Swelling Behavior of Poly(acrylamide-*co*-*N*-vinylimidazole) Hydrogels under Different Environment Conditions

Belma Işık, Banu Doğantekin

Hacettepe University, Chemistry Department, 06532 Beytepe, Ankara, Turkey

ABSTRACT: A series of random copolymers of acrylamide and *N*-vinylimidazole, poly(AAm-*co*-NVI), with various compositions were prepared using redox copolymerization. The influence of environmental conditions such as pH, temperature, and ionic strength on the swelling behavior of the copolymeric hydrogels was investigated. The hydrogels exhibited the highest equilibrium swelling in basic medium at high temperature. Equilibrium swelling decreased with rising ionic strength at pH 5.0. As pH increased, equilibrium swelling of the hydrogels increased at pH 11.0 and $I = 0.20$ M. Swelling kinetics of the hydrogels was found to be non-Fickian at 25°C. The process tended to be Fickian at higher pH and temperature. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1783–1788, 2005

Key words: acrylamide; *N*-vinylimidazole; hydrogel; swelling; diffusion

INTRODUCTION

Hydrogels are three-dimensional cross-linked polymeric structures that are able to swell in aqueous solutions. Hydrogels undergo controllable volume change in response to small variations under solution conditions such as pH,[1–6] temperature,[7–10] ionic strength,[11–13] solvent composition,[14] and electric field[15]. Temperature and pH have been the most commonly used solution variables.

Acrylamide (AAm) is a highly hydrophilic monomer and its copolymer with diprotic acids has been investigated as an adsorbent in the adsorption of some cationic dyes,[16] uranyl ions, and some heavy metal ions.[17,18] These, the acrylamide groups, hydrolize in a basic environment at high temperature.

On the other hand, poly(*N*-vinylimidazole), PVI, hydrogels are neutral, but in acid solutions the imidazole groups behaves as a weak base[19] and can be protonated. Thus, PVI hydrogels undergo volume changes in response to variations in the pH of the swelling solution. Additionally, they contain inherent properties such as the ability to regulate the pH of the bath[20] and the ability for uptake of heavy metal cations.[21,22]

The purpose of this study is to combine both monomers in one polymer. In this respect, a series of copolymeric hydrogels with pH reversibility was synthesized from copolymerizing acrylamide and *N*-vinylimidazole. Hydrogels were obtained by changing the AAm/NVI initial molar ratio. The degree of swelling of these hydrogels was determined at various pH, temperature, and ionic strength values.

EXPERIMENTAL

Materials

AAm and NVI were obtained from Merck-Schuchardt and Fluka Chemie AG and used without further purification. Poly(ethylene glycol) M_w 4000 (PEG 4000) was added as a diluent. Other chemicals used were *N*,*N*'-methylenebisacrylamide (MBAAm) from BDH as a cross-linking agent, sodium persulfate ($Na_2S_2O_8$) from BDH as an initiator, and *N*,*N*,*N*',*N*'-tetramethylene diamine (TEMED) from Merck as an accelerator. Buffer solutions were prepared using sodium hydrogenphosphate ($Na_2HPO_4 \cdot 2H_2O$) and potassium dihydrogenphosphate (KH_2PO_4, BDH). All experiments were conducted in a thermostatic water bath (Fryka, Kaltechnik KB 300, Germany).

Preparation of hydrogels

AAm and NVI random copolymers with different compositions and total monomer concentrations were prepared by radical polymerization. AAm was dissolved in 1.0 mL of distilled water. NVI was added to this solution. After the addition of the two monomers and water; 0.11 mL of the cross-linking agent solution, MBAAm (0.05 g/mL water), 0.11 mL of the initiator solution, $Na_2S_2O_8$ (0.05 g/mL water), and 0.11 mL of the accelerator solution, TEMED (0.1 mL/1.5 mL wa-

TABLE I
Production Conditions[a] of PAAm and P(AAm/NVI)
Hydrogels in Water

Gel No.	Initial molar ratio AAm/NVI	AAm (g)	NVI (mL)
1	—	1.0	—
2	89.74/10.26	1.0	0.1
3	81.25/18.75	1.0	0.2
4	74.28/25.72	1.0	0.3
5	68.42/31.58	1.0	0.4

[a] Included in the polymerization medium of all gels listed was 1.0 mL water, 0.11 mL $Na_2S_2O_8$, 0.11 mL TEMED, 0.11 mL MBAAm.

ter), were included in the polymerization medium. Polymerization was carried out in polyvinylchloride straws of 3-mm diameter. After all the chemicals were added, the PVC straws were left at 25°C until polymerization was completed. Hydrogels obtained in long cylindirical shapes were cut into pieces 4–5 mm long and washed with distilled water for removal of unreacted monomer within the gels. Hydrogels were dried in air and vacuum and stored for later evaluation. The production conditions of AAm/NVI hydrogels are given in Table I.

