylimidazole-*co*-sodium styrenesulfonate) to the formation of ionic pairs, which behave as ionic cross-linking points.[21] They have interpreted this effect, from a conciliatory and global point of view, in terms of several competing stages in the swelling mechanism: water diffusion toward the gel, chain disentanglement, sodium−proton interchange through the gel−external bath boundary, approaching of chains to allow interaction of sulfonate groups with neighboring protonated imidazole moieties, and diffusion of water outside the gel. Such ionic pairs behave as cross-linking points that decrease the swelling capacity of the hydrogel. In fact, the approaching of chains will allow the interaction of sulfonate groups with neighboring protonated imidazole moieties giving place to a physical cross-linking with subsequent water expelling.

The overshooting effect has been also observed in nonpolar systems by Vrentas et al.,[23] Smith and Peppas,[24] Peppas and Urdahl,[25−28] and Adib and Neogi.[29] Peppas and Urdahl[25−28] analyzed this effect in the transport of liquid cyclohexane through cross-linked polystyrene. After carrying out very discriminating experiments, as a function of the cross-linking ratio and geometric characteristics of the samples, they assumed that the phenomenon is related to a relaxation process of the macromolecular chains. This occurring in the polymer after the material has become rubbery, but before the real equilibrium has been attained. In the case of hydrophilic systems with some nonionizable moieties, the overshooting effect, has been also associated with molecular relaxation according to Peppas and co-workers[30,31,38] and Lee and co-workers.[32−36]

From the data found in the literature, the overshooting effect seems to be related to several factors: (i) cross-linking degree, which leads to changes on polymer mobility that affect relaxation process, no matter if the cross-linked polymer and swelling solvent are polar or nonpolar;[23] (ii) geometry of the sample,[23−25,28] i.e., dimensional changes (thickness and length of the slabs); (iii) temperature,[28,31−36] where the overshooting effect disappears with increasing temperature in some cases,[35] but it appears with increasing temperature in others;[32,35] (iv) concentration of fixed charges[37] or approaching of chains to allow interactions between neighboring charged moieties;[21] (v) pH changes;[20,22,35] (vi) in some cases, the loss of unreacted monomer or uncross-linked polymer chains diffusing out of the swollen polymer network.[38]

These explanations are essentially not contradictory, although they describe the overshooting effect from different points of view. Thus, for instance, some of them reported that it may be due to structural factors and to external morphological aspects of the gels and others to mechanisms of diffusion-controlled by molecular chain relaxation.

The equilibrium swelling behavior and dynamic swelling of a series of cross-linked P(*N*-iPAAm-*co*-MAA) copolymers and their homopolymers as a function of pH and temperature has been reported in a previous publication.[41] Their dynamic swelling curves exhibited some anomalous features: under acidic pH, they exhibited an remarkable overshoot, and under alkaline medium, sigmoidal curves were found. Both phenomena depended on composition. It is well-known that polymers having in its structure proton donor and proton acceptor groups can interact through strong specific forces forming interpolymer complexes in aqueous solution. This is the case of P(*N*-iPAAm-*co*-MAA) copolymers. By the study of the S-shaped T_g behavior of dried gels as a function of composition, the interaction among amide and carboxylic groups was suggested.[42,43] Solid-state NMR experiments brought information about the groups involved in the interaction, indicating a direct implication of MAA and *N*-iPAAm in a complex due to hydrogen bonding.[44] The differences on the mobility of hydrogels swollen in D_2O has been studied as a function of composition by means of proton wide-line spectroscopy.[45] Copolymer gels soaked under acidic conditions exhibited a very broad peak, shifted to lower field, in the ^1H water resonance region corresponding to very rigid water domains whose mobility is restricted probably due to the surrounding hydrogen bonded chains.[44] Since hydrogen bonding depends strongly on pH, it is clear that the overshooting effect under acidic pH and the sigmoidal swelling under alkaline medium are related to same process, that is hydrogen bonding.

We propose that the dynamic hydrogen bond formation promoted by the solvent under swelling is responsible for the *overshooting effect* found under acidic pHs. In this paper, the data are analyzed by means of a rigorous kinetics model based on the former assumption. A discussion about the extension of this interpretation for the overshooting found in other systems, which consider the possibility of a dynamic increase of the *physical cross-linking* during swelling, is also given.

Experimental Section

Material. *N*-Isopropylacrylamide (*N*-iPAAm) (Acros Organics) 99%, methacrylic acid (MAA) 98%, tetraethylene glycol dimethyl acrylate (TEGDMA), ammonium persulfate (APS), *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TEMED) (Fluka-Chemie, A.G., Buchs, Switzerland), ethanol, (Panreac Monplet&Esteban, S.A., Barcelona, Spain). All products were used as received, except for *N*-iPAAm, which was purified by recrystallization from a mixture of *n*-hexane/toluene (90/10, v/v) at room temperature and MAA was vacuum distilled at 50 °C/667 Pa. Deionized water from a Millipore Milli-U10 water purification facility was used where appropriate.

