Hydrogen-Bonding Effects on the Dynamic Swelling of P(*N*-iPAAm-*co*-MAA) Copolymers. A Case of Autocatalytic Swelling Kinetics

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ABSTRACT: The swelling kinetics of a series of P(*N*-iPAAm-*co*-MAA) copolymers and their P(*N*-iPAAm) and P(MAA) homopolymers previously soaked under different acidic and neutral conditions have been studied at pH 7 to probe the hydrogen-bonding ability of comonomers. Experimental data analysis has revealed that although the state due to the previous soaking pH does not exert any influence on the equilibrium swelling value of copolymers, it exerts a strong influence on their swelling kinetics. Copolymers gels ranging in composition between 30 and 70 mol % of *N*-iPAAm previously soaked under acidic conditions exhibit, when subsequently immersed in water at a neutral pH, sigmoidal swelling curves. This behavior has been interpreted according to an autocatalytic mechanism, suggesting that cooperativity on the hydrogen bond disruption controls the swelling behavior. The dynamic swelling of these hydrogels under pH 7 after soaking at this same pH is in very good agreement with a second-order kinetics. This fact corroborates that anomalous features found on the swelling dynamics of these copolymers are related to the strong hydrogen-bonding arrangement between both comonomeric units as well as to the hydrophobicity strongly enhanced by intra- or/and interchain hydrogen bonding.

Introduction

Poly(*N*-isopropylacrylamide) [P(*N*-iPAAm)] is a polymer with very interesting properties. It exhibits[1] a sharp phase transition in water (lower critical solution temperature, LCST) at 32 °C. It is a temperature-induced collapse from a perturbed coil into a globule structure which is macroscopically revealed as a sudden decrease of the degree of swelling. Poly(methacrylic acid) [P(MAA)] which contains ionizable groups shows pH dependence in its swelling behavior. Studies on polymer gels based in *N*-iPAAm and MAA have been recently reported by Peppas and co-workers.[2−4] In very recent papers, we have studied the structure and dynamic,[5] thermal properties,[6,7] and swelling behavior[8,9] of these copolymer hydrogels. Thermal studies have revealed that hydrogen bonds between amide and carboxyl exert a strong dependence on the glass transition temperature.[6,7] Double quantum NMR experiments (DQ-NMR) have brought out direct proofs of the hydrogen bonding between amide and carboxyl groups probably stabilized by hydrophobic interactions.[10] This is supported by the fact that hydrogen bond interactions seem to be stronger in P(*N*-iPAAm-*co*-MAA) copolymers than in its P(MAA) homopolymer.[10] The kinetic analysis of the dynamic swelling curves indicated some anomalous features in the samples where this hydrogen bond arrangement was detected. Thus, for instance, a swelling−deswelling process under acidic pH may be attributed to the dynamic hydrogen bond formation.[8] Hydrogen bond interactions have been found in systems containing both hydrogen donors and hydrogen acceptors. Ilmain et al.[11] presented evidence of a volume transition in the poly(acrylamide)/poly(acrylic acid) interpenetrating network (IPN). This phenomenon was claimed to be the first polymer gel transition driven independently by hydrogen bonds. They concluded that a cooperative zipping interaction involving long chain sequences is necessary to describe a complete picture of this behavior. On the contrary, Wang and Morawetz[12] pointed out that long sequences are not required to form stable hydrogen-bonding complexes. We have very recently found complexes in interpenetrating polymer networks (IPN) of P(MAA) and P(*N*-iPAAm) as well as in random P(*N*-iPAAm-*co*-MAA) copolymers in complete agreement with the hypothesis of Wang and Morawetz.[12] According to Quinn et al.,[13] some very peculiar complicating factors may affect the usual behavior of hydrogels; among them we have the following: (i) Water may act as a plasticizer or antiplasticizer depending on concentration, temperature, and pH. (ii) The structural organization of absorbed water is sensitive to polymer mobility. (iii) Polymer conformational changes can accompany hydration. (iv) The presence of a third component such as a salt can alter the way in which water behaves. (v) Effects of cross-linking can be significant. (vi) Water is affected by both equilibrium and nonequilibrium factors, the latter displaying strong temperature, concentration, and pH dependence. All of these factors must be taken into account to get the best knowledge on the swelling behavior of hydrogels.

