

# Synthesis and Properties of Radiation-Induced Acrylamide–Acrylic Acid Hydrogels

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**ABSTRACT:** Acrylamide (AAM)/acrylic acid (AAc) hydrogels in the cylindrical form were prepared by  $\gamma$ -irradiating binary systems of AAM/AAc with 2.6–20.0 kGy  $\gamma$ -rays. The effect of the dose and relative amounts of AAc and pH on the swelling properties, diffusion behavior of water, diffusion coefficients, and network properties of hydrogel systems was investigated. The swelling capacities of AAM/AAc hydrogels were in the range of 1000–3000%,

while poly(acrylamide) (PAAM) hydrogels swelled in the range of 450–700%. Water diffusion into hydrogels was found to be non-Fickian-type diffusion. Diffusion coefficients of AAM/AAc hydrogels were found between  $0.79 \times 10^{-5}$  and  $2.78 \times 10^{-5} \text{ cm}^2 \text{ min}^{-1}$ . © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3570–3580, 2002

**Key words:** diffusion, swelling, hydrogels

## INTRODUCTION

Crosslinked hydrophilic polymers capable of imbibing large volumes of water (i.e., >20%) are termed hydrogels. Interest in the preparation of hydrogels with various properties has increased considerably in recent years, due to their versatile applications in biomedicine and biotechnology and in a vast field where controlled release of chemicals is required. The first step in the preparation of hydrogels is the selection of a highly hydrophilic or even water-soluble polymer.<sup>1</sup>

Recent developments in this field call for a better understanding of the molecular structure of three-dimensional networks and our ability to predict such structures using kinetic models. Indeed, no significant work has been performed on kinetic modeling of multicomponent, multifunctional copolymerization/crosslinking reactions for the production of hydrogels. PAAM hydrogels and their derivatives have been used extensively. Polyacrylamide (PAAM) and copolymers of PAAM have the capability to absorb water, have biocompatibility with the physiology of body fluids, and are capable of protein adsorption.<sup>2–5</sup>

In this study, we report on increasing of the capability of water absorption of PAAM hydrogels with the addition of acrylic acid (AAc)-containing hydrophilic groups. Acrylamide (AAM) and AAM-containing various quantities of AAc were irradiated under  $\gamma$ -rays at various doses. Spectroscopic and thermal characterizations of AAM and AAM/AAc hydrogels were made, and then the swelling properties and dif-

fusional parameters and some parameters about the network were found at the end of the swelling studies. Janus Green B basic dye was absorbed by the AAM/AAc hydrogels used.<sup>6</sup>

## EXPERIMENTAL

### Materials

The two monomers used in this study, namely, AAM and AAc were obtained from BDH. The  $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$  used to prepare a phosphate buffer solution were obtained from BDH.

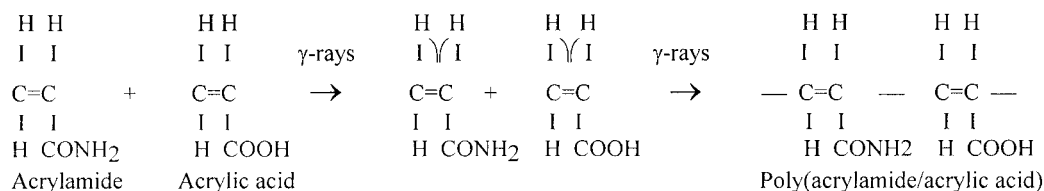
### Preparation of hydrogels

Suitable quantities of AAM and AAc and irradiation doses for AAM/AAc hydrogels were selected. The solutions of monomers of AAM and AAc were prepared in three different compositions (AAM/AAc mol ratios of 30/70, 20/80, and 15/85). These solutions were placed in poly(vinyl chloride) straws of 3-mm diameter and irradiated. Doses of 2.6, 3.0, 4.0, 8.0, 12.0, 16.0, and 20.0 kGy in air at ambient temperature in a Gamma cell 220 type  $\gamma$  irradiator were applied at a fixed rate of  $0.16 \text{ kGyh}^{-1}$ . The dose rate was determined by the conventional Fricke dosimeter. Hydrogels obtained in long cylindrical shapes were cut, washed with distilled water for removal of unreacted monomers, and dried in air and in a vacuum and stored for later evaluation. The percent conversion was determined gravimetrically.