Swelling studies

The dried cylindirical hydrogels were incubated in a solution of desired pH (5–11), ionic strength (0.05–0.2), and temperature (25, 50°C). The ionic strength of the swelling medium was controlled with the concentration of buffer solution. Swollen gels were removed from the buffer solution at regular intervals and dried superficially with filter paper, weighed, and placed back into the same bath. The measurements were continued until a constant weight was reached for each sample. The percentage of swelling of each hydrogel was calculated from the equation

$$S\% = [(m_t - m_0)/m_0] \times 100, \tag{1}$$

where m_t is the mass of swollen gel at time t, amd m_0 is the initial mass of the dry gel.

RESULTS AND DISCUSSION

Swelling studies

The swelling behavior of the hydrogels depends on the nature of the polymer (i.e., the charge, ion content, and the cross-linking agent content) and environmental conditions such as ionic strength, pH, and temperature of the swelling solution.

Inclusion of a hydrophilic and/or ionizable monomer into a gel structure is expected to enhance the water sorption capacity of the hydrogel. The effect of AAm/NVI molar ratio of the produced hydrogels was studied by changing this ratio between 89.74/10.26 and 68.42/31.58 while the AAm concentration in the polymerization medium remained constant (1.0 g/mL). Figure 1 represents poly(AAm/NVI) hydrogel swelling under separated conditions. As seen in Figure 1a, higher equilibrium swelling was obtained at constant pH 5.0, temperature, and ionic strength by increasing NVI content of the hydrogel. PVI hydrogels are neutral but at an acid pH (5.0) the NVI (a weakly basic comonomer) is present in the gel in its ionic form carrying a positive charge. Increasing the NVI content increased the quantity of ionic NVI and high swelling values were obtained in acid solution because of the repulsive interactions between neighbor protonated imidazole groups.

The temperature of the swelling medium influences water diffusion into the hydrogels in many ways. A rise in temperature enhances water diffusion and segmental mobility of polymer/copolymer chains, which causes an increment in degree of swelling. On the other hand, greater thermal energy may detach bound water molecules and may decrease swelling. The results are displayed in Figure 1a and b, which shows that the swelling increases with increasing temperature.

The effect of pH on the swelling of the hydrogels has been investigated by increasing the pH of the swelling medium from 5.0 to 11.0. The results shown in Figure 1c and d indicate that the swelling percentage values of the gels in the buffer solution with 11.0 are higher than those in the buffer solution with pH 5.0. These results displayed in Figure 1c and d show that the amide groups attached to the copolymeric gel structure can be hydrolyzed to form carboxylate groups under basic conditions. In a basic solution at higher temperature (50°C and pH 11.0), the hydrolysis reaction of the amide groups on the gel structure can be accelerated, and the repulsive interaction between negatively charged carboxylate ions in the gel would increase. As a result, hydrogel swelling increases. The results obtained are supported by the diffusion data as summarized in Table II.