In the current literature, many investigations dedicated to study the swelling behavior of hydrogels with hydrogen-bonding ability can be found. This is probably due to the importance of hydrogen bonding in the behavior of intelligent gels since many of them are sensitive to changes in pH. However, these studies are mostly concerned with equilibrium swelling values and their changes with pH, temperature, and composition. As far we are concerned, we have not been aware of any systematic study on the influence of the hydrogen-bonding degree on the gel swelling kinetics nor how the

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Table 1. Molar Composition of Cross-Linked Samples As Determined by Elemental Analysis; 0.50 mol % TEGDMA as Cross-Linking Agent Was Used

sample	(*N*-iPAAm) (mol %)	(MAA) (mol %)
P(MMA)(0/100)	0	100
P(*N*-iPAAm-*co*-MAA)(15/85)	19.5	80.5
P(*N*-iPAAm-*co*-MAA)(30/70)	38.8	61.2
P(*N*-iPAAm-*co*-MAA)(50/50)	53.3	46.7
P(*N*-iPAAm-*co*-MAA)(70/30)	73.3	26.7
P(*N*-iPAAm-*co*-MAA)(85/15)	83.3	16.7
P(*N*-iPAAm)(100/0)	100	0

swelling kinetics can reveal hydrogen bond formation.

The aim of the present work was to investigate how changes on the swelling history may alter the gel structure and therefore the subsequent dynamic swelling features of a series of P(*N*-iPAAm-*co*-MAA) hydrogels. For this reason, we have submitted the samples to controlled swelling histories to tailor the degree of hydrogen bonding in order to prove the relationship between anomalous swelling behavior and hydrogen bond interaction as controlling factors during the swelling process.

Synthesis

P(MAA) and P(*N*-iPAAm) homopolymers and P(*N*-iPAAm-*co*-MAA) random copolymers with 0.50 wt % of cross-linking agent TEGDMA were synthesized by radical copolymerization in solution. It has been described in detail elsewhere.[5,6] Each polymer composition estimated by elemental analysis is given in Table 1. Uniform disks were punched out of the hydrogel sample following the procedure described elsewhere.[8,9]

Swelling Experiments

Swelling kinetics and equilibrium values were determined gravimetrically. Gel disks were left to swell in buffer solutions to achieve the equilibrium at 25 °C. The swollen gels were taken out at regular time intervals, wiped superficially with filter paper, weighed, and placed again in the same immersion bath. Data from the swelling studies are usually expressed in terms of water uptake, defined as the weight of water imbibed by the sample per unit weight of dry polymer. The normalized swelling degree (Q_t) at time t were calculated in grams of water per gram of dry gel using the following expression:

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

where m_0 is the initial weight of the dried disk (xerogel), namely, the weight a $t = 0$, m_t is 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

$$Q_\infty = \frac{m_\infty - m_0}{m_0} = \frac{W_\infty}{m_0} \qquad (2)$$

Three different procedures were carried out in order to investigate the effect of the preswelling history of the samples. To distinguish among the different samples according to the preswelling treatment prior to the swelling experiments, a general nomenclature has been adopted:

(i) Control Samples. Dried samples as obtained from the chemical synthesis of the gels (pH ≈ 5). These samples were swelled in a pH 7 buffer solution without any previous treatment, and we will refer to them as "pH 7 (pH from synthesis)".

(ii) Dried after Soaking Samples. A second series of samples were treated by soaking in different pH media (pH 2, 4, and 7) until equilibrium was achieved and then dried. Afterward, these samples were swelled again to carry out swelling kinetic experiments in a pH 7 buffer solution. The nomenclature for these samples is, for instance, "pH 7 (pH 2)", that is, a sample soaked at pH 2, then dried, and subsequently swelled at pH 7.

(iii) Not Dried after Soaking Samples (Swelled). A third series of samples were prepared as follows. Samples soaked and equilibrated at pH 2 were directly immersed, without any drying treatment, in a buffered solution at pH 7. These samples will be referred as "pH 7 (pH 2 swelled)". It is noteworthy that the swelling equilibrium degree Q_∞ attained at pH 2 is very small compared to that attained at pH 7 and therefore negligible. Thus, for instance, let say that at time $t = 0$ the ratio Q_t/Q_∞ is less than 0.03 for samples under study.

Experimental Results

In Table 2 the equilibrium swelling values Q_∞ at pH 7 for a series of P(*N*-iPAAm-*co*-MAA) copolymers previously soaked at different pHs are collected. As can be seen, the swelling history does not significantly affect the equilibrium water uptake. The slight differences found in these values might be due to the exchange between H^+ and Na^+ ions in the carboxyl groups at the different pHs of the preswelling treatment. This will affect the weight of the dried gel (m_0) used to normalize the Q_∞ value. But also, the experimental errors should be taken into account due to the gravimetric method used for the dynamic swelling experiment. In Figure 1, the half swelling time $t_{1/2}$ at pH 7 and 25 °C is plotted against mol % *N*-iPAAm composition as a function of the previous treatment pH for a series of copolymers and their homopolymers. In Figure 1, a dramatic effect

Table 2. Equilibrium Swelling Values Q_∞ at pH 7 and 25 °C for a Series of Cross-Linked (0.50% Cross-Linking Agent) P(*N*-iPAAm-*co*-MAA) Copolymers Samples Previously Soaked at Different pHs