### Composition of hydrogels

Irradiated mixtures were dried in a vacuum oven at 305 K to a constant weight. Uncrosslinked polymer

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**Figure 1** Possible copolymerization reaction of AAm with AAc by irradiation.

and the remaining monomers were removed with Soxhlet extraction from the hydrogel structure. Extracted hydrogels were dried again in a vacuum oven at 305 K to a constant weight. The amount of uncrosslinked AAc was determined by titration of the extract against NaOH (0.05M) to the phenolphthalein end point.

### Swelling studies

Dried hydrogels (2-mm thickness, 3-mm diameter) were left to swell in a solution of the desired pH (3–8), with an ionic strength  $I$  of 0.05–0.3, at a temperature of 25°C. Swollen gels were removed from the water at regular intervals and dried superficially with filter paper, weighed, and placed in the same bath. The measurements were continued until a constant weight was reached for each sample.

To determine the pH sensitivity of the hydrogels, the hydrogels were immersed in a 20 mL pH 8.0 solution at 25°C for 3000 min. The hydrogels were weighed after removal of excess surface water and then transferred to a pH 3.0 buffer and the swelling versus the time measured again. The same procedure was repeated. In all cases, the pH of the solutions did not change. The kinetics and reversibility of the swelling were determined.

### Spectroscopic and thermal analysis

Fourier transform infrared (FTIR) spectra of the homopolymers and copolymers were recorded between

4000 and 400  $\text{cm}^{-1}$  on a Nicolet 520 FTIR spectrophotometer as KBr pellets. The copolymers were characterized by comparing the FTIR spectra of the homopolymers and copolymers. A DuPont Model 1951 thermogravimetric analyzer and DuPont 910 differential scanning calorimeter were used for determination of the thermal stabilities of the homopolymers and copolymers. Samples weighing 5–10 mg were heated in a dynamic nitrogen atmosphere from 20 to 800°C at a heating rate of 10°C  $\text{min}^{-1}$ .

## RESULTS AND DISCUSSION

In this study, ionizing radiation processing was used for the preparation of the AAm/AAc hydrogels. A possible free-radical polymerization reaction of AAm with AAc by  $\gamma$ -ray irradiation is shown in Figure 1.

When a solution of AAm and AAc was irradiated, a bond in the double bond of AAm and AAc was broken and monomer radicals were formed. These monomer radicals were combined together and the AAm/AAc copolymer was obtained. It has been reported that gelation of the poly(AAm) hydrogel occurs at 2.0-kGy  $\gamma$ -ray doses at ambient temperature.<sup>4</sup> The percent gelation of the poly(AAm/AAc) hydrogels is presented in Table I. As can be easily seen from this table, the percent gelation of these hydrogels decreases with increasing irradiation doses. The percent gelation of the poly(AAm/AAc) hydrogels was completed at an 8.0-kGy irradiation dose. So, an 8.0-kGy  $\gamma$ -ray dose was used for preparation of the AAm/AAc hydrogels.

**TABLE I**  
Percent Gelation of AAm/AAc Monomer Mixtures Irradiated at Various Doses

| Dose (kGy) | % Gelation     |                |                |
|------------|----------------|----------------|----------------|
|            | Poly(AAm/AAc)1 | Poly(AAm/AAc)2 | Poly(AAm/AAc)3 |
| 2.6        | 40.06          | 36.40          | 32.36          |
| 3.0        | 75.00          | 72.14          | 65.72          |
| 4.0        | 85.77          | 83.29          | 73.29          |
| 8.0        | 99.00          | 98.80          | 98.76          |
| 12.0       | 90.88          | 89.47          | 84.09          |
| 16.0       | 88.80          | 88.00          | 84.00          |
| 20.0       | 87.77          | 82.21          | 90.49          |
| 23.4       | 89.96          | 87.78          | 89.04          |
| 27.0       | 84.69          | 85.80          | 85.97          |

Initial mol ratios of AAm/AAc monomer mixtures are 30/70, 20/80, and 15/85 for poly(AAm/AAc)1, poly(AAm/AAc)2, and poly(AAm/AAc)3, respectively. Dose rate: 0.16 kGy  $\text{h}^{-1}$ .

