Preparation and Determination of Swelling Behavior of Poly(acrylamide-*co*-acrylic acid) Hydrogels in Water

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ABSTRACT: Hydrogels with varying crosslinking densities were prepared from the acrylamide/acrylic acid and acrylamide/acrylic/poly(ethylene glycol) systems by the redox copolymerization method. Average molecular weights between crosslinks, percent swelling, swelling equilibrium values, and diffusion/swelling characteristics (i.e., the structure of network constant, the type of diffusion the initial swelling rate, diffusion coefficients, and swelling rate constant) were evaluated for both hydrogel systems. The pre-pared hydrogels have shown mass swelling capabilities in the range of 663–755% (for AAm/AA hydrogels) and 635–800% (for AAm/AA/PEG 4000 hydrogels). Water diffusion into hydrogels was found to be non-Fickian type diffusion. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1526–1531, 2004

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

INTRODUCTION

Hydrogels are crosslinked hydrophilic polymers that are swollen in water and buffer solutions. The hydrophilicity of hydrogels is due to the presence of hydrophilic functional groups such as carboxylic acid, amines, amides, alcohols, etc. Acrylamide (AAm)-based hydrogels can be polymerized easily and they are biocompatible. Hydrogels derived from poly-(acrylamide) have many useful chemical and physical properties and have been investigated for applications as smart polymers. These applications include immobilization of biocatalysts,[1] drug delivery systems,[2–4] bioseparators,[5] and protein adsorption.[6,7]

Some authors have reported that some copolymers of the acrylamide have been used for the adsorption of the some heavy metal and uranyl ions.[8–11] On the other hand, poly(hydroxamic acid) hydrogels prepared from poly(acrylamide) have been used in the binding uranyl ions.[12]

Polyelectrolyte hydrogels are formed from polymer chains having relatively ionizable groups. These hydrogels undergo controllable volume changes in response to small environmental conditions. In recent years, many work has been carried out on surounding conditions, especially temperature and pH, because these factors have been the most commonly used solution variables in typical physiological, biological, and chemical systems.[13] Because of the presence of carboxylic acid groups, the swelling behavior of the poly(acrylic acid) (PAA) hydrogel is highly dependent on the pH of the surrounding medium.[14–18]

In the present work, poly(AAm-*co*-AA) gels were obtained by changing the total monomer concentrations. The aim of this study was to investigate the network structure, swelling behavior, and diffusion of water for hydrogels AAm/AA and AAm/AA/PEG 4000 prepared by the redox copolymerization method from their aqueous solutions, because for hydrogels swelling characteristics are very important. The gels will later be characterized in different pH solutions and will be evaluated for some applications, such as purification of waste water, immobilized enzyme systems, and separation processes.

EXPERIMENTAL

Acrylamide (AAm), acrylic acid (AA), and poly(ethylene glycol) (PEG 4000) were obtained from BDH (Poole, UK). AAm was recrystallized in methanol and AA was distilled under a vacuum before use.

The other chemicals which were used are *N,N'*-methylenebisacrylamide (MBAAm) from BDH as a crosslinking agent, potassium persulphate (KPS) as an initiator, and *N,N,N',N'*- tetramethylenediamine (TE-MED) from Merck as an accelerator. Distilled water was used in all the copolymerizations and swelling studies.

AAm/AA and AAm/AA/PEG 4000 random copolymers were prepared described as previously.[19] Prepared hydrogels were cut into pieces ~ 5 mm long,

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washed with distilled water for removal of unreacted chemicals, and dried to constant weight. The conversion of monomers was checked by gravimetric determination. In most cases, nearly quantitative conversion values and complete incorporation of AA into the gel matrix were achieved. The production conditions of the hydrogels are given in Table I.

Dried hydrogel samples were left to swell in distilled water at a constant temperature of 25°C. Swollen gels removed from the water of regular intervals were dried with filter paper weighed with an electronic balance (Shimadzu, Japan, EB. 280 + 1×10^{-3} g) 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:

$$S = [(m_t - m_0)/m_0] \times 100 \qquad (1)$$

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

RESULTS AND DISCUSSION

The swelling behavior of the hydrogels depends on the nature of the polymers and the environmental conditions. The nature of the polymer involves the nature of the charge, the ionic content, and the crosslinking agent content. The environmental conditions include pH and temperature of solution. Swelling of the crosslinked polymer structure in a chosen and suitable solvent is the most important parameter (especially one of the most important parameters is mass swelling) for swelling measurements.[20,21] The water intake of initially dry gels was followed for a long period of time in water. The measurements were continued until a constant weight was reached for each hydrogel sample. In the swelling experiments, the total monomer concentration was varied between 0.55 and 1.66 g/mL by fixing the initial AAm/AA

Figure 1 Swelling % values of the AAm/AA gels in water produced by different total monomer concentrations; AAm/AA mol ratio : 94.5/5.5.

mole ratio at 94.5/5.5. Swelling curves of the hydrogels are plotted and representative swelling curves are shown in Figure 1. All the hydrogels showed a similar swelling behavior. As can be seen from this figure, swelling capabilities of the hydrogels are increased by time, but at a certain period of time, they showed constant weight. This constant weight is the equilibrium swelling for a polymer in a given hydrogel sample swollen to equilibrium in water.