	Q_∞						
(*N*-iPAAm) (mol %)	pH 7 (pH 2)	pH 7 (pH 4)	pH 7 (from synthesis)	pH 7 (pH 7)	pH 7 (pH 2, swelled)	mean	standard error
100	14.9	14.9	13.3	14.7	13.7	14.3	0.33
85	50.0	51.6	48.4	48.3	45.2	48.7	1.06
70	43.3	45.2	43.9	40.8	43.0	43.2	0.71
50	28.7	28.1	30.4	26.3	28.0	28.3	0.66
30	22.0	22.6	21.8	20.5	22.1	21.8	0.35
15	14.9	14.9	14.7	12.2	15.2	14.4	0.55
0	21.6	20.8	19.3	15.3	19.1	19.2	1.08

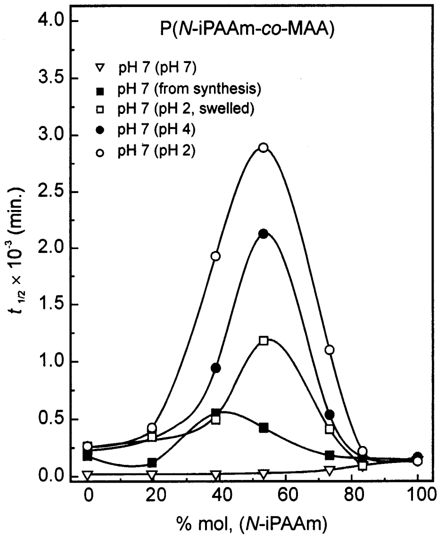

Figure 1. Plot of $t_{1/2}$ estimated from the isotherm swelling curves at pH = 7 and 25 °C vs the mol % *N*-iPAAm composition as a function of the previous soaking pH for a series of P(*N*-iPAAm-*co*-MAA) hydrogels and P(*N*-iPAAm) and P(MAA) homopolymers. For nomenclature see the text.

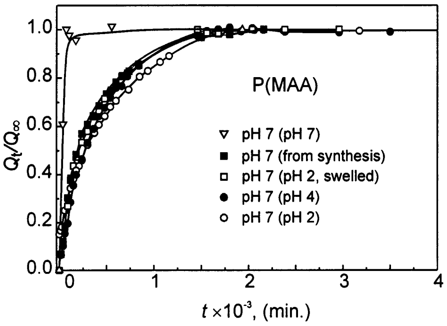

Figure 2. Effect of the previous soaking pH on the swelling isotherms at pH 7 and 25 °C on the Q_t/Q_∞ vs t plot of a P(MAA) homopolymer. For nomenclature see the text.

on the copolymer swelling rate may be observed. The swelling history does not have any significant effect on the cross-linked P(*N*-iPAAm) homopolymer as it could be expected since it does not contain any ionizable group in its structure. The greatest effect of the previous soaking pH occurs in copolymers approaching equimolecular amounts of both comonomers, namely, 30, 50, and 70 mol % of *N*-iPAAm. The slowest swelling rate, i.e., the higher time $t_{1/2}$ for the swelling, takes place for the equimolecular composition, for the sample previously soaked at pH 2 and then dried, where the half of the equilibrium swelling value is reached after 2 days. The $t_{1/2}$ increases considerably with decreasing the soaking pH, which is directly related to the amount of hydrogen bonding in the sample. However, this effect is much less remarkable in P(MAA) homopolymer.

As is very well-known, P(MAA) may form hydrogen bonds between carboxylic groups from its structural unit. Figure 2 displays swelling curves of cross-linked P(MAA) at pH 7, previously soaked at different pH and 25 °C. As can be observed, the gels soaked below the pK_a of methacrylic acid have a slower swelling rate than the one previously soaked at pH 7. The swelling curves of samples treated under different acidic pH may be almost superimposed, which means that they have almost the same swelling rate. It must be assumed that, if the swelling rate is not limited by the disruption of hydrogen bonds, it is because this process is faster than the rate of ionization of the MAA carboxyl groups.