**TABLE II**  
Initial Mol Percents of AAm and AAc in the Gel Systems and Percent Gelation

| Hydrogel       | % mol of AAm | % mol of AAc | % Gelation |
|----------------|--------------|--------------|------------|
| Poly(AAm/AAc)1 | 33.73        | 66.27        | 99.00      |
| Poly(AAm/AAc)2 | 20.78        | 79.22        | 98.80      |
| Poly(AAm/AAc)3 | 14.48        | 85.52        | 98.76      |

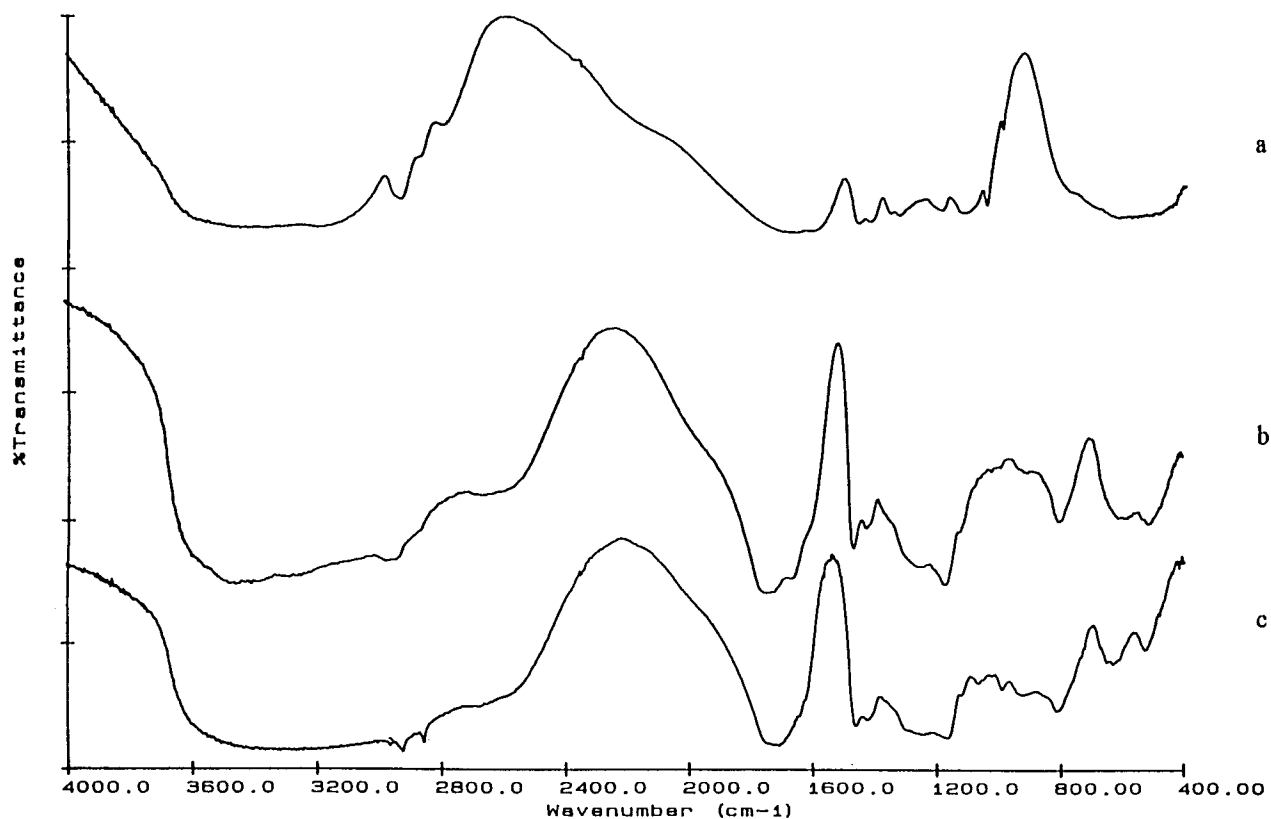
### Composition of hydrogels

Poly(AAm/AAc)1, poly(AAm/AAc)2, and poly(AAm/AAc)3 have been used for three different compositions of poly(AAm/AAc) hydrogels which were obtained by using AAm/AAc monomer mixtures at three different mol percents: 30/70, 20/80, and 15/85, respectively. Initial mol percentages of monomers in the copolymeric gels and after removing the uncrosslinked polymer and residual monomer with extraction from the gel structure were determined. The mol percentages of monomers in the hydrogel systems and percentage gelation are given in Table II.