Synthesis. Synthesis of P(MAA), P(*N*-iPAAm) homopolymers, and P(*N*-iPAAm-*co*-MAA) with 0.25 and 0.50 wt % of cross-linking agent TEGDMA has been described in detail elsewhere.[41,42,45] Polymer compositions estimated by elemental analysis are given in Tables 1 and 2. Uniform disks were punched out of the hydrogel sample using a stainless steel cork borer following the procedure described in previous papers.[19,41] The dried disks had a diameter of 9 mm and a thickness of 0.9 mm.

Swelling Experiments. Analysis of the equilibrium and dynamic swelling characteristics of all hydrogels was performed at 25.0 ± 0.1 °C. Xerogel disks were left to swell in buffer solutions at pH = 7, 4, and 2 to achieve the swelling equilibrium. The swollen gels were taken out at regular time intervals, wiped superficially with filter paper, weighed, and placed again in the same immersion bath.

The percentages of mass or normalized swelling degree Q_t at time t were calculated in grams of water per gram of dry gel using the following expression

$$Q_t = \frac{m_t - m_0}{m_0} = \frac{W_t}{m_0} \qquad (1)$$

where m_0 is the initial weight of the dried disk (xerogel),

Table 1. Rate Constants k_1, k_3, k_5, and k_6, Values of A_1 and A_3 at Equilibrium, $A_{1\infty}$ and $A_{3\infty}$, and Determination Coefficients R^2 Calculated According to Eq 16 for a Series of P(*N*-iPAAm-*co*-MAA) Hydrogels and Their Homopolymers with 0.25 wt % Cross-Linking Agent[a]

sample	composition (% mol *N*-iPAAm)	10^3k_1 (min^{-1})	10^3k_3 (min^{-1})	10^3k_5 (min^{-1})	10^3k_6 (min^{-1})	$A_{1\infty}$	$A_{3\infty} = Q_\infty$	R^2
P(MMA)(0/100)	0	21.8				4.6		0.997
P(*N*-iPAAm-*co*-MAA)(15/85)	15.4	23.1	1.7	27.0	13.7	5.1	1.7	0.990
P(*N*-iPAAm-*co*-MAA)(30/70)	32.4	7.2	2.8	7.2	4.4	2.2	0.8	0.952
P(*N*-iPAAm-*co*-MAA)(50/50)	50.5	17.8	1.9	24.8	6.2	9.6	1.9	0.990
P(*N*-iPAAm-*co*-MAA)(70/30)	66.7	7.6	2.7	28.0	3.6	34.0	3.9	0.999
P(*N*-iPAAm-*co*-MAA)(85/15)	82.6	7.2	1.9	2.7	8.7	25.7	19.6	0.975
P(*N*-iPAAm)(100/0)	100	3.6				21.6		0.997

[a] Sample protocol "pH 4 (from synthesis)" at 25 °C.

Table 2. Rate Constants k_1, k_3, k_5,and k_6, Values of A_1 and A_3 at Equilibrium, $A_{1\infty}$ and $A_{3\infty}$, and Determination Coefficients R^2 Calculated According to Eq 16 for a Series of P(*N*-iPAAm-*co*-MAA) Hydrogels and Their Homopolymers with 0.50 wt % Cross-Linking Agent[a]

sample	composition (% mol *N*-iPAAm)	10^3k_1 (min^{-1})	10^3k_3 (min^{-1})	10^3k_5 (min^{-1})	10^3k_6 (min^{-1})	$A_{1\infty}$	$A_{3\infty} = Q_\infty$	R^2
P(MMA)(0/100)	0	14.4				4.7		0.994
P(*N*-iPAAm-*co*-MAA)(15/85)	19.5	15.2	1.0	15.0	11.7	4.2	1.8	0.988
P(*N*-iPAAm-*co*-MAA)(30/70)	38.8	1.0	3.0	2.1	0.9	2.3	0.7	0.978
P(*N*-iPAAm-*co*-MAA)(50/50)	53.3	1.5	4.6	3.5	1.1	4.7	1.1	0.945
P(*N*-iPAAm-*co*-MAA)(70/30)	73.3	7.2	2.2	12.1	2.6	14.0	2.5	0.996
P(*N*-iPAAm-*co*-MAA)(85/15)	83.3	7.9				15.8		0.999
P(*N*-iPAAm)(100/0)	100	5.0				14.0		0.998

[a] Sample protocol "pH 4 (from synthesis)" at 25 °C.

namely, the weight at $t = 0$, and m_t is the weight after a time t and W_t is the weight of the water uptake at a time t. The normalized equilibrium swelling Q_∞ is given by

$$Q_\infty = \frac{m_\infty - m_0}{m_0} = \frac{W_\infty}{m_0} \tag{2}$$

According to the general nomenclature adopted in a previous paper,[19] two series of samples were investigated. (i) The first was *control samples,* namely, samples obtained from the chemical synthesis of the gels (pH = 5) purified in distilled water and dried. Therefore, they are free of residual monomers, traces of initiator, etc., They are only partially protonated because the traces of sodium hydroxide used to neutralize the reaction mixture. (ii) The second was *dried after soaking samples*; these samples were treated by soaking in pH 7 until equilibrium was achieved and then dried. Then these samples were swelled again to carry out swelling kinetic experiments in a pH 2 buffer solution. The nomenclature for these samples is "pH 2 (pH 7)".

