Swelling Behavior and Determination of Diffusion Characteristics of Acrylamide–Acrylic Acid Hydrogels

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ABSTRACT: In this study, a random copolymer of acrylamide and acrylic acid [poly(AAm-*co*-AA)] was prepared by a redox copolymerization method of their aqueous solutions. The effects of initial AAm/AA mole ratio, PEG 4000 content, and *N,N′*-methylenebisacrylamide concentration on swelling behavior were investigated in water. Average molecular weights between crosslinks, percentage swelling, swelling equilibrium values, and diffusion/swelling characteristics (i.e., the structure of network constant, the type of diffusion, the initial swelling rate, swelling rate constant) were evaluated for every hydrogel systems. The hydrogels showed mass swelling capabilities in the range 789–1040% (for AAm/AA hydrogels), 769–930% (for AAm/AA hydrogels in the presence of PEG 4000), and 716–1040% (for AAm/AA hydrogels containing different concentrations of the crosslinker). The swelling capabilities of the hydrogels decreased with the increasing AA, PEG 4000, and crosslinker concentrations. The diffusion of water into AAm/AA hydrogels was found to be a non-Fickian type. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1289–1293, 2004

Key words: hydrogels; acrylic acid; crosslinking; diffusion; swelling

INTRODUCTION

Hydrogels, which are crosslinked hydrophilic polymers, have been used in bioengineering, biotechnology, medicine, pharmacy, agriculture, food industry, and other fields. The hydrophilicity of hydrogels is attributed to the presence of hydrophilic functional groups such as alcohols, carboxylic acid, and amides. Acrylamide (AAm)-based hydrogels can be polymerized easily and they are biocompatible. Poly(acrylamide) and its derivates are the most preferred members of this family in application fields from agriculture to controlled drug delivery systems. In recent studies, the copolymers of AAm with the diprotic acids were tested as adsorbent in the adsorption of some cationic dyes,[1–3] uranyl ions,[4] and the adsorption of bovine serum albumin.[5]

Polyelectrolytes are polymers that contain relatively ionizable groups such as polymeric acids and polymeric bases. Examples of common polyelectrolytes include poly(acrylic acid),[6,7] poly(methacrylic acid),[8,9] poly(acrylamide-*co*-itaconic acid),[10] poly(acrylamide-*co*-maleic acid),[11] and poly(vinylamine).[12] Polyelectrolyte-type hydrogels undergo controllable volume changes in response to small environmental conditions such as pH, temperature, and ionic strength.[13–15] pH- and temperature-sensitive hydrogels have recently been the focus of increasing interest in new applications including controlled drug delivery[16] and immobilized enzyme systems.[17] In our previous studies, poly(*N*-isopropylacrylamide-*co*-*N*-hydroxymethyl acrylamide),[18] poly(*N*-isopropylacrylamide-*co*-acrylamide),[19] and poly(*N*-isopropylacrylamide-*co*-acrylamide-*co*-hydroxyethyl methacrylate)[20] copolymer gels were prepared as alternative thermoresponsive gels. In our other previous study, copolymeric gels of dimethylaminoethylmethacrylate and acrylamide having pH-sensitive character were prepared and used the adsorption of uranyl acetate.[21]

In the present work, poly(AAm-*co*-AA) gels were obtained by changing the initial mole ratio, PEG 4000, and *N,N′*-methylenebisacrylamide (MBAAm) concentrations. The hydrogels prepared were characterized with respect to their swelling properties, network structures, and diffusion of water. The gels will later be characterized in different pH solutions and some applications will be evaluated such as purification of waste water, immobilized enzyme systems, and separation processes.

EXPERIMENTAL

The two monomers used in this study, acrylamide (AAm) and acrylic acid (AA), were obtained from BDH (Poole, UK). Acrylic acid was distilled under vacuum.

Poly(ethylene glycol) (PEG 4000; BDH, Poole, UK) was used as a diluent. The other chemicals used were *N,N′*-methylenebisacrylamide (MBAAm) from BDH as a crosslinking agent, potassium persulfate (KPS) as an initiator, and *N,N,N′,N′*-tetramethylenediamine

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(TEMED) from Merck (Darmstadt, Germany) as an accelerator. Distilled water was used in all copolymerizations and swelling studies.