As shown in Table II, an increasing mol percentage of AAc in the initial mixture increases the amount of AAc in the gel system. Dried gels are in a glassy form and too hard, but swollen gels are very soft. These hydrogels are obtained in the form of cylinders. Upon swelling, these hydrogels retained their shapes.

### Spectroscopic characterization

To understand the forming and crosslinking of the poly(AAm/AAc) hydrogel, obtained from AAm and AAc monomers, FTIR spectra of poly(AAm), poly(AAc), and poly(AAm/AAc) were evaluated and are presented in Figure 2. In the FTIR spectra of poly(AAm/AAc), the absorbances appearing in the range of 3100–3500  $\text{cm}^{-1}$  are due to O—H and N—H bands. The reason for this wide band may be explained by hydrogen bonding between the molecules. The absorbances at 1100–1200  $\text{cm}^{-1}$  can be attributed to C—N absorption and were also observed in the poly(AAm) and poly(AAm/AAc) hydrogels. The weak peaks at about 2900  $\text{cm}^{-1}$  are C—H stretching vibrations. —CH<sub>2</sub>— groups on the chain give absorption at 1460  $\text{cm}^{-1}$ . The absorbances at 1661 and 1641  $\text{cm}^{-1}$  are of the —CONH<sub>2</sub> group absorption in poly(AAm) and IR absorbances at 1570, 1400, and 1714



