

# Swelling Kinetics of Poly(*N*-vinylimidazole-*co*-sodium styrenesulfonate) Hydrogels

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**ABSTRACT:** Hydrogels of *N*-vinylimidazole and sodium styrenesulfonate were synthesized by radical crosslinking copolymerization. Transient swelling measurements in water, at room temperature, reveal an unusual behavior. For some gel compositions, the swelling time dependency is about a  $\delta$  function: dry hydrogel pellets swell up readily to reach a high degree of swelling and, spontaneously, they deswell to collapse. Such peculiarity was interpreted in terms of several competing events 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. The results of cyclic swelling–deswelling following abrupt changes of composition in the external bath, from water to sodium hydroxide solution, support that mechanism. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 191–200, 2002

**Key words:** hydrogels; swelling kinetics; deswelling; ionic crosslink; poly(*N*-vinylimidazole-*co*-sodium styrenesulfonate)

## INTRODUCTION

In the last two decades the consideration of hydrogels by researchers changed from rare, almost unknown materials, to materials with unique properties and potential application in many different fields. Of particular interest are smart or responsive gels, found at first by Tanaka.<sup>1</sup> Responsive gels respond to changes in environmental conditions with drastic changes of volume<sup>1–4</sup> or any other property such as fluorescent emission.<sup>5,6</sup> Most of the applications proposed for responsive gels depend on the kinetics of changes of the observed property.

Poly(*N*-vinylimidazole) (PVI) and poly(*N*-vinylimidazole-*co*-sodiumstyrenesulfonate) (PVI–SSS) hydrogels have several potential applications<sup>7–11</sup> because of their ability to regulate the pH of an aqueous solution<sup>8</sup> and to uptake heavy-metal cations.<sup>9,10</sup> PVI–SSS gels show polyampholytic or polyelectrolytic behavior, depending on the SSS content of the gel, and they experience transitions between superabsorbent and collapsed states induced by small changes of ionic strength and SSS compositions.<sup>7</sup>

The swelling degree of a hydrogel is known to depend on its network structure,<sup>11,12</sup> which is controlled by the conditions of the crosslinking polymerization.<sup>13–15</sup> The swelling degree of neutral PVI hydrogels depends inversely on the crosslinking ratio and the total concentration of comonomers in the feed.<sup>11</sup> In this work, the feeding mixture composition of PVI–SSS hydrogels

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was selected to get transparent gels with different total comonomer concentrations and different ionization degrees, but constant crosslinker ratio. Transient swelling measurements were performed on such PVI–SSS hydrogels trying to elucidate compositional effects on the swelling kinetic behavior.

Indeed, the rate of volume change in response to an external perturbation depends on the size and shape of the gel pellet. Pellets in the centimeter size scale may need several weeks to reach equilibrium, whereas micrometric gel particles undergo complete volume changes in fractions of a second.<sup>16</sup> For a given pellet size, swelling kinetics depends on the crosslink density<sup>11</sup> and on gel composition. In general, swelling kinetics is analyzed in terms of stepwise processes.<sup>17</sup> In the first swelling steps, swelling is considered to be governed by Fick's law,<sup>18</sup> although non-Fickian behavior was also frequently found.<sup>19</sup> For long periods of time, swelling increases and levels off to the equilibrium value and swelling kinetic results were analyzed with a second-order kinetic law.<sup>18,20,21</sup> In this work, pellets of about 1 cm were employed and thus long periods of time (months) were considered.

## EXPERIMENTAL

### Preparation of Hydrogels

*N*-Vinylimidazole, purchased from Aldrich (Milwaukee, WI), was distilled under reduced pressure at 55°C just prior to use. Sodium styrenesulfonate (Aldrich) was used as received. Water was distilled and deionized by a Milli-Q system from Millipore (Bedford, MA). *N,N'*-Methylene-bisacrylamide (Aldrich) and AIBN (Fluka, Milwaukee, WI) were high-quality products, used as received.

Hydrogel samples (PVI–SSS) were synthesized by radical crosslinking polymerization of *N*-vinylimidazole (VI), sodium styrenesulfonate (SSS), and *N,N'*-methylene-bisacrylamide (BA) in aqueous solution, with AIBN ( $6 \times 10^{-3} M$ ) as initiator. Neutral hydrogels without SSS (PVI) were also obtained under the same conditions, to be used as a reference.

The aqueous solution of VI, SSS, BA, and AIBN was sonicated at 60°C for 10 min and was then immersed in a bath at 90°C for 2 h. The hydrogels were taken out of molds and cut in pieces, which were mostly unshaped because of their mechanical properties. Afterward, the hydrogel was

washed repeatedly with an excess of water (Milli-Q) for about 1 month. Washing water was replaced every day. Clean hydrogels were dried in an oven at 80°C for 24 h. The yield of the reaction was between 80 and 100% in all cases.