The differences in equilibrium swelling degree (ΔESD) in different environments are shown in Figure 2 for sample 2, which has the least NVI, and sample 5, which has the largest NVI content. As seen here, the equilibrium swelling degrees of the hydrogels increase with increasing pH and temperature. This is due to amide groups becoming more prone to hydrolysis under basic and high-temperature conditions, and this causes the ESDs of the hydrogels to be higher at 50°C than at 25°C. Differences in ESDs of the produced AAm/NVI hydrogels under different conditions are also shown in Table III. Comparing the ΔESD values between 25 and 50°C shows that all values at 50°C are larger than those at 25°C. An increase in
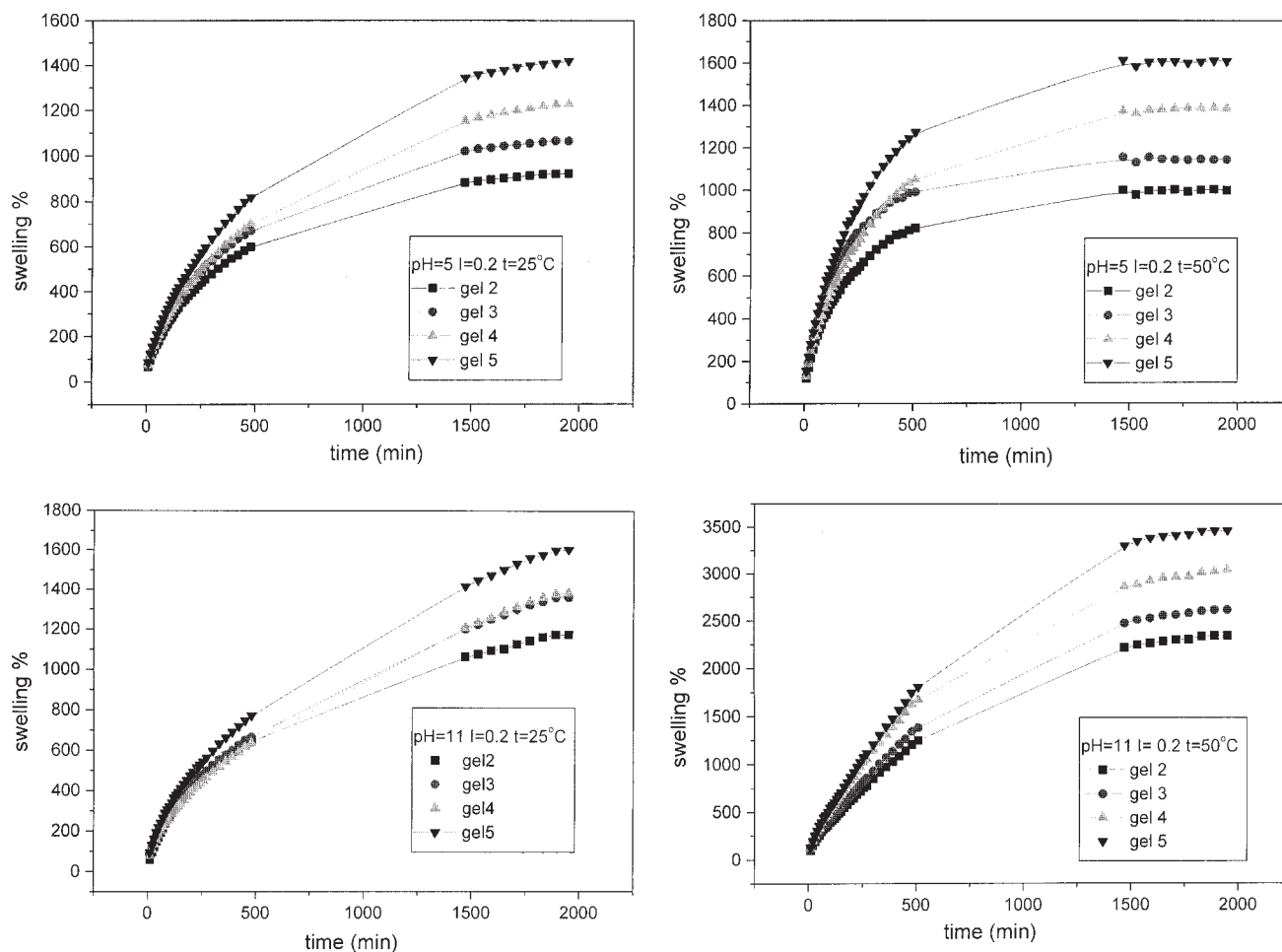
Figure 1 Percentage mass swelling as a function of time for the copolymeric gels at different environments.

temperature from 25 to 50°C caused a significant increase in equilibrium swelling of the hydrogels. At higher temperatures amide group hydrolysis to carboxylic acid groups increases. Since negatively charged carboxylate groups are incorporated into the copolymer network, the hydrophilicity of the hydrogel increases. The greater the hydrophilicity of the hydrogels, the stronger affinity toward water and thus a larger ΔESD.