Experimental Results

1. Dynamic Swelling and Equilibrium Swelling Values under Acidic Medium. Influence of the Swelling History on the Overshooting Effect. In Figure 1 swelling curves at pH 4 for P(*N*-iPAAm), P(MAA), and a series of P(*N*-iPAAm-*co*-MAA) copolymers with 0.50 wt % cross-linking agent are shown. Some of these dynamic swelling curves corresponding to copolymers exhibit an overshoot. Its absolute value depends on copolymer composition. In a first step, the samples increase their swelling ratio, later on they reach a maximum, and finally they deswell until an equilibrium value is reached. We have attributed this feature to a lower degree of ionization of the acid, which produces the dynamic formation of hydrogen bonds between both comonomeric units. It has been observed that the macroscopic appearance, before the maximum is reached, is almost transparent, and after the overshooting, the opacity increases. The opacity of the gel was found to depend on polymer composition. It has been reported that when a polymer−polymer complex is formed due to hydrogen bonds, the polymer solution becomes turbid, which arises from the aggregation of the polymer chains.[46] The greatest overshooting effect takes place at the 70% mol *N*-iPAAm content copolymer.

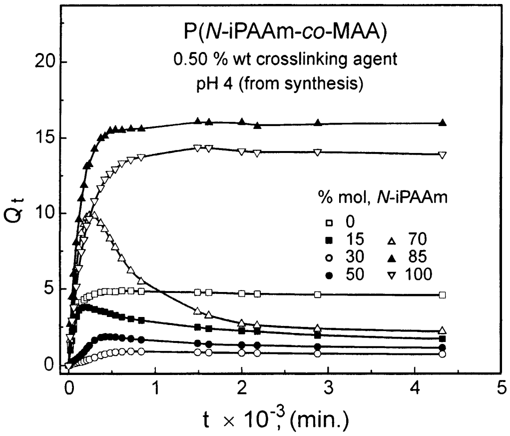

Figure 1. Plot of Q_t experimental data vs t for a series of P(*N*-iPAAm-*co*-MAA) copolymers and their homopolymers with a 0.50 wt % of cross-linking agent. Sample protocol "pH 4 (from the synthesis)".

Equilibrium swelling values at pH 4 and 2, for two series of samples cross-linked with 0.25 and 0.50 wt % cross-linking agent at 25 °C are shown in Figure 2. Q_∞ values are higher for pH 4 (full symbols) than for pH 2 (open symbols). At this temperature, the equilibrium values are higher with increasing *N*-iPAAm concentration and reach a minimum for enriched MAA copolymers. Pure P(MAA) cross-linked homopolymer exhibit higher Q_∞ values than some of the copolymers, indicating that the interaction between both comonomeric units leads to a more collapsed structure than the interaction between MAA units alone. The Q_∞ dependence on copolymer composition is similar for both series of samples. The absolute Q_∞ values are very similar for the equivalent composition of both series of copolymers, indicating that the swelling response is more affected

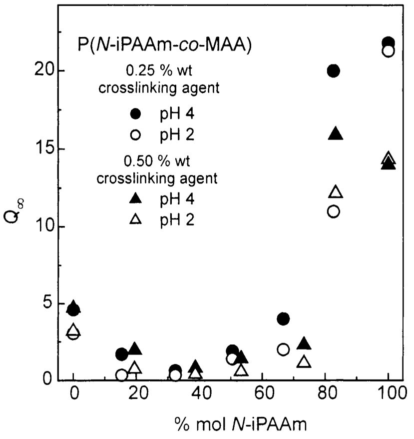

Figure 2. Equilibrium swelling values Q_∞ at pHs 4 and 2 for a series of P(*N*-iPAAm-*co*-MAA) and their homopolymers with 0.25 and 0.50 wt % of cross-linking agent.

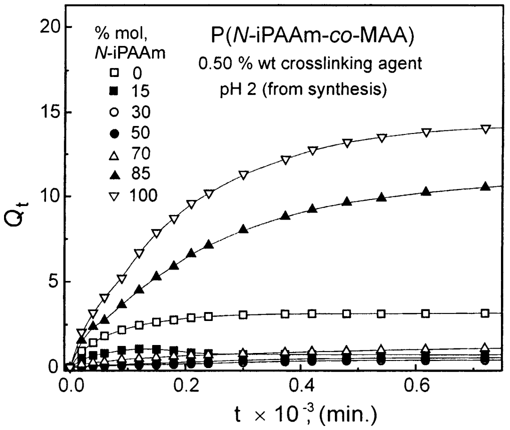

Figure 3. Plot of Q_t experimental data vs t for a series of P(*N*-iPAAm-*co*-MAA) copolymers and their homopolymers with 0.50 wt % of cross-linking agent. Sample protocol "pH 2 (from synthesis)".

by the interaction between both comonomers than by the cross-linking degree.