The total concentration of monomers  $C_T$  (in g/100 mL or % w/v) in the reacting solution, as much as the crosslinker ratio  $C$  (% w/w of BA) and the SSS weight fraction ( $w_{SSS}$  in % w/w) in the mixture of comonomers in the feed, determines the optical, thermal, mechanical, and swelling properties of the final hydrogel. In the following, any sample will be denoted by the symbol ( $C_T/C/w_{SSS}$ ). For example, (40/2/5) represents a hydrogel obtained with the following feeding mixture composition: 40 g/100 mL total concentration of monomers and a mixture of comonomers having 2% w/w BA and 5% w/w SSS. When results were analyzed in terms of interactions between monomeric units, mole fractions of SSS units in the feed ( $f_{SSS}$ ), rather than weight fractions, were employed.

The mole fractions of SSS in the hydrogels ( $F_{SSS}$ ) were spectrophotometrically determined in a Shimadzu UV240 (Shimadzu, Japan). Swollen PVI–SSS samples of known mass and swelling degree were placed in a homemade prism with quartz windows whose optical path length was previously determined. The absorption spectra were corrected<sup>22,23</sup> for light scattering with a baseline proportional to  $\lambda^{-4}$ . The molar extinction coefficient of SSS at 260 nm was taken as  $228 M^{-1} \text{ cm}^{-1}$ .

### Swelling Measurements

Swelling measurements were performed gravimetrically. Dry pellets were immersed in deionized water baths for several weeks. Samples were periodically removed from the bath, weighed, and then returned to a new water bath of the same final volume as before. The swelling degree  $S$  was calculated in grams of water per gram of dry gel, as

$$S = \frac{m_h - m_0}{m_0} \quad (1)$$

where  $m_0$  is the weight of the dry pellet and  $m_h$  is the weight of the swollen pellet at a given time or at equilibrium ( $S_{eq}$ ).  $S$  was measured at room temperature, keeping constant the gel effective concentration ( $C_{eff}$ ), that is to say, the ratio of  $m_0$  to the volume of the liquid in which the dry pellet

was immersed. The standard deviation of time-dependent  $S$  measurements was less than 10% but still quite large. It was attributed to the difficulty of cutting regular pellets of the material, even in the swollen state, because of its internal stress. The surfaces of unshaped pieces were difficult to dry before weighing and, besides, some samples broke during swelling. Thereafter, samples had to be handled in Gooch crucibles without drying before weighing, to avoid losing material.

## RESULTS

Characterization of PVI-SSS samples requires determining the mole fraction of predominant comonomers (VI and SSS) and the degree of crosslinking of the network through, for example, the molecular weight of chains between crosslinks ( $M_c$ ). The Flory-Rehner equation,<sup>24</sup> modified by Peppas and Merrill,<sup>25</sup> allows calculation of  $M_c$  for neutral hydrogels with known  $\chi$  (Flory-Huggins polymer-solvent interaction parameter),  $\rho_2$  (xerogel density),  $V_1$  (solvent molar volume), and  $v_{2r}$  (polymer volume fraction in the relaxed state):

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + \frac{V_1 \rho_2}{M_c} (v_2^{1/3} v_{2r}^{2/3} - v_2/2) = 0 \quad (2)$$

whereas  $v_2$ , the polymer volume fraction in the swollen gel, is

$$v_2 = \frac{m_0 \rho_2}{\rho_2 \frac{m_0}{\rho_2} + \frac{m_h - m_0}{\rho_1}} \quad (3)$$

where  $\rho_1$  represents solvent density. Equation (2) was applied to methanol-PVI systems with  $\chi = 0.472$  (calculated from the second virial coefficient given in Ref. 26),  $V_1 = 40.45 \text{ cm}^3/\text{mol}$ , and taking  $\rho_2$  from Refs. 7 and 27.  $v_{2r}$  represents the polymer volume fraction at the reference or relaxed state. Properly, the reference state is that in which polymer chains have random walk configurations but it is usually identified<sup>25</sup> with the state of the network just after synthesis. In this case  $v_{2r} = 0.088, 0.224, \text{ and } 0.366$  for  $C_T = 10, 25, \text{ and } 40\%$ , respectively. Table I summarizes  $M_c$  values obtained for PVI hydrogels with  $C = 2\%$  and  $C_T$  employed in this work. As expected,  $M_c$  decreases upon increasing  $C_T$  because of: (1) the

**Table I** Molecular Weight of Chains Between Crosslinks and Equilibrium Swelling Degree in Pure Water, as a Function of the Total Comonomer Concentration in the Feeding Mixture Employed to Synthesize PVI Gels<sup>a</sup>

$C_T$ (% w/v)	$M_c$ ( $10^4$ g/mol)	$S_{eq}$ (g <sub>H<sub>2</sub>O</sub> /g <sub>dry gel</sub> )
10	6.2	59.1
25	2.4	4.8
40	2.9	3.7

<sup>a</sup> Molecular weights of chains were calculated from swelling results in methanol.