The effect of external ionic strength on the equilibrium swelling degree of AAm/NVI hydrogels is given in Figure 3. The solution pH was fixed at 5.0 and 11.0 to obtain the equilibrium swelling degree for each gel sample. An increase in ionic strength generally decreased the swelling, because the difference in concentration of mobile ions between the gel and solution is reduced with a decrease in osmotic swelling pressure of these mobile ions inside the hydrogel. As shown in Figure 3a, by increasing ionic strength of the swelling solution, the ESD values decrease under acidic conditions (pH 5.0). ESD values in basic solutions decreased slightly to 0.10 M ionic strength and increased after this value; this effect becomes more pronounced at

50°C than at 25°C (Fig. 3b). This interesting behavior can be explained with variation in the percentage of hydrolysis of amide groups within the hydrogel structure. The (carboxylate groups/total amide groups) ratio decreases with binding of Na^+ ions in the swelling solution to carboxylate groups formed by hydrolysis, so blocking carboxylate groups increases the percentage of hydrolysis and repulsive interactions.

Diffusion studies

When a glassy hydrogel is brought into contact with water, water diffuses into the polymer structure, thus causing it to swell. Analysis of the mechanism of water diffusion into a polymeric matrix has recently been of increasing interest because of important applications of swellable polymers in biomedical, pharmaceutical, agricultural, and engineering fields. The swelling curves of the produced poly(AAm/NVI) hydrogels were used for the calculation of diffusional properties. The following equation was used to determine the nature of the diffusion of water into hydrogels.[23]

TABLE II
Diffusion Characteristics of the Poly(AAm) and Poly(AAm/NVI) Hydrogels at Various pH,
Ionic Strength, and Temperature (D: cm^2 min^{-1})

| Gel No., compositon | Ionic strength | pH 5.0 | | | | | | pH 11.0 | | | | | |
| | | 25 °C | | | 50 °C | | | 25 °C | | | 50 °C | | |
		n	$k \times 10^2$	$D \times 10^2$	n	$k \times 10^2$	$D \times 10^2$	n	$k \times 10^2$	$D \times 10^2$	n	$k \times 10^2$	$D \times 10^2$
1 P(AAm)	0.05	0.58	2.42	3.76	0.43	7.44	5.93	0.56	2.05	2.96	0.46	3.88	3.21
	0.10	0.57	2.02	3.16	0.52	3.19	3.83	0.56	2.15	3.33	0.49	2.68	2.28
	0.20	0.48	4.42	4.10	0.38	9.23	5.56	0.54	2.36	2.46	0.49	4.02	4.70
2 89.74/10.26	0.05	0.62	1.73	2.65	0.52	3.02	3.75	0.59	1.54	2.76	0.52	2.22	2.44
	0.10	0.58	1.70	2.80	0.54	2.57	3.53	0.57	1.68	2.60	0.50	3.25	2.97
	0.20	0.58	1.73	2.88	0.49	3.88	3.61	0.55	1.51	2.02	0.65	0.84	2.99
3 81.25/18.75	0.05	0.66	0.90	2.70	0.58	1.91	3.51	0.59	1.61	2.79	0.53	2.21	2.47
	0.10	0.58	2.28	3.57	0.58	1.98	3.80	0.57	1.79	2.72	0.51	2.52	2.48
	0.20	0.58	1.61	2.84	0.51	3.81	4.50	0.54	1.67	2.14	0.67	0.74	2.99
4 74.28/25.72	0.05	0.66	0.92	2.77	0.63	1.71	4.01	0.63	1.13	2.66	0.54	2.00	3.05
	0.10	0.64	1.11	2.93	0.59	2.15	3.93	0.56	2.13	3.06	0.55	2.01	2.62
	0.20	0.58	1.47	2.59	0.53	2.67	3.38	0.55	1.40	2.00	0.67	0.79	3.13
5 68.42/31.58	0.05	0.68	0.82	2.92	0.61	1.79	3.76	0.60	1.71	3.21	0.56	1.88	2.81
	0.10	0.64	1.23	3.04	0.62	1.89	3.78	0.59	1.69	2.93	0.54	1.97	2.49
	0.20	0.60	1.38	2.66	0.54	2.66	3.66	0.55	1.49	2.10	0.68	0.71	2.94