The samples analyzed in Figure 1, correspond to the called c*ontrol samples*, but we have also investigated samples which were soaked under a pH prior to record a swelling curve under a second medium. In a previous paper,[19] it has been established that the amount of hydrogen bonding in the sample can be tailored by soaking the sample under a buffer solution. This simple treatment has a dramatic influence on the swelling kinetics. P(*N*-iPAAm-*co*-MAA) copolymer hydrogels soaked under acidic media and reswelled at pH 7 exhibited an anomalous swelling behavior and a low swelling rate. The lower the pH of the previous soaking solution, the slower the swelling rate at pH 7.[19] In this previous study, the slow disruption of the hydrogen bonds was shown to be responsible of the swelling kinetics. Under acidic medium, the opposite phenomenon occurs, i.e., the dynamic formation of hydrogen bonding. Figure 3 displays dynamic swelling curves of samples without treatment, with 0.50 wt % cross-linking agent at pH 2. At first sight, it can be said that the swelling process is not anomalous, at least concerning the overshooting effect. Copolymers and P(MAA) reach their low swelling equilibrium very rapidly, only the copolymer with the highest *N*-iPAAm amount and pure P(*N*-iPAAm) preserve a relative high water uptake capability. An obvious question arises, if the overshooting effect is related to the hydrogen bond formation, it should be logical that it would occur in higher levels at pH 2 than at pH 4. We propose that this fact is a consequence of differences on the time scales of the initial swelling and the hydrogen bond formation, taking place at pH 2. In the next figure, Figure 4, can be observed what happens when the samples are soaked at pH 7, previous to being reswelled at pH 2. The overshooting appears in copolymers as well in P(MAA). The maximum of the water uptake occurs earlier than for samples swelled at pH 4. We have to mention that an analogous experiment was performed on samples soaked at pH 7 and reswelled at pH 4. Unfortunately, it was not possible to keep constant the pH of the buffer solution during the experiment, which affects the experimental results and therefore were not taken into account.

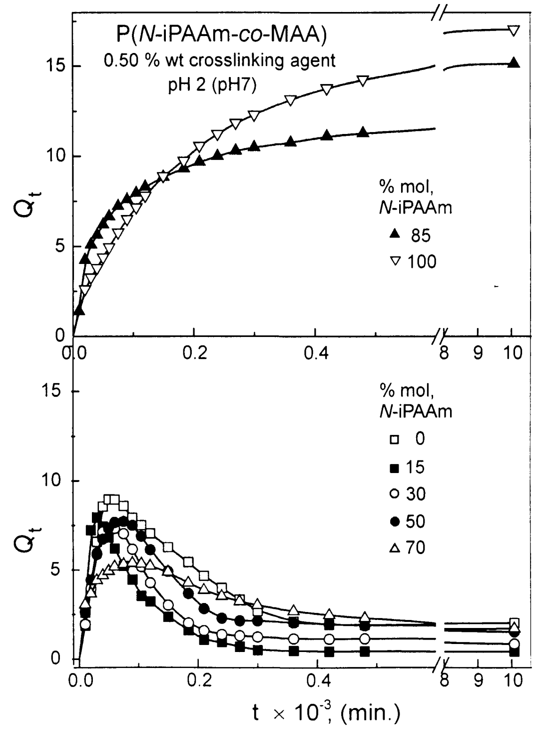

Figure 4. Plot of Q_t experimental data vs t for a series of P(*N*-iPAAm-*co*-MAA) copolymers and their homopolymers with 0.50 wt % of cross-linking agent. Sample protocol "pH 2 (pH 7)".

2. A Kinetics Model for the Interpretation of the Overshooting Effect. The existence of different types of water with different mobility depending on the soaking pH has been shown by wide-line NMR.[44] The kinetics model we are going to describe is based on the existence of different *species of water,* which are a consequence of the hydrogel topology.

At the beginning of the swelling process, amide and carboxylic groups of copolymer hydrogel are unbounded and possess a capability of water uptake that we will call A_1; the absorbed water at each time for this hydrogel is called A_2. The low pH of the medium promotes the rearrangement of the hydrogel structure through hydrogen bonding, leading 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 3.

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 written by means of the following scheme

$$A_1 \underset{k_2}{\overset{k_1}{\rightleftarrows}} A_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} A_3 \underset{k_6}{\overset{k_5}{\rightleftarrows}} A_4 \tag{3}$$

that is, three consecutive reversible first-order reactions.[47,48]

The problem undergoes a remarkable simplification by setting certain of the rate constants equal to zero. Thus, 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

$$\begin{aligned} \frac{\mathrm{d}A_1}{\mathrm{d}t} &= -\,k_1A_1 \\ \frac{\mathrm{d}A_2}{\mathrm{d}t} &= k_1A_1 - k_3A_2 \\ \frac{\mathrm{d}A_3}{\mathrm{d}t} &= k_3A_2 - k_5A_3 + k_6A_4 \\ \frac{\mathrm{d}A_4}{\mathrm{d}t} &= k_5A_3 - k_6A_4 \end{aligned} \tag{4}$$

The set of differential equations for the first-order reversible consecutive reactions was integrated by Rakowski.[49] The kinetics have been derived using dimensionless variables by Lowry and John.[50] Lewis and Johnson[51] solved a similar mathematical problem using matrix methods. The solution by this last method involves the secular equation

$$\begin{bmatrix} k_1-\lambda & 0 & 0 & 0 \\ -\,k_1 & k_3-\lambda & 0 & 0 \\ 0 & -\,k_3 & k_5-\lambda & -\,k_6 \\ 0 & 0 & -\,k_5 & k_6-\lambda \end{bmatrix} = 0 \tag{5}$$