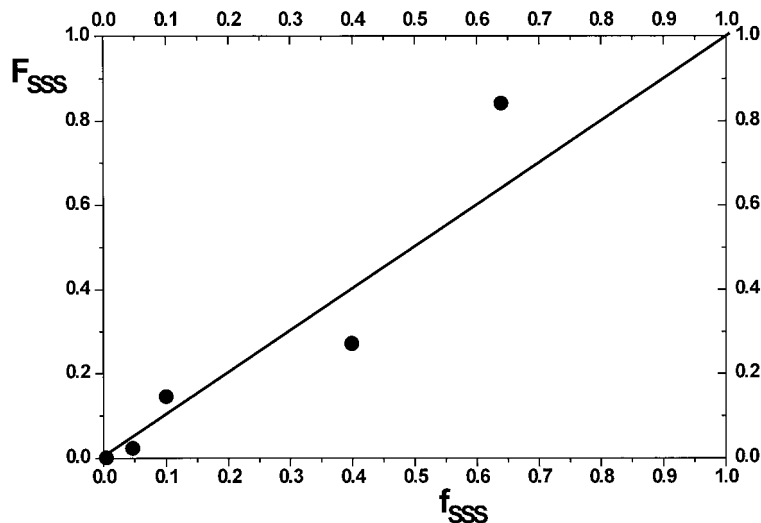
increasing contribution of entanglements to the effective degree of crosslinking and (2) the decreasing probability of formation of network defects such as intramolecular cyclization.<sup>28-30</sup> In any case, chains between crosslinks have more than 100 monomeric units and similar values should be expected for PVI-SSS.

SSS contents in PVI-SSS hydrogels were spectrophotometrically determined. It was found that the composition of the hydrogel was about the same as that of the mixture of comonomers in the feed (Fig. 1), in accordance with yields of the reaction of polymerization close to 100%. The same result was found for similar hydrogels.<sup>31</sup> In the following, the mole fraction of SSS in the hydrogel will be identified with  $f_{SSS}$ , the mole fraction of SSS in the feed.

Several theories on swelling kinetics have been proposed.<sup>20,32-34</sup> When a dry gel is immersed in water, it penetrates into the gel pellet in the form of a front, which shifts from the surface to the core. The rate of translation of the solvent front depends on both the shape<sup>32</sup> and the history of the polymer sample.<sup>35</sup> Figure 2 shows a typical time dependency of swelling, observed for neutral PVI in deionized water baths. As usual,<sup>11,18,21</sup>  $S$  increases at short times and levels off to the maximum swelling degree at longer times ( $S_{max}$ ). For low  $w_{SSS}$  values, the swelling kinetic behavior of PVI-SSS is similar to that of neutral PVI, as shown in Figure 2.  $S$  data plotted in Figure 2 were fitted to rectangular hyperbolic functions with

$$S = \frac{S_{max} t}{t + \tau_S} \quad (4)$$

where  $\tau_S$  (Table II) represents the time needed to reach half the maximum swelling value. This type of functionality represents a second-order de-



**Figure 1** Composition of PVI-SSS hydrogels ( $F_{\text{SSS}}$ ) synthesized with  $C_T = 25\%$  and  $C = 2\%$ , as a function of the mole fraction of SSS in the comonomer feeding mixture ( $f_{\text{SSS}}$ ). The degree of conversion of the polymerization for this particular  $C_T$  value is in the range 95–100%.

scription of swelling processes<sup>20</sup> and it was applied for long periods of time.

For the largest  $w_{\text{SSS}}$  values, 40% and above, the maximum swelling is reached almost instantly (Fig. 3) and from then on,  $S$  decreases slowly with time. To fit the experimental results of gel deswelling in this range of  $w_{\text{SSS}}$  values, a linear regression was employed:

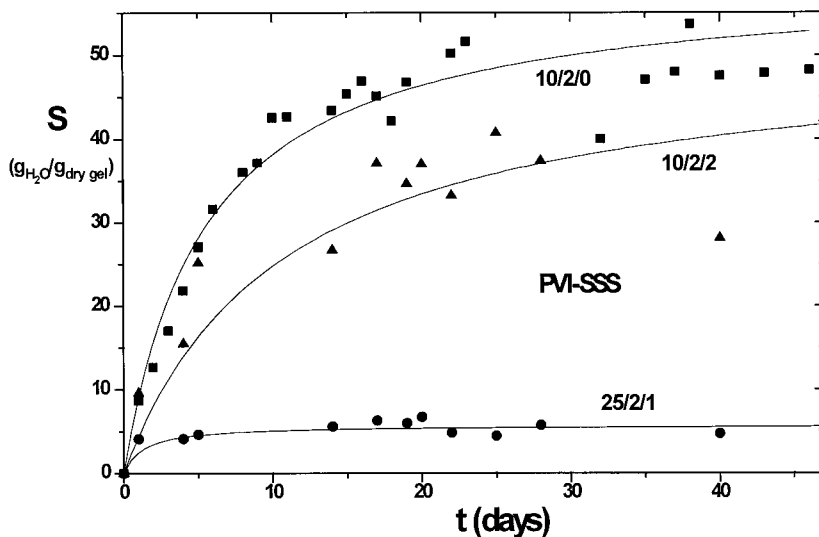
$$S = S_{\text{max}} + \Delta S_D \frac{(t - t_0)}{2(\tau_D - t_0)} \quad (5)$$