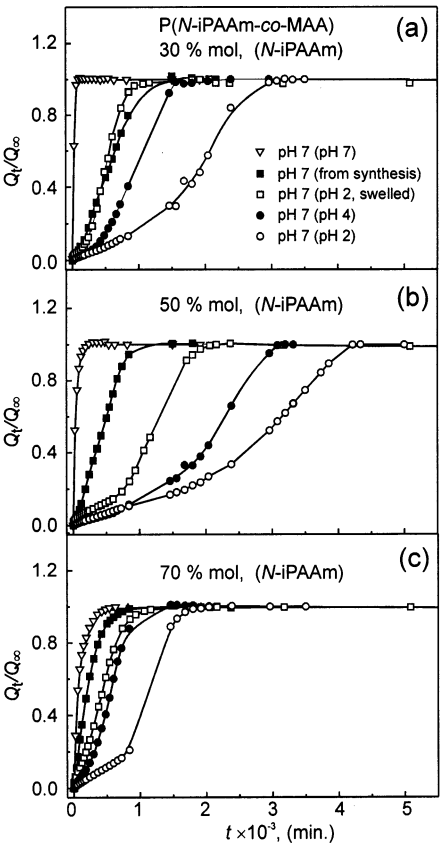

Figure 3. Effect of the previous soaking pH on the swelling isotherm in water of three P(*N*-iPAAm-*co*-MAA) copolymers at pH 7 and 25 °C. For nomenclature see the text.

Figure 3a–c shows dynamic swelling curves of a series of copolymers having 30, 50, and 70 mol % *N*-iPAAm content at pH 7, previously soaked according to the three protocols described in the experimental part. Generally speaking, it can be said that the swelling behavior of these copolymers is very different from that of P(MAA) displayed in Figure 2. Both the swelling rate and the shape of the curve depend strongly on the previously pH used to soak the sample. The sigmoidal shape of the dynamic swelling curve for gels treated under acidic pH becomes more accentuated as the acidity of the previous soaking medium increases. It should be noted that, in the case of gels soaked at pH 2, the reswelling is faster when the gels remain swelled at pH 2 than when they were dried before the experiments at pH 7. This sigmoidal shape clearly seen in some of the curves suggests that the swelling may follow autocatalytic kinetics. In fact, this can be clearly seen in Figure 4, where the rate of water uptake per minute, $d(Q_t/Q_\infty)/dt$, as a function of the normalized amount of water inside the gel, Q_t/Q_∞, has been plotted for the 70 mol % *N*-iPAAm copolymer hydrogel previously soaked at different pHs. The rate of water uptake reaches a maximum when nearly half of the equilibrium swelling value has been reached. This behavior is also peculiar and typical of processes that obey autocatalytic mechanisms. This may suggest that hydrogen bond disruption results from a cooperative process, and the unzipping of the close sites may follow an autocatalytic

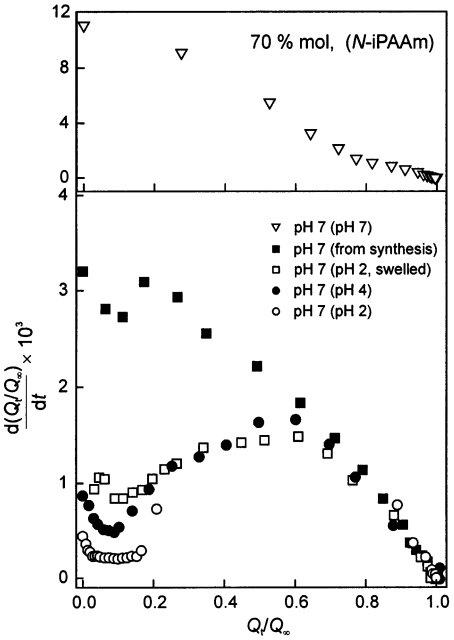

Figure 4. Effect of the previous soaking pH as plots of the swelling rates $d(Q_t/Q_\infty)/dt$ against the swelling degree Q_t/Q_∞ of a P(*N*-iPAAm-*co*-MAA) of 70 mol % *N*-iPAAm content at pH = 7 and 25 °C. For nomenclature see the text.

mechanism. The uptake of the first water molecule helps the uptake of the next one.

Let us assume that the water uptake (swelling process) under consideration is as follows:

$$H_2O \xrightarrow{k_1} H_2O^\bullet$$

$$H_2O + H_2O^\bullet \xrightarrow{k_2} 2H_2O^\bullet \qquad (3)$$

where $H_2O^\bullet$ represents water molecules inside the gel; the first water molecule that penetrates inside the polymer helps the next one to go inside the gel, so that $k_2 \gg k_1$. This is a water penetrating kinetics scheme for a simple autocatalytic process. In the present case, the swelling rate is proportional to the amount of sites still available for water, $1 - Q_t/Q_\infty$, and to the water already inside the gel, Q_t/Q_∞. Therefore we can write

$$d(Q_t/Q_\infty)/dt = k_1[1-(Q_t/Q_\infty)] + k_2Q_t/Q_\infty[1-(Q_t/Q_\infty)] \qquad (4)$$

which after arrangement and integration yields the following integrated equation:[14]

$$\ln\left[\frac{(k_1/k_2)+(Q_t/Q_\infty)}{1-(Q_t/Q_\infty)}\right] = \ln\left[\frac{k_1}{k_2}\right] + (k_1+k_2)t \qquad (5)$$