Acrylamide and acrylic acid random copolymers were prepared by radical polymerization. AAm was dissolved in 1.0 mL of distilled water; AA was added to this solution and PEG 4000 should be dissolved if the hydrogel would contain PEG. After the addition of the two monomers, water and PEG 4000, 0.11 mL of the crosslinking agent solution MBAAm (0.05 g/mL water), 0.05 mL of the initiator solution KPS (0.05 g/mL water), and 0.05 mL of the accelerator solution TEMED (0.1 mL/1.5 mL water) were included in the polymerization medium. In general, a type of persulfate initiators, chemicals that contain diamine (ethylene diamine, tetramethylene diamine, etc.) are used to initiate the polymerization reaction at low temperature. KPS and TEMED formed a redox pair for the purpose of radical polymerization. Polymerization was carried out in poly(vinyl chloride) straws of 3-mm diameter. The straws were maintained at 4°C until polymerization was completed. After the reaction the hydrogels were cut into cylinders about 5 mm long, washed with distilled water for removal of unreacted chemicals, and vacuum dried until they reached a constant weight. The conversion of monomers was confirmed by gravimetric determination. In most cases, nearly quantitative conversion values and complete incorporation of AA into the gel matrix were achieved.

Measurement of swelling

Dried hydrogels were allowed to swell in distilled water at room temperature. Swollen gels removed from the water at regular intervals were dried with filter paper weighed by an electronic balance (280 + 1 $\times 10^{-3}$ g; EB, Shimadzu, Kyoto, Japan) and placed in the same bath. The measurements were continued until a constant weight was achieved for each sample. The densities of the hydrogels were determined by a picnometer at room temperature. The percentage swelling (%S) of each hydrogel was calculated from the following expression:

$$\%S = \frac{m_t - m_0}{m_0} \times 100 \quad (1)$$

where m_t is the weight of swollen gel at time t and m_0 is the weight of dry gel at time 0.

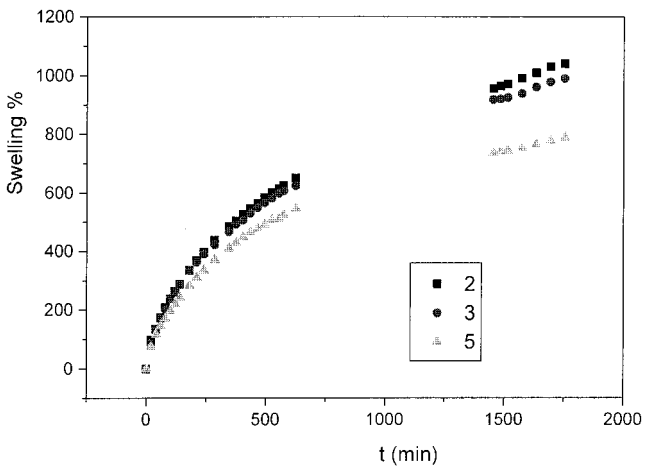

Figure 1 Swelling percentage values of the AAm/AA hydrogels in water produced by different AA concentrations. AAm concentration: 1.0 g/mL, MBAAm concentration: 7.7%.

TABLE I
Production Conditions of AAm/AA Hydrogels and Values of Equilibrium Mass Swelling of the Same Hydrogels in Water[a]

Sample	AAm (g)	AA (mL)	MBAAm solution (%)	PEG 4000 (g)	%S
2	1.0	0.1	7.7	—	1040
3	1.0	0.2	7.7	—	990
5	1.0	0.4	7.7	—	789
6	1.0	0.1	7.7	0.11	930
1E	1.0	0.2	7.7	0.11	808
3E	1.0	0.4	7.7	0.11	769
2	1.0	0.1	7.7	—	1040
6	1.0	0.1	7.7	0.11	930
7	1.0	0.1	7.7	0.22	760
2	1.0	0.1	7.7	—	1040
8	1.0	0.1	8.3	—	890
9	1.0	0.1	9.0	—	820
10	1.0	0.1	9.6	—	720
11	1.0	0.1	10.2	—	716

[a] Included in polymerization media of all gels listed was 1.0 mL water.