where  $\Delta S_D$  represents the difference between the equilibrium and the maximum swelling degree,

$$\Delta S_D = S_{\text{eq}} - S_{\text{max}} \quad (6)$$

$t_0$  is the time at which the maximum swelling is reached (taken as 1 day when unknown), and  $\tau_D$  (Table II) represents the time needed to reach half the total jump in deswelling  $\Delta S_D$ .

Surprisingly, samples of PVI-SSS hydrogels having  $w_{\text{SSS}}$  in the range 2 to 40% (Fig. 4), swelled



**Figure 2** Time dependency of swelling in pure water of PVI-SSS hydrogels with weight fractions of SSS in the feeding ranging from 0 to 2%,  $C_T = 10$  and 25%, and  $C = 2\%$ . Solid lines represent the best-fitting curves of eq. (4) to the experimental data.

**Table II Fitting Parameters to Eqs. (4) to (7) of the Time Dependency of PVI-SSS Hydrogels' Swelling and Deswelling in Deionized Water at Room Temperature**

Sample	$\tau_S$ (days)	$\tau_D$ (days)	$S_{\max}$ ( $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{dry gel}}$ )	$\Delta S_D$ ( $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{dry gel}}$ )
25/2/0	0.7	—	4.8	—
25/2/1	1.3	—	5.7	—
25/2/2	0.02	0.63	6.0	-1.2
25/2/5	0.06	7.7	6.9	-4.0
25/2/10	0.13	3.1	13	-11
25/2/20	0.07	13	14.5	-13
25/2/40	—	24	21	-17
25/2/60	—	26	21	-7

up readily and, afterward,  $S$  decreased exponentially to a minimum value much smaller than  $S$  values characteristic of neutral PVI (see Table I). In this range of compositions,  $\tau_D$  values (Table II) were calculated with exponential fitting functions:

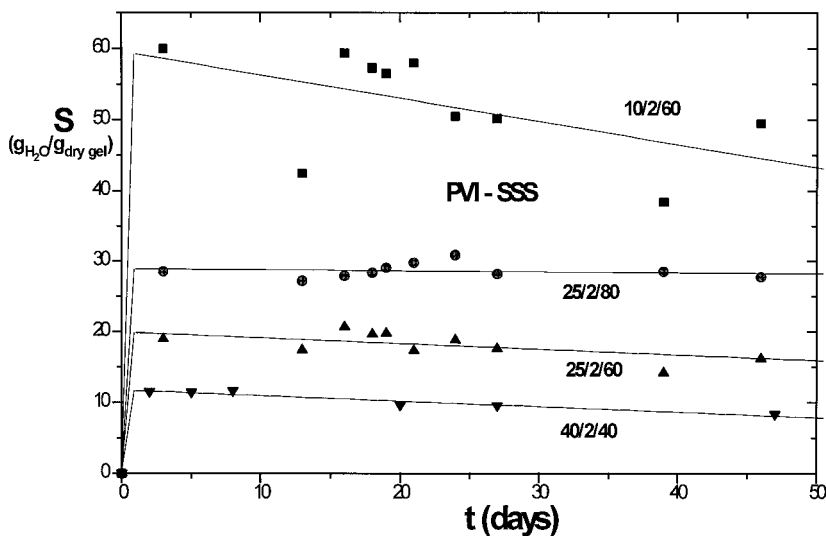
$$S = S_{eq} - \Delta S_D \exp\left(\frac{(t - t_0) \ln 2}{\tau_D - t_0}\right) \quad (7)$$

and  $\tau_S$  (Table II) with eq. (4) in the time range of decreasing and growing swelling, respectively.