After expansion the four roots are given by

$$\begin{aligned} \lambda_1 &= 0 \\ \lambda_2 &= k_1 \\ \lambda_3 &= k_3 \\ \lambda_4 &= k_5 + k_6 \end{aligned} \tag{6}$$

As described by Lewis and Johnson,[51] the B coefficients can be deduced by setting $B_{3r} = 1$. In matrix form this may be written as

$$\mathbf{B} = \begin{bmatrix} 0 & \left(\frac{k_1-k_3}{k_3}\right)\left(\frac{k_6+k_5-k_1}{k_5}\right) & 0 & 0 \\ 0 & k_1\left(\frac{k_1-k_5-k_6}{k_3k_5}\right) & \frac{k_3-k_5-k_6}{k_5} & 0 \\ \frac{k_6}{k_5} & \frac{k_6-k_1}{k_5} & \frac{k_6-k_3}{k_5} & -\,1 \\ 1 & 1 & 1 & 1 \end{bmatrix} \tag{7}$$

Let us define the following series of matrices

$$\mathbf{A} = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \end{bmatrix} \tag{8}$$

$$\mathbf{A_0} = \begin{bmatrix} a \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{9}$$

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \mathrm{e}^{-k_1t} & 0 & 0 \\ 0 & 0 & \mathrm{e}^{-k_3t} & 0 \\ 0 & 0 & 0 & \mathrm{e}^{-(k_5+k_6)t} \end{bmatrix} \tag{10}$$

where $\mathbf{A_0}$ matrix represents the conditions at $t = 0$; therefore $A_1 = a$ and $A_2 = A_3 = A_4 = 0$. Thefore the matrix $\mathbf{A}$ may be rewritten as

$$\mathbf{A} = \mathbf{B}\cdot\mathbf{E}\cdot\mathbf{B}^{-1}\cdot\mathbf{A_0} \tag{11}$$

The explicit solution of this equation then gives the dependence of each water concentration on time. They can be written in conventional form as

$$A_1 = a\mathrm{e}^{-k_1t} \tag{12}$$

$$A_2 = \left(\frac{k_1}{k_1-k_3}\left(\mathrm{e}^{-k_3t} - \mathrm{e}^{-k_1t}\right)\right)a \tag{13}$$

$$\begin{aligned} A_3 = \Bigg(&\frac{k_3}{k_1-k_3}\,\frac{k_1-k_6}{k_1-k_5-k_6}\,\mathrm{e}^{-k_1t} - \\ &\frac{k_1}{k_1-k_3}\,\frac{k_3-k_6}{k_3-k_5-k_6}\,\mathrm{e}^{-k_3t} + \\ &\frac{k_1}{k_1-k_5-k_6}\,\frac{k_5}{k_5+k_6}\,\frac{k_3}{k_3-k_5-k_6}\,\mathrm{e}^{-(k_5+k_6)t} + \\ &\frac{k_6}{k_5+k_6}\Bigg)a \end{aligned} \tag{14}$$

$$\begin{aligned} A_4 = \Bigg(&\frac{k_3}{k_3-k_1}\,\frac{k_5}{k_1-k_5-k_6}\,e^{-k_1}t + \\ &\frac{k_1}{k_1-k_3}\,\frac{k_5}{k_5+k_6}\,\frac{k_5}{k_3-k_5-k_6}\,\mathrm{e}^{-k_3t} + \\ &\frac{k_3}{k_1-k_3}\,\frac{k_5}{k_5+k_6}\,\frac{k_1}{k_1-k_5-k_6}\,\mathrm{e}^{-(k_5+k_6)t} + \\ &\frac{k_1}{k_1-k_3}\,\frac{k_5}{k_5+k_6}\,\frac{k_3-k_6}{k_3-k_5-k_6}\,\mathrm{e}^{-(k_5+k_6)t} - \\ &\frac{k_1}{k_1-k_3}\,\frac{k_6}{k_5+k_6}\left(\mathrm{e}^{-(k_5+k_6)t} - \mathrm{e}^{-k_3t}\right) + \frac{k_6}{k_5+k_6}\Bigg)a \end{aligned} \tag{15}$$

The overall content of water imbibed by the gel at time t is then given by Q_t

$$Q_t = A_2 + A_3 = \left(\frac{k_1}{k_1 - k_3} (e^{-k_3 t} - e^{-k_1 t}) + \frac{k_3}{k_1 - k_3} \frac{k_1 - k_6}{k_1 - k_5 - k_6} e^{-k_1 t} - \frac{k_1}{k_1 - k_3} \cdot \frac{k_3 - k_6}{k_3 - k_5 - k_6} e^{-k_3 t} + \frac{k_1}{k_1 - k_5 - k_6} \frac{k_5}{k_5 + k_6} \frac{k_3}{k_3 - k_5 - k_6} e^{-(k_5 + k_6)t} + \frac{k_6}{k_5 + k_6} \right) a \quad (16)$$