RESULTS AND DISCUSSION

Swelling of the gel structure is the most important parameter for swelling measurements.[22] The water intake of initially dry gels was followed for a long period of time. The effect of AAm/AA mole ratio on the swelling curve of the produced hydrogels was studied by changing this ratio 100/0 and 81.1/18.9. AAm concentration in the polymerization was fixed at 1.0 g/mL. Representative swelling curves are shown in Figure 1 for samples 2, 3, and 5. As seen here, swelling capabilities of the gels increase with time, but after a certain period, they show constant swelling. This constant value may be called equilibrium mass swelling. Table I shows that lower equilibrium mass swelling values were obtained by increasing the AA

content of the copolymer structure. The values of equilibrium mass swelling of AAm/AA gels range from 1040 to 789%. In the AA-rich gels, the percentage swelling was possibly controlled by the AA portion of the copolymer. The reason for this is probably attributable to the intermolecular hydrogen bonding between carboxylic acid and amide groups and intramolecular hydrogen bonding between amide groups, and thus the numbers of hydrophilic groups of the gels decrease. The presence of hydrogen bonding in the copolymer matrix caused the network to be less swollen.

Swelling behavior of the gels prepared from AAm/AA/PEG 4000 mixtures was also followed gravimetrically; the swelling curves are shown in Figure 2. When the swelling behaviors given in Figure 2 are compared with the results in Figure 1, it may be observed that the equilibrium mass swelling decreasing effect of PEG 4000 was valid in all compositions. Equilibrium mass swelling values are indicated as 1040, 990, and 789% for AAm/AA gels in the absence of PEG 4000. However, in the case of PEG 4000 containing AAm/AA gels, these values are decreased 930, 808, and 769%, respectively (Table I). The effect of PEG 4000 on the swelling behavior at constant total monomer concentration and monomer composition was studied by varying PEG 4000 concentration between 0 and 0.22 g/mL. The total monomer concentration and AAm/AA mole ratio were fixed at 1.11 g/mL and 94.5/5.5, respectively. The decrease in the equilibrium mass swelling of the gels may be explained by the formation of additional crosslinks between AA and PEG 4000.[23]

To observe the effect of crosslinker concentration on the swelling behavior, crosslinker concentration was varied between 7.7 and 9.6%. The total monomer concentration and AAm/AA mole ratio were fixed at 1.11 g/mL and 94.5/5.5, respectively. The effect of crosslinker concentration on the swelling behavior of hydrogels is given in Table I. It is known that the swelling capabilities decrease because the molecules of the crosslinker are placed between the chains of monomers. Then the hydrophilic group number and the swelling percentage decrease. The more crosslinker molecules there are in the hydrogel, the lower the swelling ratio is in the hydrogel system.

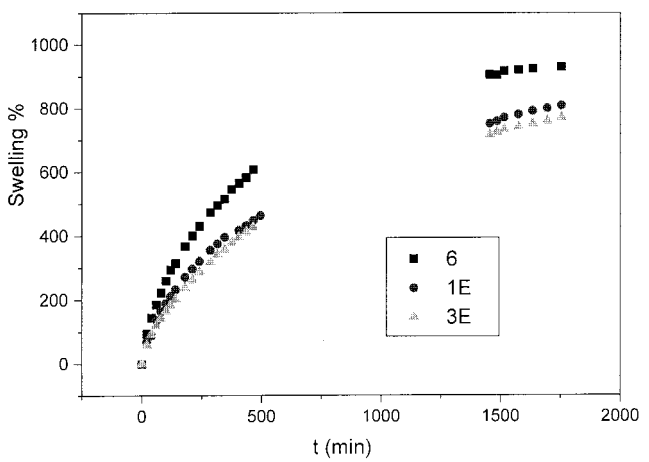

Figure 2 Swelling percentage values of the AAm/AA/PEG 4000 hydrogels in water by different AA concentrations. PEG 4000 concentration: 0.11 g/mL, MBAAm concentration: 7.7%.