This means that a plot of the left-hand-side term of this equation vs t will lead to a straight line. In pure autocatalytic processes, when $k_2 \gg k_1$, k_1/k_2 is negligible compared to Q_t/Q_∞, and therefore a plot of the left-hand-side term $\ln\{(Q_t/Q_\infty)/[1-(Q_t/Q_\infty)]\}$ vs t yields a straight line except for very short times. From the intercept and slope of the straight part of the plot, k_1 and k_2 can be accurately estimated. When k_1 is of the same order that k_2, k_1/k_2 is not negligible, and the rate constant has to be calculated by means of a trial-and-error process using the complete expression given by eq 5. However, eq 5 may be also arranged to the following form:

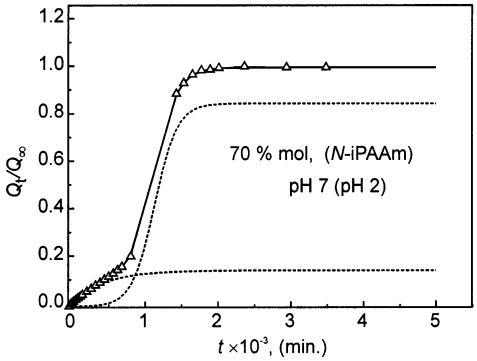

Figure 5. Deconvolution of a first-order and an autocatalytic process for the swelling of a 70% mol *N*-iPAAm copolymer at pH 7, previously soaked at pH 2.

$$\frac{Q_t}{Q_\infty} = \frac{(k_1/k_2)(1-e^{-(k_1+k_2)t})}{(k_1/k_2)+e^{-(k_1+k_2)t}} \qquad (6)$$

This equation has been employed when the first derivative did not exhibit a clear maximum, for instance, for samples swelled directly from the synthesis as it can be observed in Figure 4. If we have a look at this expression when $k_1 \gg k_2$, $(k_1 + k_2) \approx k_1$ and therefore $(k_1/k_2) \gg e^{-(k_1+k_2)}$, it is oversimplified to a first-order rate of swelling,

$$\frac{Q_t}{Q_\infty} \approx 1 - e^{-k_1t} \qquad (7)$$

where now k_1 is a true first-order rate constant. Coming back to Figure 3, samples treated under pH 2 exhibit an almost constant swelling rate until a degree of swelling ranging approximately between 0.15 and 0.2. This part of the plot may correspond to a zero- or first-order kinetics and appears in all copolymers soaked at pH 2 and in 50 mol % *N*-iPAAm for pH 2, 4, 2 (swelled). However, as we will see later, the possibility of zero-order rate has to be ruled out. Nevertheless, it seems that for these cases an induction or delay period exits, which may be caused by a higher hydrogen bond strength when copolymers are treated under more acidic conditions, especially for 50 mol % *N*-iPAAm, i.e., the equimolecular composition. It can be interpreted in terms of two simultaneous processes: the first one that follows a first-order kinetics with a very small rate constant and the second one the overall autocatalytic process with its two rate constants. These two simultaneous processes may be represented by eqs 6 and 7 by the following equation:

$$\frac{Q_t}{Q_\infty} = (1-\beta)\frac{(k_1/k_2)(1-e^{-(k_1+k_2)t})}{(k_1/k_2)+e^{-(k_1+k_2)t}} + \beta(1-e^{-k_3t}) \qquad (8)$$

where β is a parameter which represents the percentage of each one of the two contributions to the overall process. In Figure 5, the deconvolution curves of these two simultaneous processes represented by eq 8 for a 70% mol *N*-iPAAm copolymer at pH 7 previously soaked at pH 2 as dotted, dashed, and full lines, respectively, are displayed. This confirms the assumption we have

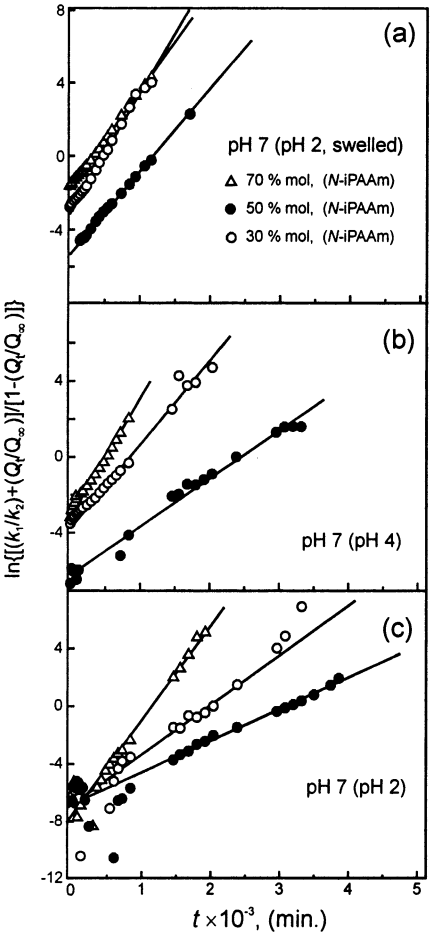

Figure 6. Autocatalytic effect as a plot of $\ln\{[(k_1/k_2) + (Q_t/Q_\infty)]/[1 - (Q_t/Q_\infty)]\}$ vs t from eq 5 of a series of P(*N*-iPAAm-*co*-MAA) hydrogels at pH 7 and 25 °C. For nomenclature see the text.