The equilibrium value Q_∞ is the concentration of A_3 species in the equilibrium. It is a function of the rate constants k_5 and k_6

$$Q_\infty = A_{3\infty} = \frac{k_6}{k_6 + k_5} a \quad (17)$$

In Figure 5, a scheme representing the structural reorganization inside the gel, which produces the water expelling after the first initial swelling, is shown. The values of the four rate constants calculated by the fitting of the experimental data to eq 16 are gathered in Tables 1−3. In Tables 1 and 2, for samples swelled directly from the synthesis at pH 4 with 0.25 and 0.50 wt % cross-linking agent and in Table 3 for samples with 0.50 wt % cross-linking agent at pH 2 and previously soaked at pH 7. As it can be seen, the values of the determination coefficients are quite good, in most of the cases $R^2 > 0.9$. In parts a and b of Figure 6, the experimental swelling values for 70% mol *N*-iPAAm samples with 50 wt % cross-linking agent, swelled directly from the synthesis at pH 4 and previously soaked at pH 7 and then dried and reswelled at pH 2, are presented with the theoretical curves calculated by the best fitting to eq 16, as well as the theoretical curves for the four *water species* calculated by means of eqs 12−15 and assuming the rate constants extracted from the fitting to eq 16. In Figures 7 and 8, experimental swelling values for a series of copolymers swelled directly from the synthesis at pH 4 with 0.25 and 0.50 wt % cross-linking agent are compared with the theoretical curves extracted from the fitting to eq 16. In these figures, a good agreement between the values obtained experimentally and those calculated with the proposed model is observed.

Discussion of Results

It is obvious that a fitting with five adjustable parameters (the four rate constants and *a*) could lead to some uncertainties, and therefore, the values extracted from the fittings have to be interpreted from a qualitative point of view. However, we have made some assumptions to obtain the most realistic results. A second series of good fits were also obtained for the sample protocol "pH 4 (from synthesis)", from which, the values of k_3, related to the hydrogen bond formation, were extremely high. But this implies that the values of the deswelling constant, k_5, had to be unrealistically low. For this reason this second possibility was disregarded. In general, from the fittings corresponding to both series of samples at pH 4, it can be said that the slow k_3 rate is controlling the swelling behavior of copolymers, whereas swelling and deswelling rates are of the same order of magnitude, as could be expected. There are no qualitative differences between both series of samples because of their different amounts of cross-linking agent. On the contrary, the magnitude of the overshooting depends strongly on composition. This dependence is attributed to the advantage of some copolymer compositions to form hydrogen bonds, as well as to the differences on chain mobility and hydrophilicity, which produces a higher and faster water uptake prior to the polymer rearrangement. At pH 2 (pH 7) (Table 3), all the processes are faster than at pH 4; the k_3 rate constant increases, and it is related to the characteristic time at which the overshoot maximum appears. We attribute the absence of the overshooting in the samples from the synthesis and swelled at pH 2 to an increasing of the k_3 constant with decreasing pH. The value of k_1 for these nonsoaked samples should be lower than when the samples are totally ionized under basic pH. Then when k_3 is much higher than k_1, the overshoot does not appear. The ratio between these two characteristic times, the time of the water to penetrate into the gel, and the time to reorganize the polymer

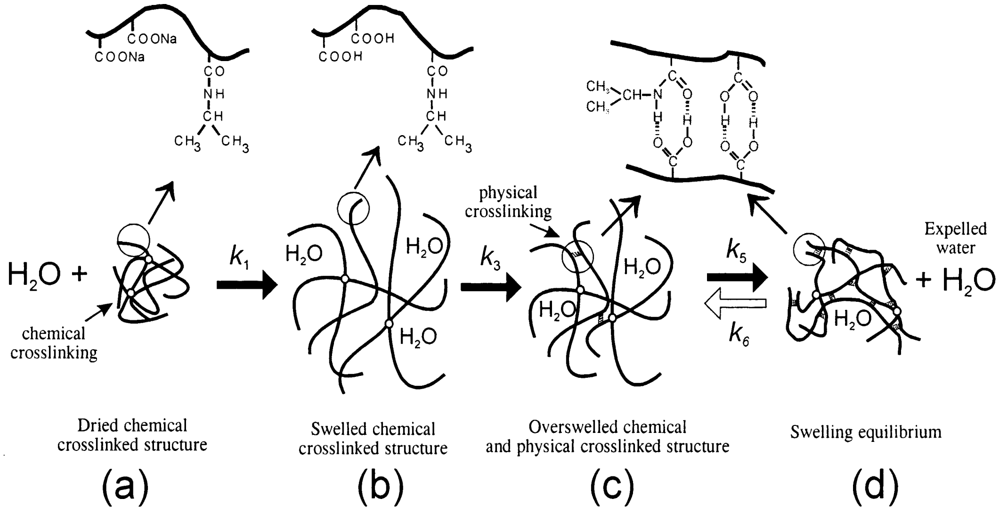

Figure 5. Four-state model of the swelling-mediated "overshooting effect" equilibrium for a sample soaked at pH 7 and reswelled under acidic medium: (a) structure of a chemical cross-linked collapsed gel with sodium carboxylate groups; (b) expanded structure after swelling, protonation of the carboxyl groups; (c) formation of the noncovalent structure through hydrogen bonds; (d) new equilibrium structure and equilibrium of swelling after water expelling.