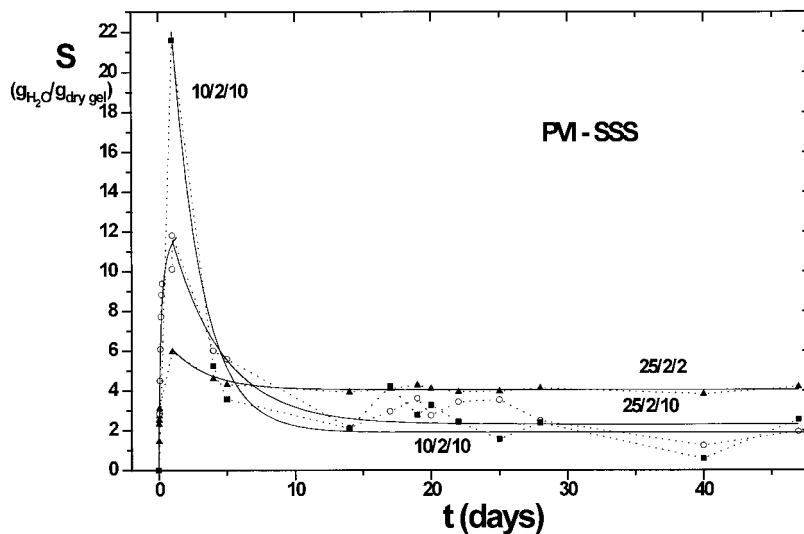
Swelling of several samples deserves special mention (i.e., 10/2/10, 25/2/10, and 40/2/10) because it is practically a  $\delta$  function: it goes from zero to a maximum value, which can be very large, and again to almost zero, without external stimulus. This spontaneous swelling-collapse behavior, with changes of volume by as much as 10-fold, was not frequently observed. There are some reports in the literature on spontaneous sequences of swelling-deswelling or even the opposite, deswelling-swelling, but they are concerned with rather complex systems such as polyelectrolyte-loaded gels placed in water<sup>36</sup> or gels swollen in water and immersed in a solution of an amphiphilic surfactant.<sup>37</sup> In some conditions, ionic gels also show<sup>35,38-40</sup> an overswelling or overshoot representing about 10% of the equilibrium swelling. This effect has not yet been clearly understood but seems to be related to the thickness,<sup>35</sup> the concentration of fixed charges,<sup>40</sup> and degree of crosslinking of the sample.<sup>39</sup>

## DISCUSSION

Table II summarizes  $\tau_S$ ,  $\tau_D$ ,  $\Delta S_D$ , and  $S_{\max}$  values for  $C_T = 25\%$  and different  $w_{\text{SSS}}$  in the feed. They are representative of the other samples studied here.  $\tau_S$  decreases with increasing  $C_T$ , keeping the same pattern for the dependency on  $w_{\text{SSS}}$ . For



**Figure 3** Time dependency of swelling in pure water of PVI-SSS hydrogels with weight fractions of SSS in the feeding mixture in the range  $40 < w_{\text{SSS}} < 80\%$ ;  $C_T = 10, 25,$  and  $40\%$ ; and  $C = 2\%$ . Solid lines represent the best-fitting curves of eq. (5) to the experimental data.



**Figure 4** Time dependency of swelling in pure water of PVI-SSS hydrogels with weight fractions of SSS in the feeding mixture in the range  $2 < w_{\text{SSS}} < 40\%$ ,  $C_T = 25\%$ , and  $C = 2\%$ . Polymer effective concentration  $C_{\text{eff}}$  is between 0.5 and 0.75 g/100 mL. Solid lines represent the best-fitting curves of eqs. (4) and (7) to the experimental data.

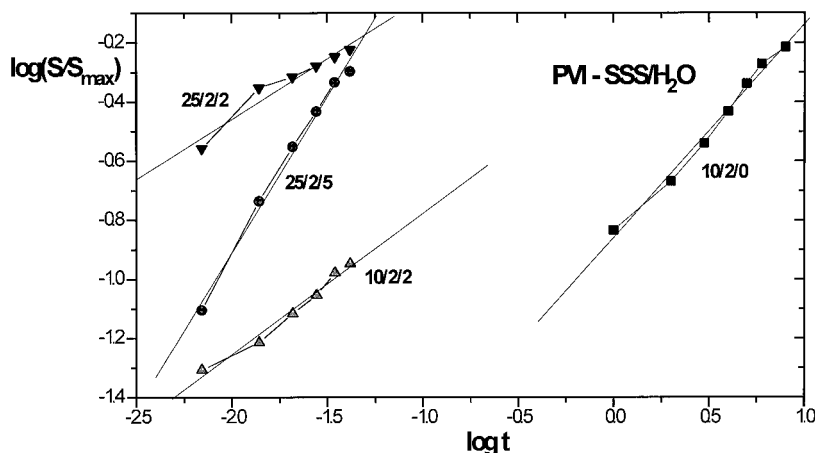
example,  $\tau_S$  of sample 10/2/1 is 7.0 days, whereas for sample 25/2/1 it is 1.3 days and for sample 40/2/1 it is 0.7 days. The maximum swelling reached follows the same trend: it equals 45, 5.7, and 3.6  $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{dry gel}}$ , respectively. For any  $C_T$ , there is a sudden decrease of  $\tau_S$  at  $w_{\text{SSS}}$  around 5%, which is not correlated with a decrease of  $S_{\text{max}}$  and needs explanation. The spontaneous sequence swelling-deswelling is the other unexpected result, which is considered below.