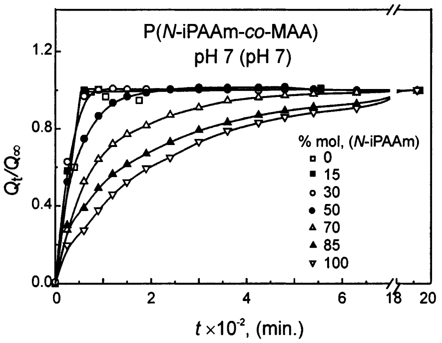

Figure 7. Plot of Q_t/Q_∞ vs t of a series of P(*N*-iPAAm-*co*-MAA) hydrogels at pH 7 and 25 °C previously soaked at the same pH 7. For nomenclature see the text.

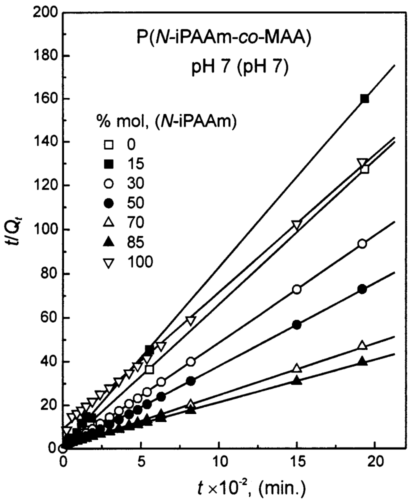

Figure 8. Robinson–Schott's second-order kinetics plot from swelling isotherms at pH 7 of a series of P(*N*-iPAAM-*co*-MAA) hydrogels previously soaked at pH 7. For nomenclature see the text.

made above on a first-order process for the initial part of the curves and rules out the existence of a zero-order rate for the initial regime.

In Figure 6 the applicability of eq 5 to the observed swelling curves at pH 7 previously soaked as indicated is shown. The experimental results have been previously corrected by subtracting the first part of the process by means of eq 7, using parameters determined by eq 8. Rate constants k_1 and k_2 obtained from the best fitting are collected in Table 3. As can be observed, the noncatalytic rate constant, k_1, decreases considerably with decreasing the soaking pH; however, the autocatalytic one, k_2, changes only very slightly. The lowest values of k_2 and k_1 are found for the 50% mol *N*-iPAAm copolymer.

A series of experimental results were also obtained with copolymer hydrogels, which were soaked at pH 7, dried, and subsequently swelled at the same pH. Normalized swelling curves are plotted in Figure 7. They do not show any characteristic sigmoidal trend. It can be seen that in this case a direct relationship between the normalized swelling ratio and the amount of MAA comonomeric units in the copolymer exists.

First-order rate constants and correlation coefficients R^2 are included in Table 4 for comparison purposes. Therefore, we have also examined as a possibility that the swelling process for these systems given in Figure 7 may follow a second-order kinetics. Second-order rates may be expressed by means of the well-known Robinson–Schott's equation:[15–17]

$$t/Q_t = [1/KQ_\infty^2] + [1/Q_\infty]t \qquad (9)$$

where K is a second-order rate constant. Therefore, by plotting our experimental results as t/Q_t against t, a straight line with a slope = $1/Q_\infty$ and an intercept = $1/KQ_\infty^2$ from which Q_∞ and K may be estimated. From this equation the half-swelling time can be estimated as $t_{1/2} = 1/KQ_\infty$. Experimental data given in Figure 7 have been plotted in Figure 8 according to eq 9. As can be very easily seen, almost all the experimental points lie on a series of straight lines, even for the first 30 h. These initial values are very often ignored in the literature. Parameters corresponding to second-order kinetics as well as correlation coefficients R^2 also given in Table 4. Much better correlation coefficients are obtained in the case of a second-order rate equation. As the molar amount of MAA in the composition increases, the second-order rate constant also increases, and $t_{1/2}$ decreases, showing a much faster swelling process. The values obtained from the best fitting of polymers with 0 and 15% *N*-iPAAm molar amounts should not be taken into account. They are due to the lack of experimental data in the first part of the process. For these compositions swelling is so fast that it is almost equilibrated