**Figure 2** FTIR spectra of poly(AAm)(a), poly(AAm/AAc)3(b), and poly(AAc)(c).

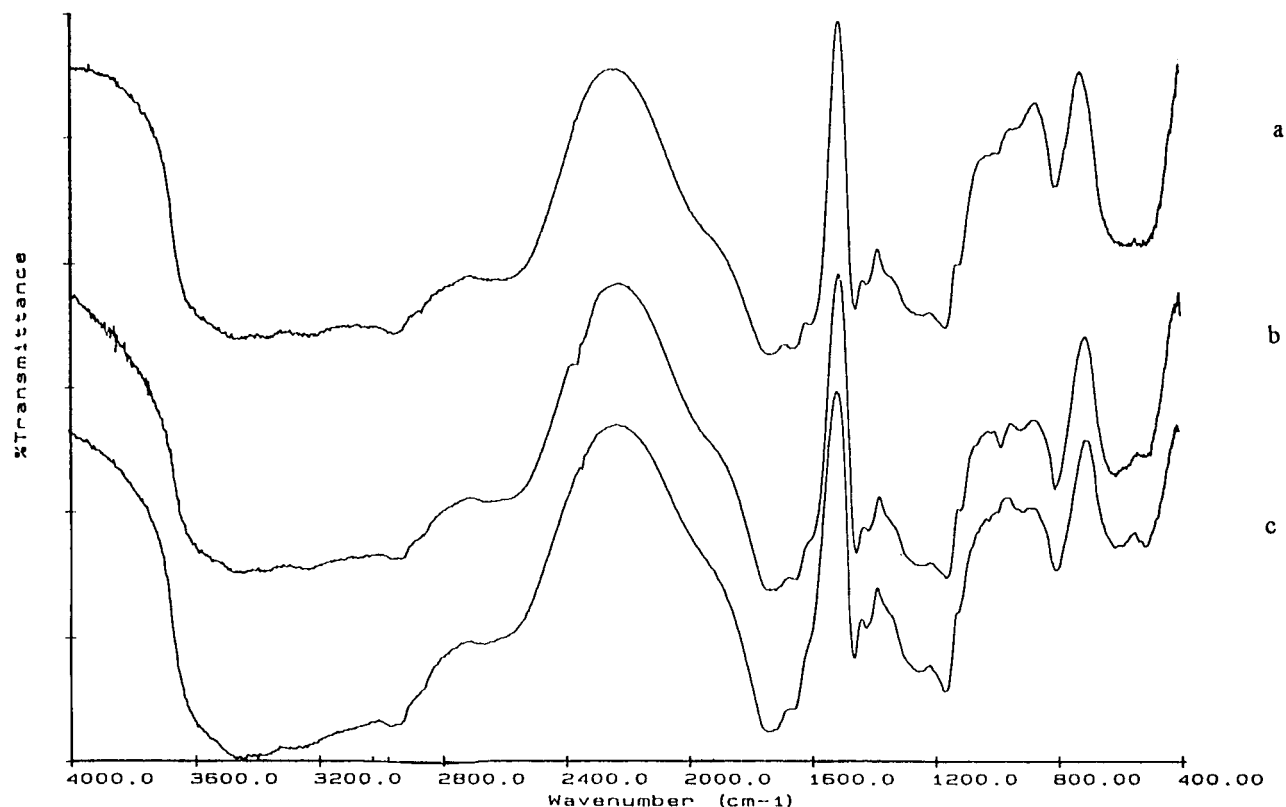


Figure 3 FTIR spectra of poly(AAm/AAc)1(a), poly(AAm/AAc)2(b), and poly(AAm/AAc)3(c).

$\text{cm}^{-1}$  can be attributed to carboxyl absorption. The  $\text{C}=\text{O}$  bond of the amide group was observed at  $1658 \text{ cm}^{-1}$  in poly(AAm/AAc). These data indicated that the synthetic copolymer was poly(AAm/AAc).

The infrared spectra of poly(AAm/AAc) hydrogels at different compositions are shown in Figure 3. The most important peaks appear at  $1743$  and  $3100\text{--}3500 \text{ cm}^{-1}$ . The peaks at this region have increased gradually with an increasing AAc percent in the hydrogels. The absorbances in the range of  $3100\text{--}3500 \text{ cm}^{-1}$  are due to  $\text{O}\text{--H}$ , and  $\text{N}\text{--H}$  absorptions. The peaks at  $1743 \text{ cm}^{-1}$  can be attributed to a shift in the stretching vibration associated with hydrogen that is bonded directly to an overtone of the strong carbonyl absorption. The  $\text{--CONH}_2$  group gives an absorption peak at  $1661\text{--}1658 \text{ cm}^{-1}$ , and a carbonyl group of carboxylic acid is observed at  $1714\text{--}1735 \text{ cm}^{-1}$ . The weak peaks at about  $2952 \text{ cm}^{-1}$  are due to  $\text{C}\text{--H}$  stretching vibrations.  $\text{--CH}_2\text{--}$  groups on the chain give absorption at  $1454 \text{ cm}^{-1}$ . There is a shift in the  $\text{C}\text{--N}$  peaks in the case of increasing AAc content in the hydrogels.

### Thermal characterization

To investigate the thermal properties of poly(AAm), poly(AAc), and poly(AAm/AAc) hydrogels, their glass transition temperatures ( $T_g$ ) were determined. While the glass transition temperature of poly(AAm)