$$F = M_t/M_s = kt^n. \tag{2}$$

Here F is the fractional uptake, M_t/M_s, where M_t is the amount of diffusant sorbed at time t, M_s is the maximum amount absorbed, k is a constant related to the structure of the network, and n is the diffusional exponent that describes the type of diffusion. For cylindrical shapes, $n = 0.45$–0.50 corresponds to Fickian diffusion, wheras $0.50 < n < 1.0$ indicates the non-Fickian-type diffusion. This equation is applied to the initial stages of swelling and plots of ln$F$ versus ln$t$ yielded straight lines. The values of n and k, as calculated from the slopes and intercepts of the straight lines, are listed in Table II as a function of gel composition, ionic strength, temperature, and pH of the swelling medium.

For hydrogel characterization, the short-time approximation is used for calculation of the diffusion coefficients of the hydrogels. The short-time approximation is valid for the first 60% of the swelling. The diffusion coefficients of the hydrogels are calculated from the equation[24,25]

$$F = 4(Dt/\pi r^2)^{1/2} - \pi(Dt/\pi r^2) - \pi/3(Dt/\pi r^2)^{3/2}, \tag{3}$$

where D is in square centimeters per minute, t is the time at which the swelling is one-half the equilibrium value ($V/V_0 = 1/2$), and r is the radius of the swollen cylindirical hydrogel. A graphical comparison of Eqs.
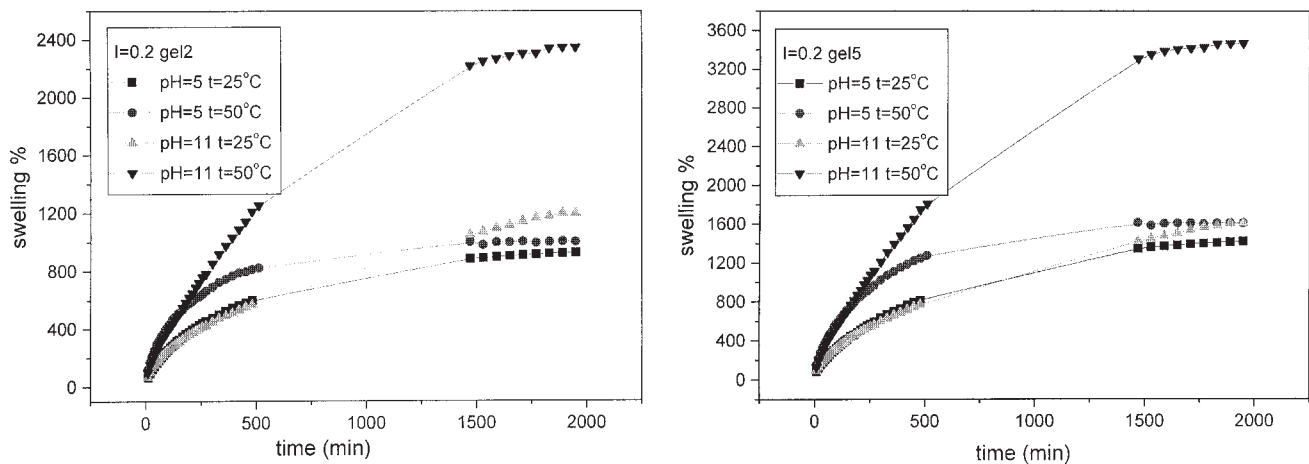

Figure 2   Percentage mass swelling as a function of time for samples 2 and 5 under the separated conditions.

TABLE III
Differences in Equilibrium Swelling Degree for PAAm and Poly(AAm/NVI) Hydrogels
under Different Conditions, $I = 0.20 M$

Gel No.	$\Delta ESD_{50-25\ °C}$		$\Delta ESD_{pH\ 5.0-7.45}$		$\Delta ESD_{11.0-7.45}$		$\Delta ESD_{11.0-5.0}$	
	pH = 11.0	pH = 5.0	25 °C	50°C	25 °C	50 °C	25 °C	50 °C
1	687	30	12	19	648	1336	704	1317
2	1152	75	75	118	317	1467	198	1368
3	1257	80	157	221	455	1696	298	1475
4	1651	159	331	492	486	2139	155	1647
5	1860	190	650	763	836	2619	186	1856