Table 3. Autocatalytic Rate Constant k_2, Noncatalytic Rate Constant k_1, and Noncatalytic−Autocatalytic Ratio k_1/k_2

	70 mol %, (*N*-iPAAm)			50 mol %, (*N*-iPAAm)			30 mol %, (*N*-iPAAm)		
procedure	10^4k_1 (min^{-1})	10^3k_2 (min^{-1})	k_1/k_2	10^4k_1 (min^{-1})	10^3k_2 (min^{-1})	k_1/k_2	10^4k_1 (min^{-1})	10^3k_2 (min^{-1})	k_1/k_2
pH 7 (from synthesis)	30.1	2.9	1.038	7.64	4.1	0.1863	5.45	3.4	0.1621
pH 7 (pH 2, swelled)	7.1	4.7	0.1590	0.21	4.5	0.0046	2.58	6.3	0.0407
pH 7 (pH 4)	2.7	6.0	0.0408	0.06	2.7	0.0022	0.98	4.3	0.0226
pH 7 (pH 2)	0.04	6.5	0.0005	0.03	2.2	0.0014	0.04	3.5	0.0011

Table 4. Second- and First-Order Kinetic Parameters at pH 7 for Hydrogels Previously Soaked at pH 7

(*N*-iPAAm) (mol %)	second-order kinetic				first-order kinetic			
	Q_∞	*K* (min^{-1})	$t_{1/2}$ (min)	R^2	Q_∞	*K* (min^{-1})	$t_{1/2}$ (min)	R^2
100	16.0	4.2×10^{-4}	147.5	0.9993	14.1	5.0×10^{-3}	138.3	0.9904
85	51.1	2.1×10^{-4}	94.5	0.9997	45.6	7.3×10^{-3}	94.8	0.9677
70	42.3	6.9×10^{-4}	43.7	0.9997	39.9	1.1×10^{-2}	62.4	0.9918
50	26.5	6.0×10^{-3}	6.3	0.9999	26.3	2.5×10^{-2}	27.6	0.9942
30	20.6	6.8×10^{-2}	0.7	0.9999	20.7	4.2×10^{-2}	16.5	0.9966
15	12.2	9.6×10^{-3}	8.5	0.9998	11.8	4.2×10^{-2}	16.5	0.9310
0	15.3	7.1×10^{-3}	9.2	0.9999	15.3	2.8×10^{-2}	24.6	0.9755

for the first data point, leading to experimental difficulties and considerable errors that turn out in odd values for the fit.

Discussion of Results

As far we are concerned, we have not been aware of any study on the autocatalytic water uptake by polymeric gels. However, we have observed in the literature curves a sigmoidal tendency.[18,19] Falamarzian and Varshosaz[18] have determined swelling isotherms of hydrogels of methyl methacrylate/(dimethylamino)-ethyl methacrylate homologue series with 0.1% DVB (divinylbenzene) at pH 3, and they found that experimental data do not follow the Robinson−Schott's second-order rate equation.[15−17] Those curves show sigmoidal shape that may be due to an autocatalytic behavior. For the interpretation, these authors[18] proposed that this deviation may be related to the multilayer adsorption of water molecules to the hydrophilic segments of the polymer, similar to the adsorption of gases to the surface of the solids proposed by Langmuir.[20] However, this is only a plausible hypothesis. Siegel[19] attributed this effect to the glassy state of the copolymer which leads a swelling front separating the glassy core from the rubbery periphery. This rigid core constrains the swelling of the outer part. Only when the front reaches the core is the swelling permitted in three dimensions, leading to swelling acceleration and to the sigmoidal shape.[19] However, that is a macroscopic explanation; at the molecular level, the main factor responsible for this trick behavior may be the disruption of strong hydrogen bonds, which occurs at low pH due to the basic character of this hydrogel.[18,19]

Throughout the paper we have proposed hydrogen bonding as responsible for the peculiar swelling behavior found in P(*N*-iPAAm-*co*-MAA) copolymers. At least two factors derived from hydrogen bond formation between amide and carboxyl groups have to be taken into account to understand the whole swelling process. First, hydrogen bond decreases polymer mobility increasing T_g, and second, the complexes formed possess hydrophobic character. These facts have been put forward for some other copolymers by other procedures. Thus, Staikos et al.[21] concluded that the presence of the isopropyl groups in P(*N*-iPAAm) contributes to a major stabilization of the complex between P(*N*-iPAAm) and P(AA) through hydrogen bonding in aqueous solutions at low pH due to an important hydrophobic interaction. It is also well-known that interpolymer association via hydrogen bonding leads to very compact structures.[22,23] In the case of P(*N*-iPAAm-*co*-AA) copolymers in solution, Bokias et al.[24] showed that its hydrophobicity is strongly enhanced by intrachain hydrogen bonding. In the present case, we have two simultaneous effects: one represented by a more compact structure and the other and a higher hydrophobicity enhanced by inter- and intrachain hydrogen bonding. The lower the pH of soaking, the higher the influence of these two effects on the rate of swelling, as has been observed experimentally in the case of the present series of P(*N*-iPAAm-*co*-MAA) copolymers.