Table 3. Rate Constants k_1, k_3, k_5, and k_6, Values of A_1 and A_3 at Equilibrium, $A_{1\infty}$ and $A_{3\infty}$, and Determination Coefficients R^2 Calculated According to Eq 16 for a Series of P(*N*-iPAAm-*co*-MAA) Hydrogels and Their Homopolymers with 0.50 wt % Cross-Linking Agent[a]

sample	composition (% mol *N*-iPAAm)	10^3k_1 (min^{-1})	10^3k_3 (min^{-1})	10^3k_5 (min^{-1})	10^3k_6 (min^{-1})	$A_{1\infty}$	$A_{3\infty} = Q_\infty$	R^2
P(MMA)(0/100)	0	29.3	8.0	60.1	7.7	12.2	1.4	0.966
P(*N*-iPAAm-*co*-MAA)(15/85)	15.4	75.0	13.0	121.9	4.2	10.1	0.3	0.951
P(*N*-iPAAm-*co*-MAA)(30/70)	32.4	22.7	33.4	30.1	2.5	14.2	1.1	0.982
P(*N*-iPAAm-*co*-MAA)(50/50)	50.5	19.9	26.1	22.9	3.2	14.1	1.7	0.997
P(*N*-iPAAm-*co*-MAA)(70/30)	66.7	45.7	6.3	8.4	3.5	5.9	1.7	0.969
P(*N*-iPAAm-*co*-MAA)(85/15)	82.6	10.8				12.1		0.874
P(*N*-iPAAm)(100/0)	100	5.3				16.1		0.988

[a] Sample protocol "pH 2 (pH 7)" at 25 °C.

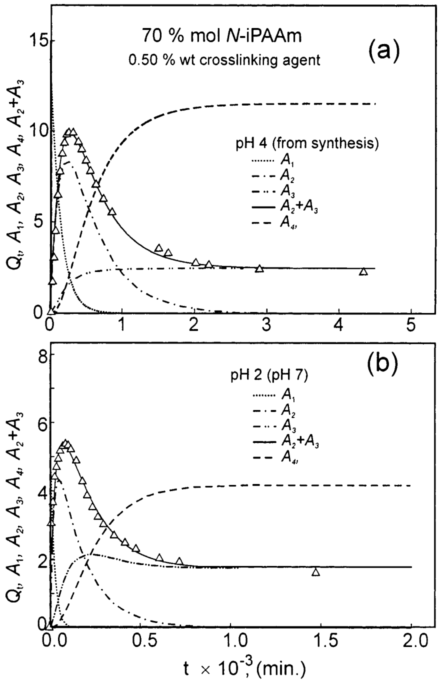

Figure 6. Plot of Q_t experimental data vs t for a 70 wt % *N*-iPAAm copolymer: (a) samples referred as "pH 4 (from synthesis)" and (b) samples referred as "pH 2 (pH 7)". Key: Q_t (open triangles); A_1 (dotted line); A_2 (dotted and full line); A_3 (two dots and full line); $A_2 + A_3$ (full line); A_4 (dashed line).

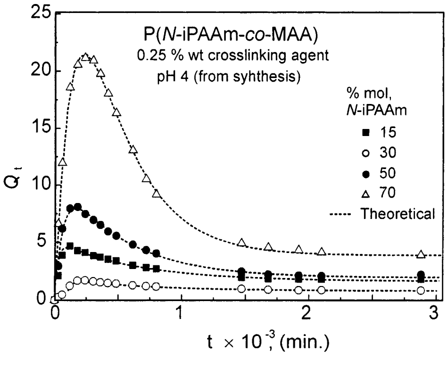

Figure 7. Plot of Q_t experimental data vs t for a series of four P(*N*-iPAAm-*co*-MAA) hydrogels with 0.25 wt % of cross-linking agent. Sample protocol "pH 4 (from synthesis)". Theoretical values calculated according to eq 16 are represented by a dotted line. Adjustable kinetics parameters are given in Table 1.

structure will determine whether the process is anomalous or not.

As we have anticipated in the Introduction, one of the most extended interpretations to explain the overshooting phenomenon is based on relaxational effects. Thus, for instance, in the case of hydrophilic systems with some nonionizable moieties, the overshooting effect according to Peppas and co-workers[30,31,38] and Lee and co-workers[33−36] has been attributed to molecular relaxation. The water diffuses into the network before the chains have enough time to relax (diffusion is faster than relaxation), and the fractional uptake curve reaches a maximum, the overshoot value. When the chains do finally relax, water is forced out of the network and the water uptake eventually reaches its equilibrium value (different rates of diffusion and molecular chain relaxation effects). The slow reorientation of polymer molecules can lead to a wide variety of anomalous effects for both, permeation and sorption experiments, particularly when such experiments are conducted near or below the glass transition temperature of the system.[22] But in some cases, the overshooting has been found at swelling rates where the polymer is well above its T_g.[32] This is also the case of the overshooting found in P(*N*-iPAAm-*co*-MAA) copolymers. Other sign of complexity of this feature is its temperature dependence. If it would be only a relaxation phenomenon, it should decreases with increasing temperature; however, Lee and Shieh[32] have found that dynamic swelling curves of copolymers based on *N*-iPAAm and acrylic acid neutralized by sodium hydroxide exhibited an overshoot under high-temperature conditions, in opposite to the behavior found for the poly(2-hydroxyethyl methacrylate) P(HEMA),[30,31,33−36,38] which exhibits an overshoot with decreasing temperature.