(2) and (3) shows the semiempirical Eq. (2). with n = 0.5 and $k = 4(D/\pi r^2)^{1/2}$. The diffusion coefficients of the hydrogels were calculated from the slopes of the lines of F versus $t^{1/2}$. The results in Table II indicate that the n values decrease with increasing ionic strength and temperature at pH 5.0. As the pH was increased, the swelling process was closer to Fickian kinetics at 25°C. This is because when the pH is decreased the hydrolysis of amide groups is a part of rate limiting. For an ionizable hydrogel, the swelling rate is more complicated, since fixed charge group ionization rates must be considered in addition to solvent diffusion. If the ionization rate is much slower than the diffusion, the ionization process is rate limiting and

the swelling kinetics will be non-Fickian. The hydrogels used in this study have amide groups and can be hydrolyzed. If pH and temperature are increased more amide groups are hydrolyzed to the carboxylate group and ionization becomes partially rate limiting. The exponent n increased in an aqueous solution of pH 11.0 and 0.20 M ionic strength at 50°C because of the increasing of hydrolysis of the amide groups in the hydrogel at the basic medium with increasing ionic strength.

Diffusion coefficients of the hydrogels are listed in Table II. Penetration of the solvent into the hydrogel is easier and the diffusion rate is faster in aqueous solutions of pH 11.0 at 50°C, due to an increased rate of
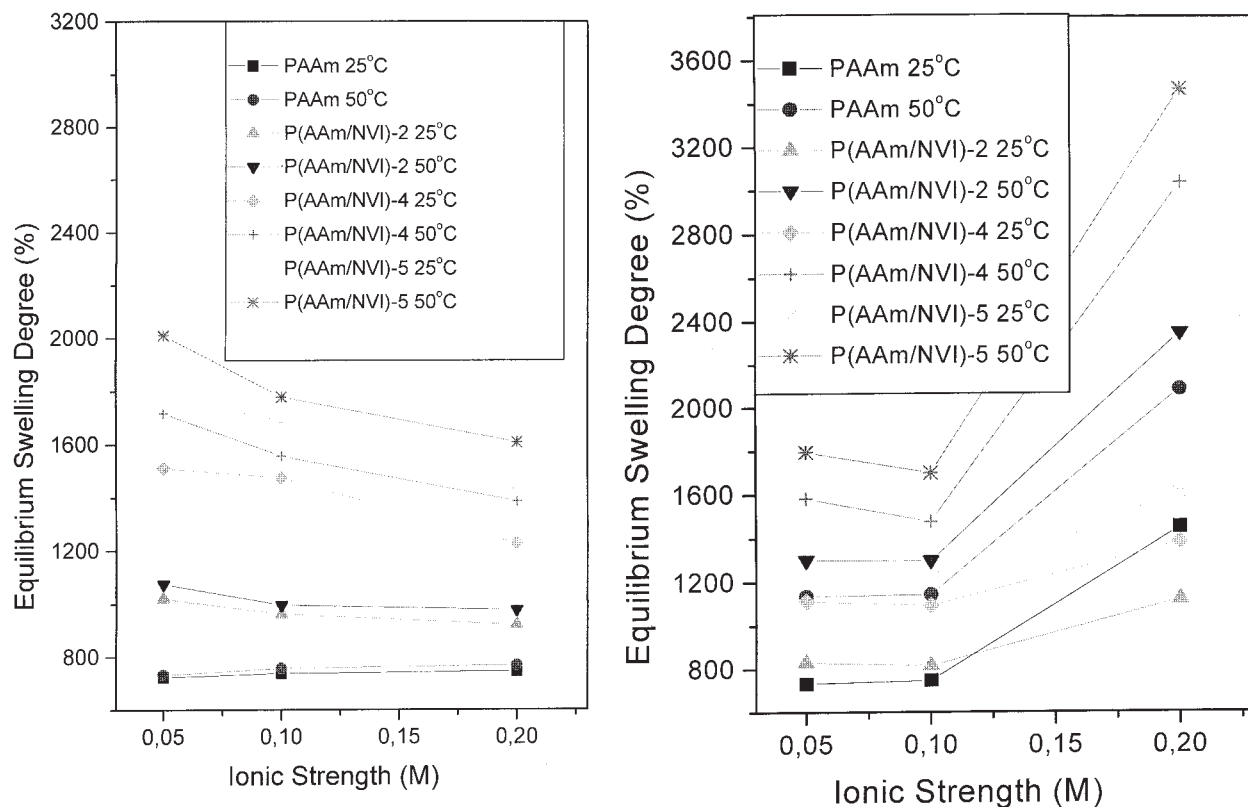

Figure 3 Effect of ionic strength on the equilibrium swelling degree values of PAAm and P(AAm/NVI) hydrogels: (a) pH 5.0, (b) pH 11.0.

hydrolysis of amide groups to carboxylate groups at higher temperatures.