TABLE II
Values of M_c and the Crosslink Densities of AAm/AA Hydrogels in Water

Sample	$M_c \times 10^{-4}$	$\rho \times 10^3$ (mol/cm^3)
2	10.7	0.67
3	8.8	0.81
5	4.1	1.75
6	8.1	5.25
1E	4.9	7.21
3E	4.6	8.64
7	3.5	20.6
2	10.7	0.67
8	6.5	1.10
9	6.0	1.19
10	2.8	2.56
11	2.4	2.99

The average molecular weight between consecutive crosslinks (M_c) is another structural parameter characterizing the three-dimensional network structure. It is directly related to the crosslink density. M_c can be determined by swelling experiments according to the Flory–Rehner equation[24]:

$$M_c = -\frac{V_1 d_p(\phi_p^{1/3} - \phi_p/2)}{\ln(1-\phi_p) + \phi_p + \chi\phi_p^2} \quad (2)$$

where V_1 is the molar volume of solvent, d_p is the density of polymer, ϕ is the volume fraction of polymer in the swollen gel, and χ is the Flory–Huggins interaction parameter between polymer and solvent molecules.

The M_c values determined from eq. (2) for every gel system are given in Table II. The results obtained show that the average molecular weight between the crosslinks is affected by the AA and crosslinker concentration and introduction PEG 4000. It is possible to control the average dimensions of pores by changing these parameters.

The crosslink density ρ is defined as the mol fraction of crosslinked units[25]:

$$\rho = M_0/M_c \quad (3)$$

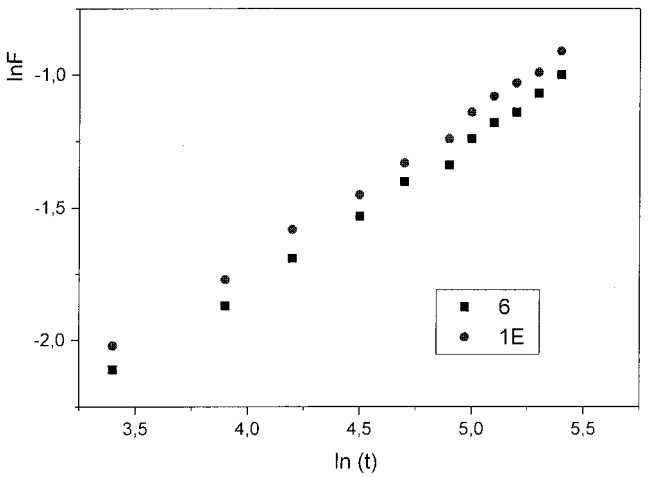

Figure 3 Curves of swelling kinetics of AAm/AA hydrogels.

where M_0 is the molecular weight of the polymer repeating unit. The calculated crosslink density values are given in Table II for the hydrogel systems. As seen here, the crosslink density increased with increasing AA and crosslinker concentration and the values of crosslink density of AAm/AA/PEG gels are higher than the values of AAm/AA gels.

The data of the gels were fit to the following equation[26]:

$$F = M_t/M_s = kt^n \tag{4}$$

where M_t and M_s denote the amount of solvent diffused into the gel at time t and infinite time, respectively; k is a constant related to the structure of the network; and the exponent n is a number to determine the type of diffusion. For cylindrically shaped samples, for Fickian kinetics in which the rate of penetrant diffusion is rate limiting, n equals 0.5. If during the swelling, non-Fickian diffusion occurs, n will have a value between 0.5 and 1.0.

This equation is applied to the initial stages of swelling and plots of ln F versus ln t are shown in Figure 3. The exponents in eq. (4) were calculated from the slope of the lines. The values of n are listed in Table III as a function of the AA, PEG 4000, and crosslinker concentrations. It can be seen from this table that n takes values between 0.50 and 0.54, and values were found to be over 0.50. Hence the diffusion of water into the gels was taken to be of non-Fickian character.[27] The values given in this table show that the higher AA and crosslinker concentration and introduction of PEG (i.e., the higher the crosslink density), the more non-Fickian becomes the transport of water into the hydrogels. This is generally explained as a consequence of the slow relaxation rate of the polymer.