Another observation is the swelling of the hydrogels depends on the total monomer concentration. The hydrogels produced with lower total monomer concentration exhibited higher swelling capability, and the equilibrium mass swelling of the gels decreased with increasing total monomer concentraion. For the constant gel volume, the decrease in the total monomer concentration causes an increase in the degree of dilution of the matrix. This case involves an increase in the equilibrium water content of the gel. Therefore, the observed increase in the swelling of the hydrogel may be explained by the increase formed in the microporosity of the gel with the decreasing monomer concentration.

To increase the swelling of the produced gels by creating additional microporosity within the gel matrix, we tried PEG 4000 in our previous studies.[22,23] PEG 4000 was examined for this purpose since it was soluble in the initial copolymerization medium and its molecular weight was sufficiently low to remove it from the gel matrix after copolymerization. Swelling behavior of the gels prepared from AAm/AA/PEG 4000 mixtures were also followed gravimetrically. The variation of the swelling of the produced hydrogels with the time is given in Figure 2. When the swelling behaviors given in Figure 2 were compared with the results in Figure 1, the equilibrium mass swelling decreasing effect of PEG

TABLE I
Production Conditions of Hydrogels[a]

No	AAm (g)	AA (mL)	MBAAm (%)	PEG 4000 (g)
7E	0.5	0.05	7.7	—
2	1.0	0.10	7.7	—
6E	1.5	0.15	7.7	—
4E	0.5	0.05	7.7	0.11
6	1.0	0.10	7.7	0.11
5E	1.5	0.15	7.7	0.11

[a] .05 mL of initiator solution, KPS (0.05 g/mL water), 0.05 mL accelerator solution, TEMED (0.05 g/mL water), and 0.4 mL water were included polymerization mediums of all the gels listed.
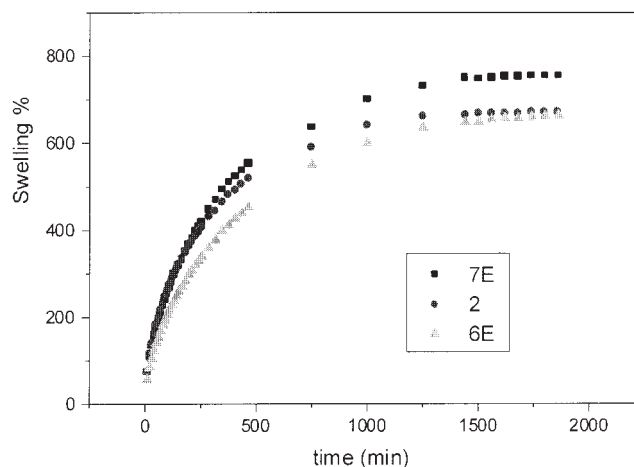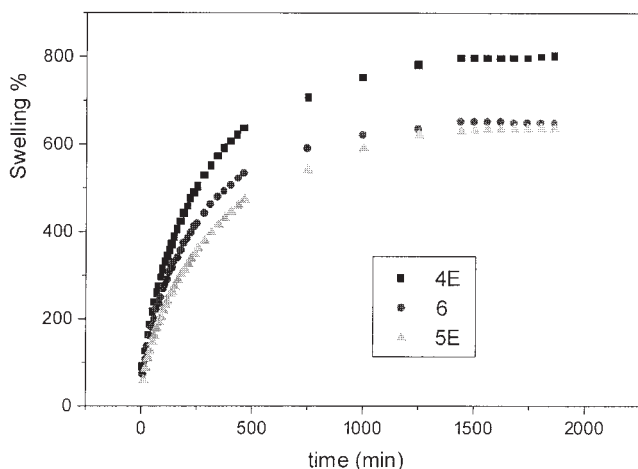
Figure 2 Swelling % values of the AAm/AA/PEG 4000 gels in water produced by different total monomer concentrations; AAm/AA mol ratio : 94.5/5.5.

4000 was valid in higher total monomer concentrations. Equilibrium mass swelling values are 755, 671, and 663% for AAm/AA gels in the absence of PEG 4000. In the case of PEG 4000 containing the AAm/AA gel, these values are determined to be 800, 648, and 635%, respectively (Table II). The gels produced by using PEG 4000 exhibited lower swelling relative to those produced without using PEG 4000. This effect was clear for the gels produced with higher total monomer concentration.