CONCLUSIONS

1. Poly(AAm/NVI) hydrogels were prepared at four different initial molar ratios by redox polymerization. The effect of external stimuli, pH, temperature, and ionic strength on the swelling of the hydrogels was investigated.
2. The effect of temperature on the gel swelling has been shown at 25 and 50°C. The equilibrium swelling degree increased with increasing temperature.
3. The equilibrium swelling degree decreased with increasing ionic strength at pH 5.0. As the pH is increased, equilibrium swelling degree of the gels increased at pH 11.0 and $I = 0.20$ M.
4. Swelling kinetics of the hydrogels was non-Fickian at 25°C. At pH 11.0, $I = 0.20$ M and 50°C, the transport of water into the hydrogels is non-Fickian.

REFERENCES

1. Grignon, J.; Scallan, A. M. J Appl Polym Sci 1980, 25, 2829.
2. Brannon-Peppas, L.; Peppas, N. A. J Cont Rel 1989, 8, 267.
3. Kataoka, K.; Koyo, H.; Tsuruta, T. Macromolecules 1995, 28, 3336.
4. Vazquez, B.; Gurruchaga, M.; Goni, I.; Narvarte, E.; Roman, J. S. Polymer 1995, 17, 3327.
5. Lee, Y. M.; Su, H. K.; Cho, C. S. J Appl Polym Sci 1996, 62, 301.
6. Yaung, J. F.; Kwei, T. K. J Appl Polym Sci 1998, 69, 921.
7. Freitas, R. F. S.; Cussler, E. L. Chem. Eng Sci 1987, 42, 97.
8. Bae, Y. H.; Okano, T.; Kim, S. W. J Polym Sci Polym Phys 1990, 28, 923.
9. Yu, H.; Grainger, D.W. Macromolecules 1994, 27, 4554.
10. Zhang, X. Z.; Zhuo, R. X. Eur Polym J 2000, 36, 643.
11. Ricka, J; Tanaka, T. Macromolecules 1984, 17, 2916.
12. Siegel, R. A.; Firestone, B. A. Macromolecules 1988, 1, 3254.
13. Nishi, S.; Kotaka, T. Polym J 1989, 21, 393.
14. Tanaka, T. In Encyclopedia of Polymer Science and Technology; Mark, H. F.; Kroschwitz, J. J., Eds.; Wiley: New York, 1985; p. 514.
15. Eisenberg, S. R.; Grodzinski, A. J. J Membr Sci 1984, 19, 173.
16. Karadağ, E.; Saraydin, D.; Güven, O. Sep Sci Technol 1996, 61, 2367.
17. Karadağ, E.; Saraydin, D.; Güven, O. Sep Sci Technol 1995, 30, 3747.
18. Saraydin, D.; Karadağ, E.; Güven, O. Sep Sci Technol 1995, 30, 3291.
19. Molina, M. J; Anton, M. R. G.; Pierola, I. F. Int J Polym Mater 2002, 51, 477.
20. Anton, M. R. G.; Molina, M. J.; Morales, E.; Pierola, I. F. US Patent 5 1995, 393, 853.
21. Rivas, B. L.; Maturana, H.; Molina, M. J; Anton, M. R. G.; Pierola, I. F. J Appl Polym Sci 1998, 67, 1109.
22. Molina, M. J; Anton, M. R. G.; Rivas, B. L.; Maturana, H.; Pierola, I. F. J Appl Polym Sci 2001, 79, 1467.
23. Peppas, N. A.; Franson, N. F. J Polym Sci Polym Phys 1983, 21, 983.
24. Saraydin, D.; Karadağ, E.; Güven, O. Polym Bull 1998, 41, 577.
25. Berens, A. R.; Hopfenberg, H. B. Polymer 1978, 19, 489.