TABLE III
Diffusion Characteristics of AAm/AA Hydrogels in Water

Sample	$k \times 10^2$	n
2	1.72	0.52
3	1.91	0.51
5	2.22	0.51
6	2.18	0.51
1E	2.31	0.52
3E	1.96	0.54
7	3.05	0.50
2	1.72	0.52
8	2.14	0.51
9	2.50	0.50
10	2.95	0.50
11	2.80	0.52

For extensive swelling of poly(AAm-*co*-AA) hydrogels, it may be expressed by the following equation[28]:

$$t/S = A + Bt \tag{5}$$

where $B = 1/S_{eq}$ is the reverse of the maximum or equilibrium swelling, $A = 1/(k_s S_{eq}^2)$ is the reciprocal of the initial swelling rate of the gel, and k_s is the swelling rate constant. This relation represents second-order kinetics.[24] Figure 4 shows the linear regression of the swelling curves obtained by means of eq. (5) for poly(AAm-*co*-AA) hydrogels. The initial rate of swelling (r_i), swelling rate constant, and theoretical equilibrium swelling (S_{eq}) of the hydrogels were calculated from the slope and intersection of the lines, presented in Table IV.

Table IV shows that the values of the theoretical equilibrium swelling of the hydrogels are in good agreement with the results of equilibrium swelling of

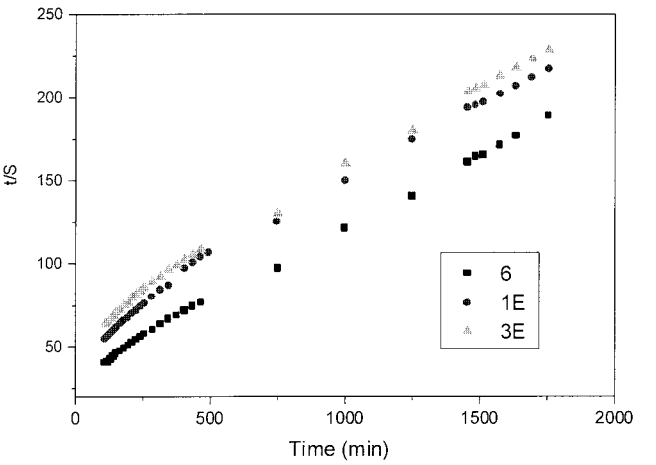

Figure 4 Plot of t/S versus t curves for AAm/AA hydrogels in water.

TABLE IV
Swelling characteristics of AAm/AA Hydrogels

Sample	$r_i \times 10^{a}$	$k_s \times 10^{4\,b}$	$S_{eq}{}^{c}$
2	0.75	1.35	13.3
3	0.80	1.53	12.5
5	1.03	2.31	9.7
6	0.88	2.30	11.4
1E	0.97	1.86	10.2
3E	0.98	1.64	10.2
2	0.75	1.35	13.3
6	0.88	2.30	11.4
7	1.10	2.90	9.3
2	0.75	1.35	13.3
8	0.91	2.07	10.9
9	0.89	2.14	11.2
10	1.20	3.43	8.5
11	1.10	2.91	9.2

[a] (g water/g gel)/min.
[b] (g gel/g water)/min.
[c] (g water/g gel).

poly(AAm-*co*-AA) hydrogels (Fig. 2). It is well known that the swelling phenomena are directly related to the structure of crosslinked polymer and/or density of the hydrogel.

CONCLUSIONS

A new series of AAm/AA hydrogels was produced in aqueous solution and characterized in terms of equilibrium mass swelling, average molecular weights, crosslink density, and diffusion/swelling characteristics. It is seen that the swelling of the hydrogels decreased with increasing AA, PEG, and crosslinker concentration. The diffusion type of hydrogel systems was of a non-Fickian diffusion character.

As a result, poly(AAm-*co*-AA) hydrogels with differing crosslink densities can be used as water retainers for carrying some substances in aquatic fields in pharmaceutical, agriculture, environmental, and biomedical applications, or in the application of immobilized biologically active molecules.

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