The decrease in the equilibrium mass swelling of the gels may be explained by the formation of additional crosslinks between AA and PEG.[24]

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:[25]

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

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 III. The results obtained show that the average molecular weight between the crosslinks is affected by the total monomer concentration and introduction of PEG 4000. It is possible to control the average dimensions of pores by changing these parameters.

The crosslink density, ρ, is defined as the mole fraction of crosslinked units:[26]

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

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

The swelling curves of AAm/AA and AAm/AA/PEG 4000 hydrogels in water were used for the calculation of a certain diffusion characteristics. The following equation was used to determine the nature of diffusion of water into hydrogels:[27]

TABLE III
Values of M_c for AAm/AA and AAm/AA/PEG 4000 Hydrogels

Sample no.	M_c
AAm/AA	
7E	24,500
2	17,000
6E	16,000
AAm/AA/PEG 4000	
4E	27,000
6	15,500
5E	14,500

TABLE II
Equilibrium Mass Swelling of AAm/AA and AAm/AA/ PEG 4000 Hydrogels in Water

Sample no.	% Swelling
AAm/AA	
7E	755
2	671
6E	663
AAm/AA/PEG 4000	
4E	800
6	648
5E	635

TABLE IV
The Crosslink Densities of AAm/AA and AAm/AA/PEG 4000 Hydrogels

Sample no.	ρ (cm^3/mol)
AAm/AA	
7E	2.94×10^{-3}
2	4.21×10^{-3}
6E	4.47×10^{-3}
AAm/AA/PEG 4000	
4E	2.66×10^{-3}
6	2.74×10^{-2}
5E	2.77×10^{-2}
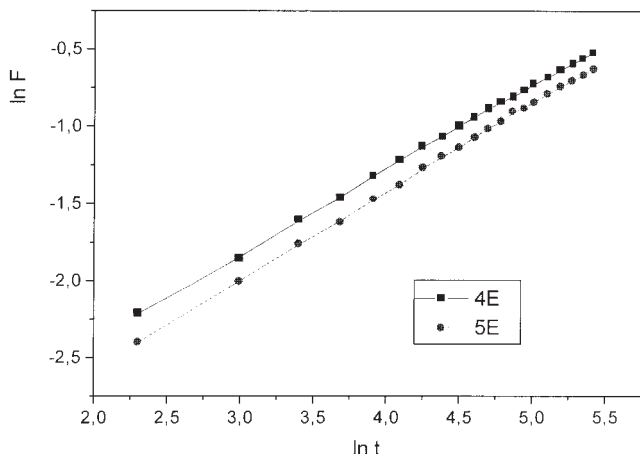
Figure 3 The curves of kinetics of AAm/AA/PEG 4000 hydrogels.

Figure 4 F versus $t^{1/2}$ curves for AAm/AA and AAm/AA/PEG 4000 hydrogels.

$$F = M_t/M_s = kt^n \qquad (4)$$

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 cylindrical shapes, if n is in the range of 0.45–0.50, diffusion is Fickian; the range $0.50 < n < 1.0$ indicates that diffusion is non-Fickian. Representative curves of swelling kinetics of hydrogels are given in Figure 3.

This equation is applied to the initial stages of swelling and and plots of ln$F$ versus ln$t$ yielded straight lines from the slope and intercept of the lines listed in Table V. It can be seen from this table that n takes values between 0.50 and 0.56, and are found to be over 0.50. Hence the diffusion of water into the gels was taken to be non-Fickian.[28] The values given in this table show that with the introduction of PEG to the copolymer matrix, the transport of water into the hydrogels is more non-Fickian. This is generally explained as a consequence of a slow relaxation rate of the polymer matrix or that relaxation and diffusion have the same properties, simultaneously, on the

TABLE V
Diffusion Characteristics of AAm/AA and AAm/AA/PEG 4000 Hydrogels

Sample no.	n	$k \times 10^2$
AAm/AA		
7E	0.54	2.8
2	0.52	2.5
6E	0.56	2.3
AAm/AA/PEG 4000		
4E	0.55	3.1
6	0.55	3.2
5E	0.56	2.4

swelling of these hydrogels.[29] For the characterization of hydrogels, the diffusion coefficient (D) can be calculated by various methods. The short-time approximation method is used for the calculation of the diffusion coefficients of the hydrogels. The short-time approximation method is valid for the first 60% of swelling of crosslinked polymers in a chosen solvent. The diffusion coefficients of the cylindirical hydrogel are determined by the following equation:

$$F = M_t/M_s = 4(Dt/\pi r^2)^{1/2} - \pi(Dt/\pi r^2)$$
$$- \pi/3(Dt/\pi r^2)^{3/2} + \ldots \ldots \ldots \quad (5)$$

where D is the diffusion coefficient in cm^2 min^{-1}, t is the time (min) at which the swelling is one-half the equilibrium value ($V/V_0 = 1/2$), and r is the radius (cm) of the swollen cylindirical sample. A graphical comparison of eqs. (4) and (5) shows the semiempirical eq. (4) and $k = 4(D/\pi r^2)^{1/2}$, $n = 1/2$, and $D = 0.049/(t/4r^2)^{1/2}$. For the AAm/AA hydrogel, F versus $t^{1/2}$ curves are given in Figure 4. The diffusion coefficients of the hydrogels were calculated from the slopes of these lines and listed in Table VI for both the hydrogel systems. It can be seen from the table that the values of the diffusion coefficients of AAm/AA/PEG 4000 hydrogels are lower than the values observed for AAm/AA hydrogels. Penetration of the solvent into the AAm/AA hydrogels is easier and the diffusion rate of these hydrogels is fast in water.

For extensive swelling of poly(AAm-co-AA) hydrogels, the following equation can be written:[30]

$$t/S = A + Bt \qquad (6)$$

where $B = 1/S_{eq}$ is the reverse of the maximum or equilibrium swelling, $A = 1/(k_s \times S_{eq}^2)$ is the recipro-

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TABLE VI
The Diffusion Coefficients of AAm/AA and AAm/AA/ PEG 4000 Hydrogels

Sample no.	$D \times 10^5$ (cm^{2}min^{-1})
AAm/AA	
7E	1.61
3	1.45
6E	1.16
AAm/AA/PEG 4000	
4E	1.70
7	1.42
5E	1.01

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TABLE VII
The Swelling Characteristics of AAm/AA and AAm/AA/ PEG 4000 Hydrogels

Sample no.	$r_i{}^a$	$k_s \times 10^{4b}$	$S_{eq}{}^c$
AAm/AA			
7E	0.114	4.25	8.76
2	0.132	6.23	7.56
6E	0.128	4.05	7.40
AAm/AA/PEG 4000			
4E	0.114	6.50	8.79
6	0.141	9.49	7.07
5E	0.140	6.24	7.16

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

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cal of the initial swelling rate of the gel, and k_s is the swelling rate constant. This relation represents second order kinetics.[30] Figure 5 shows the linear regression of the swelling curves obtained by means of eq. (6) 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 are calculated from the slope and intersection of the lines and are presented in Table VII.

Table VII shows that the values of the theoretical equilibrium swelling of the hydrogels are in good agreement with the results of equilibrium swelling of poly(AAm-*co*-AA) hydrogels (Figs. 1 and 2). It is well known that the swelling phenomena are directly related to the structure of the crosslinked polymer and/or density of the hydrogel.

CONCLUSION

In this study, the swelling behavior of two groups (AAm/AA and AAm/AA/PEG 4000) of hydrogels has been investigated. The equilibrium swelling studies were used to determine important parameters of the crosslinked structure of the hydrogels, including
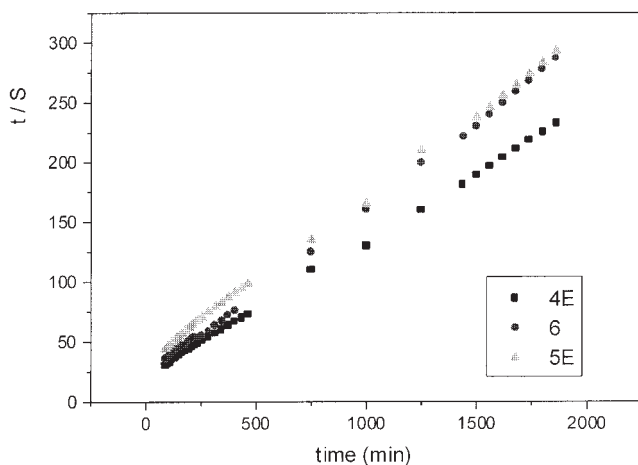
the average molar mass between two consecutive crosslinks. It has been detected that, when two hydrogel systems are compared, The AAm/AA/PEG 4000 hydrogel system with higher crosslink density has lower equilibrium swelling, theoretical equilibrium swelling, and higher initial rate of swelling at higher total monomer concentrations. The type of diffusion of both hydrogel systems was non-Fickian.

As a result, produced hydrogels with differing crosslink densities can be used as a water retainer for carrying some substances in aquatic fields in agriculture, environmental, and biomedical applications or in the application of immobilized biologically active molecules.

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Figure 5 t/S versus t curves for AAm/AA/PEG 4000 hydrogels in water.

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