The kinetics of swelling may be understood by considering several simultaneous effects. At the first stages of swelling, as long as the pellet keeps the glassy core, the rate-limiting steps are solvent diffusion or network response. The relative importance of both effects, solvent diffusion and polymer relaxation, may be analyzed with the expression<sup>3,38</sup>

$$S/S_{\text{max}} = kt^n \quad (8)$$

where  $k$  is a rate constant characteristic of the polymer-solvent system and  $n$  is a kinetic parameter indicating the transport mechanism: Fickian diffusion or Case I transport ( $n = 0.5$ ), relaxation-controlled or Case II transport ( $n = 1$ ), anomalous transport ( $0.5 < n < 1$ ) or super Case II transport ( $n > 1$ ). Figure 5 shows the time evolution of  $S$  just after immersion in the water bath, plotted in the form of eq. (8), for several PVI-SSS hydrogels. As shown in Table III,  $n$  covers a broad range,

from 0.4 to 1. In any case the upper limit of  $S/S_{\text{max}}$  was 0.6 but the lower limit, determined by the time after immersion of the first measurement, changed significantly. For example, sample 10/2/0 was measured for the first time 1 day after immersion and 10 days were needed to cover the whole range of  $S/S_{\text{max}}$ , from 0.1 to 0.6. On the other hand, sample 25/2/5 required only 1 h to cover the same range of  $S/S_{\text{max}}$ . Sets of measurements covering that range 0.2–0.6 of  $S/S_{\text{max}}$  yield  $n$  values between 0.5 and 1 (Table III), whereas shorter-range measurements as for sample 25/2/2, yield  $n < 0.5$ , indicative of a downward curvature (swelling deceleration) even for  $S/S_{\text{max}} < 0.6$ . It is also interesting to notice that for  $S/S_{\text{max}}$  below 10% (see sample 10/2/2 in Table III),  $S$  scales with time with  $n \cong 0.5$ . The conclusions drawn from these results are (1) that penetration of water in the first stage is a Fickian solvent-diffusion process ( $n \cong 0.5$ ); (2) at intermedium swelling degrees there is an anomalous type of transport mechanism with partial control of polymer chain relaxation ( $0.5 < n < 1$ ); and (3) for  $S$  values approaching 60%  $S_{\text{max}}$ , swelling is decelerated with respect to solvent-diffusion control ( $n = 0.5$ ). Given that most of the time swelling is under chain relaxation control, the sudden increase of the rate of swelling (decrease of  $\tau_S$ , see Table II) at  $w_{\text{SSS}}$  around 5% must be related to an increase of chain mobility.



**Figure 5** Double logarithmic plot of swelling versus time for PVI-SSS samples with different  $C_T$  and  $w_{SSS}$ .

Both deswelling and swelling deceleration may be explained with the following argument, visualized in Scheme 1. Xerogels are quite hydrophilic and, in the form of sodium salt, they have a very low crosslinking degree (large  $M_c$ , Table I) in such a way that a large quantity of water diffuses inside the gel. Simultaneously, in gel regions reached by water, sodium cations diffuse outside the gel to reach Donnan equilibrium. To keep electrical neutrality, protons move from the external solution across the gel-water boundary. This loss of protons in the external solution is in accordance with the observed change of pH, from around 6.5 (Milli-Q water) to more than 8, depending on the gel effective concentration. Inside the gel, a portion of protons is cached by basic imidazole groups to reach the degree of protonation in equilibrium with the pH of the solution swelling the gel.<sup>8,11</sup> Protonated imidazole moieties interact electrostatically with neighboring sulfonate groups, thus forming ionic pairs