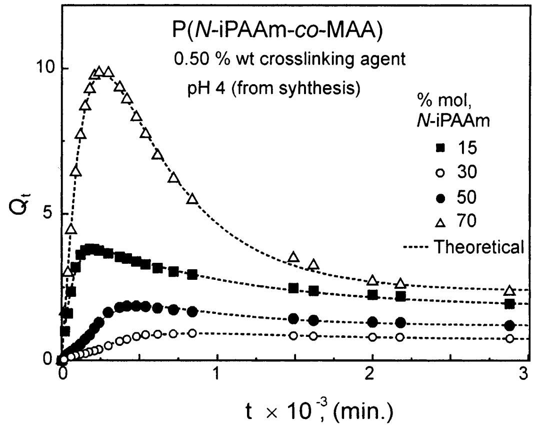

Figure 8. Plot of Q_t experimental data vs t for a series of four P(*N*-iPAAm-*co*-MAA) hydrogels with 0.50 wt % of cross-linking agent. Sample protocol "pH 4 from the synthesis". Theoretical values calculated according to eq 16 are represented by a dotted line. Adjustable kinetic parameters are given in Table 2.

After the examination of the present experimental results and a large number of data from the literature, we propose that the overshooting phenomena can be considered in some other terms. The overshooting effect cannot be explained solely by assuming different rates of diffusion and simple molecular chain relaxation effects. Such relaxational effects might be controlled by some types of chemical or physical interactions. It is very well-known that the amount of water absorbed depends on the cross-linking degree of the hydrogel. During the swelling or deswelling processes, the chemical cross-linking degree must remain constant unless some type of chemical degradation takes place. The only cross-linking that during swelling may change is the physical one, which in some cases may be very noticeable.[19] The appearance of intermolecular forces, which change the degree of cross-linking, is promoted in the swelled state by the solvent, whatever it is, organic or polar, as is water. This is the reason the overshooting effect may be affected by external factors as temperature, pH, or the initial size of the gel or by structural factors and polymer mobility, which allows chain rearrangement. Thus, the presence of strong polyelectrolyte groups giving place to cluster formation by nondipolar interactions (ionic interactions) may justify the appearance of the overshooting effect[20,22] In the case of ionic systems as sodium styrenesulfonate and *N*-vinylimidazole containing hydrogels, Valencia and Piérola[21] have interpreted this effect in terms of ionic pairs formation, which behave as cross-linking points that decrease the swelling capacity of the hydrogel. Similarly, other cause for the overshooting effect is the hydrogen bond interactions in a hydrophobic environment, as it is the case for hydrogels studied in the present paper. In the case of the overshooting feature reported on P(HEMA) and its copolymers,[30,31,33−36,38] it is known that the degree of swelling of P(HEMA) gels in water shows little variation as a function of the degree of cross-linking. On the basis of this fact and on the anomalous swelling behavior shown in the presence of urea solutions, there seems to exist a secondary noncovalent network structure that results in the very high degree of cross-linking in the polymer. This structure may consist of hydrogen bonds between pendant hydroxyl and carbonyl groups in a hydrophobic environment.[52] The slow dynamic modification of this secondary structure under swelling, also due to the glassy state of the polymer, may be responsible of the overshooting phenomenon.[30,31,33−36,38] And finally, charge transfer and $\pi-\pi$ interactions[53] may be responsible for the overshooting effect found in the case of cross-linked polystyrene and cyclohexane as solvent described by Peppas and Urdahl.[25−28]

Conclusions

From the work presented in this study, the following conclusions can be derived:

The dynamic swelling experimental results indicated that some P(*N*-iPAAm-*co*-MAA) hydrogels exhibit the “overshooting effect” under acidic conditions. It may be interpreted as two consecutive swelling−deswelling processes. The deswelling process is attributed to a reorganization of the own gel structure due to the hydrogen bond formation among the amide groups of *N*-iPAAm and the carboxyl groups of MAA in a hydrophobic environment. This fact may be considered responsible for dynamical formation of physical cross-linkages, which diminishes the swelling capacity and therefore leads to a water expelling during the dynamic swelling measurements.

A kinetics model has been proposed that takes into account the different processes that yield the overshooting effect: the first water uptake of an initial hydrophilic gel, the transformation of this gel into a more compact and hydrophobic cross-linked structure with a lower water uptake capability, and finally the water expelling until the new equilibrium is reached. The kinetics model, with four rate constants, can reproduce adequately the experimental data at any time and swelling degree.

We postulate that in the most of the cases reported in the literature, the overshooting effect might be a consequence of a spontaneous rearrangement of the gel structure on the dynamic swelling. To prove this hypothesis, refined experiments should be done on these systems in order to have an accurate control of the system structure prior the swelling experiment. In the case of P(*N*-iPAAm-*co*-MAA) copolymers, this control has been easily achieved by soaking the samples under different pHs.

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