As we have just noticed above, P(MAA) homopolymer, which is also able to form hydrogen bonds in acidic pHs, does not show any sigmoidal swelling behavior under neutral conditions. However, this behavior is exhibited by some of its *N*-iPAAm copolymers. In addition, the swelling rate at pH 7 is quite similar provided that P(MAA) has been previously soaked at a pH below its pK_a. This feature can be only explained on the basis of characteristic differences between MAA−MAA and MAA−*N*-iPAAm hydrogen bonds. In light of ^{1}H double-quantum-filtered DQF-MAS NMR experiments, it has been possible to show that the hydrogen bonds between carboxylic and amide groups are stronger than between carboxyl−carboxyl groups, and therefore their stability with respect to the pH is higher.[10] In addition, the hydrophobic character of the complexes between the P(*N*-iPAAm-*co*-MAA) copolymers should hinder the access of water to the surface. However, once the water initiates penetration and hydrogen bonds start to disrupt, carboxylic groups ionize and therefore the hydrophobicity of the medium is decreased. In fact, this means that each time the penetration of new water molecules will be easier because the medium becomes more and more hydrophilic, thus increasing the rate of water uptake by the gel. This may be an explanation to justify macroscopically the autocatalytic process. Results obtained when studing thermal transition in copolymers may also support this hypothesis.[8] As was noted in the Introduction, P(*N*-iPAAm) gels undergo a temperature-induced phase transition in water, where hydrophobic interactions play an important role.[25] This transition can be modified by copolymerization with charged monomers. As a result, high *N*-iPAAm content copolymer hydrogels do not show the discontinuous thermal transition at high pH values, when the carboxylic groups are ionized. On the contrary, the transition can be detected at low pHs after the protonation of MAA carboxylic moieties.[8] The introduction of fixed ionic monomers accommodates an additional osmotic contribution to the swelling. This additional pressure competes with attractive hydrophobic interactions preventing the thermal collapse of the entire structure.[26]

Considering the process at a molecular level, we can make use of the existence of active and inactive sites on the gel surface postulated by Wang and Morawetz[12] in the case of complex formation of poly(acrylic acid) (PAA) with the *N*,*N*-dimethylacrylamide (DAAm) homopolymer and its copolymers with acrylamide (AAm) in water solution. It is very possible that at the very beginning of the swelling process may exist on the gel surface two different types of sites or places, one which it is fully exposed to water molecules and other in which polymer complexation, no matter whatever its nature is, protects it from water molecules from the aqueous medium. In a second stage water molecules that have penetrated through the xerogel from the exposed regions may initiate the plasticization of the complexated zones in the surface creating new unprotected zones to the water molecules, giving place to a significant increment of the absorbed water. In fact, this may lead to a complete process with autocatalytic characteristics.

The existence of an induction period is probably caused by the glassy state of the dry polymer where the diffusion coefficient is very small.[27,28] The polymer requires a conditioning time, during which is swelled and platicized by water absorption to allow accessibility to complexed sites. This induction period probably exists in all the copolymers but in the copolymer with higher degree of hydrogen bonds is a very limiting factor. Copolymers, soaked at pH 2, which were not dried, pH 7 (pH 2 swelled) samples, did not exhibit such long induction period, because since the beginning, hydrogen bonding sites are more accessible to water. A practical consequence derived from this behavior may be that gels with this type of treatments may have initially a slower sorption velocity but a higher maximum swelling capacity and may therefore be used for sorption of large amounts of water. This fact may be also important and could be utilized to prepare some very specific drug delivery systems (DDS).

Conclusions

1. The swelling behavior of a series of P(*N*-iPAAm-*co*-MAA) copolymers and their P(*N*-iPAAm) and P(MAA) homopolymer hydrogels at pH 7 after soaking under different acidic and neutral conditions has been studied in order to establish a relationship between hydrogen bond ability and swelling dynamics. Some of the experimental data suggest that the swelling process does not obey either first-order or second-order kinetics.

2. Mechanistically speaking, the sigmoidal kinetics obtained for this series of hydrogels may be the result of several consecutive and/or simultaneous processes: namely, one that follows a first-order kinetics with a very small rate constant; the second one, an overall autocatalytic process with its two rate constants.

3. It has been recognized for a long time that in general the swelling kinetics of a hydrogel depends on both the chemical composition and the cross-linking degree. In this paper, it has been shown that for a given sample the swelling kinetics response may also depend on the swelling history. The effect of the previous soaking pH changes dramatically the kinetics order.

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