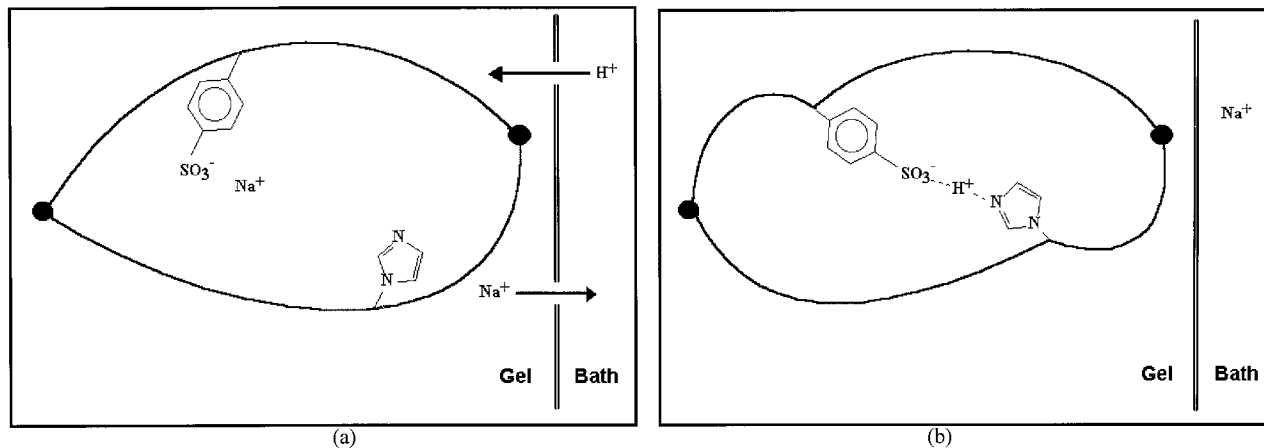
**Table III** Fitting Parameters to Eq. (8) of PVI-SSS Swelling in a Given  $S/S_{\max}$  Range

Sample	$n$	$S/S_{\max}$	$k^a$
10/2/0	$0.72 \pm 0.03$	0.1–0.6	0.14
10/2/2	$0.48 \pm 0.04$	0.05–0.1	0.50
25/2/2	$0.41 \pm 0.05$	0.3–0.6	2.3
25/2/5	$1.05 \pm 0.05$	0.1–0.6	16
25/2/10	$0.72 \pm 0.02$	0.25–0.6	2.1
25/2/20	$0.95 \pm 0.04$	0.2–0.6	4.6

<sup>a</sup> Time was measured in days and therefore the units of  $k$  are days<sup>- $n$</sup> .

(Scheme 1), which behave as ionic crosslinking points. Such ionic interaction of sulfonic and imidazole groups was previously observed in complexes of noncrosslinked poly(styrenesulfonic acid) with poly(*N*-vinylimidazole).<sup>41</sup> Ionic crosslinking by bivalent ions<sup>11,42</sup> and other types of complexations was observed<sup>43</sup> in similar copolymer gels and, as for PVI-SSS, the consequence was to produce gel deswelling. It may thus be concluded that the swelling decelerating process and deswelling of PVI-SSS gels is attributed to the formation of ionic crosslinking points whose maximum effect (minimum  $\tau_D$ ) should occur in systems with balanced protonated imidazole-sulfonate groups,  $w_{SSS}$  around 2–5% for  $C_T = 25\%$ . This interpretation is supported by the dependency of equilibrium swelling on both the sample composition and the ionic strength of the swelling aqueous solution.<sup>7</sup>

Deswelling of PVI-SSS is slower than swelling ( $\tau_D > \tau_S$ , Table II), the opposite of that for other similar hydrogels.<sup>44,45</sup> It is also slower (larger  $\tau_D$ , Table II): (1) for larger  $C_T$ , probably because more compact networks disfavor conformational changes of chains between crosslinks, and (2) for larger SSS contents, because increasing ionic crosslinks give place to shorter chains between crosslinks with less mobility. The deswelling jump between  $S_{\max}$  and  $S_{eq}$  is also dependent on  $C_T$  and  $f_{SSS}$ . Samples with the lowest  $f_{SSS}$  values for any  $C_T$  behave as neutral gels and deswelling was not observed because it might be too small. For larger  $f_{SSS}$ ,  $S_{\max}$  increases (Table II) because, in the first step, the concentration of mobile sodium cations inside the gel increases and outside it still remains negligible. Be-



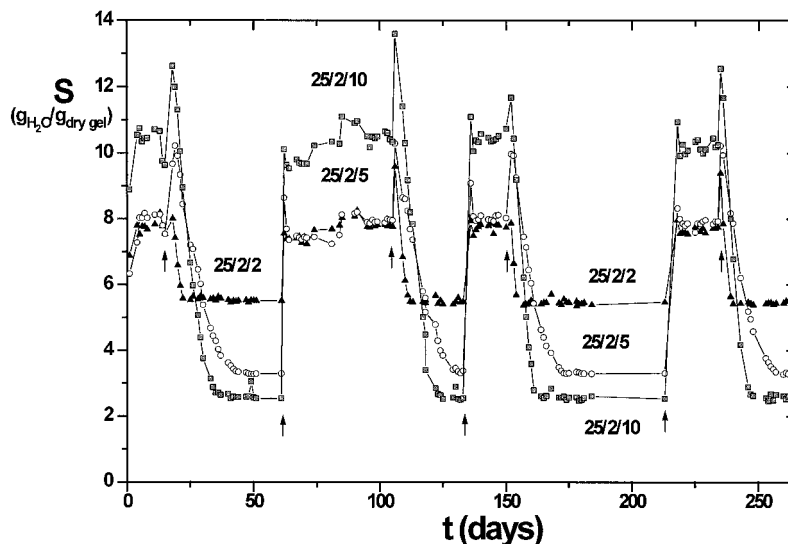
Scheme 1

cause the equilibrium swelling changes less than  $S_{\max}$ ,  $\Delta S_D$  also increases in absolute value (Table II). Again, for larger  $C_T$ ,  $S_{\max}$  and  $\Delta S_D$  decrease because entanglements diminish the effect of mobile ions on swelling.

Cyclic swelling–deswelling results, shown in Figures 6 and 7, support that argument. Remarkably, the final states in the different cycles measured over 9 months are reproducible. Swelling measures water transport, whereas pH depends on ion gel–bath interchange. When a PVI–SSS sample is immersed in a 0.01N NaOH aqueous solution,  $S$  increases sharply, as expected for the sodium salt of styrenesulfonate

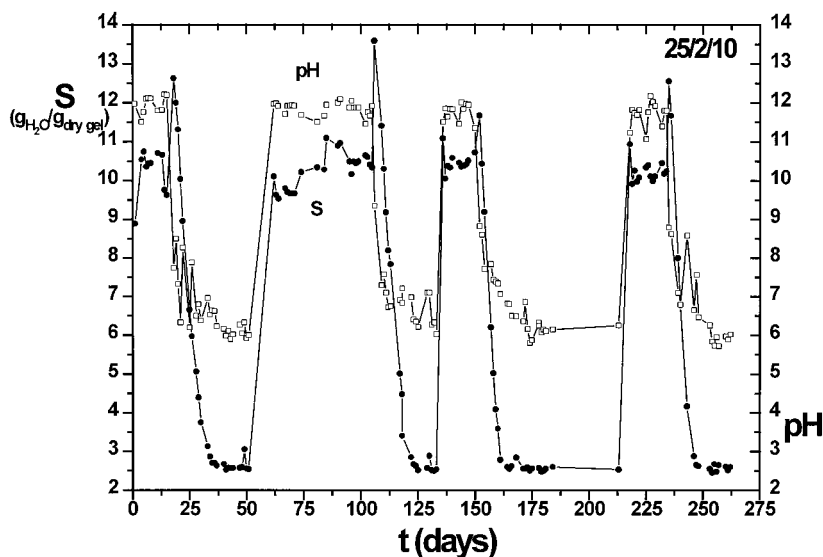
moieties, because of the osmotic pressure contribution of mobile ions. A small (about 10%) overswelling is observed in the two last cycles but it is immediately recuperated and from then on,  $S$  increases very slightly. pH goes instantly (in the time scale considered here) to 12 and remains constant with only random oscillations, indicating that there is no significant ion interchange, although slow chain relaxation broke remnants of interchain contacts of the ionic pairs previously formed at lower pH values.

At a given moment, samples were immersed in deionized water. Then, the gel overswells and im-



**Figure 6** Cyclic swelling–deswelling of three PVI–SSS samples with intermedium  $w_{\text{SSS}}$  and  $C_T = 25\%$ . Arrows denote the moment in which the external bath composition was changed from deionized water to 0.01N NaOH or vice versa.





**Figure 7** Time dependency of pH and  $S$  in cyclic changes of the external bath composition from pure water to 0.01N NaOH or vice versa.

mediately it deswells. Overswelling was not observed for some cycles of sample 25/2/2. The rate of deswelling (or  $\tau_D^{-1}$ ) is lower than that for swelling; it is reproducible cycle to cycle and is not correlated with the deswelling jump, in accordance with results shown in Table II. During deswelling pH decreases, although more slowly than  $S$  (Fig. 7). Gel deswelling requires sodium-proton interchange, interchain approaching to form ionic crosslinks, and diffusion of water outside the gel. Diffusion of ions, water, and chains takes place at different rates and, according to Figure 6, the slowest process is ionic diffusion (pH decay), which may be quite slow for systems with ion-binding interactions,<sup>16</sup> as proposed here. Nevertheless, it is not the process controlling deswelling, given that after complete deswelling, the gel continues releasing sodium cations and taking protons from the external bath. Moreover, taking into account that water diffusion was quicker (during swelling) than chain relaxation, it may be assumed that gel deswelling, which is slower than swelling, is also better controlled by chain motions than by solvent diffusion.

## CONCLUSIONS

Swelling-deswelling kinetics of PVI-SSS hydrogels is the result of several simultaneous processes. Swelling is controlled by chain motions. Simultaneously to swelling, sodium-proton inter-

change takes place across the gel-bath boundary, which initiates a swelling deceleration and subsequent deswelling pathway through the formation of sulfonate-protonated imidazole ionic crosslinks. Chain motions to approach sulfonate and protonated imidazole moieties control deswelling at longer times. They are slower than chain disentanglement motions that control swelling.

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