is  $106^\circ\text{C}$ , that of poly(AAc) is about  $182^\circ\text{C}$ . The DSC curve of poly(AAm/AAc)3 in Figure 4 showed that the  $T_g$  value of poly(AAm/AAc)3 is between those of the corresponding poly(AAm) and poly(AAc) and corresponds to  $132^\circ\text{C}$ . Thermogravimetric analysis curves were used for the determination of decomposition temperatures and the thermal stabilities of poly(AAm), poly(AAc), and poly(AAm/AAc)3. The thermograms of poly(AAm), poly(AAc), and poly(AAm/AAc)3 are given in Figure 5. To determine the thermal stability of poly(AAm), poly(AAc), and poly(AAm/AAc)3, the temperature for the maximum weight loss ( $T_{\text{max}}$ ) and the temperature for the half-life ( $T_{1/2}$ ) were found directly from their dynamic thermograms given in Figure 5. Poly(AAm) gives a 20% residue at  $500^\circ\text{C}$ . The temperature for the maximum weight loss of poly(AAm) is  $T_{\text{max}} = 396^\circ\text{C}$  and  $T_{1/2} = 408^\circ\text{C}$ . There are two decomposition stages for poly(AAc): The temperature for maximum weight loss is  $T_{\text{max}} = 410^\circ\text{C}$  and the temperature for half-life is  $T_{1/2} = 390^\circ\text{C}$ . Poly(AAc) degrades by forming an anhydride structure and it gives a 10% residue at  $500^\circ\text{C}$ . There are three decomposition peaks on its thermogram and they are  $249$ ,  $300$ , and  $410^\circ\text{C}$ , respectively. On further heating, the anhydride decomposes. Heating poly(AAc) at about  $400^\circ\text{C}$  results in rapid decomposition to carbon dioxide and volatile hydrocarbons.<sup>7</sup>

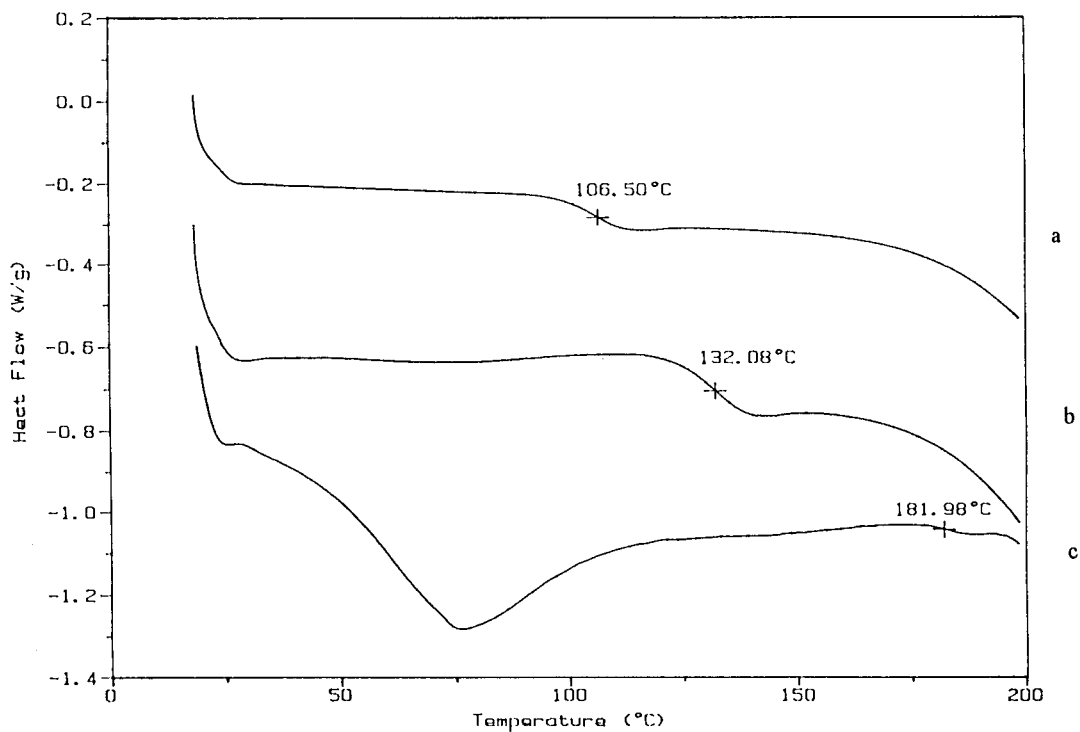


Figure 4 DSC curves of poly(AAm)(a), poly(AAm/AAc)3(b), and poly(AAc)(c).

Upon investigating the thermogram of the poly-(AAm/AAc)3 hydrogel, it was observed that, when a less stable species combined with a species of a higher

thermal stability, this hydrogel gained new thermal characteristics.  $T_{\max}$  for poly(AAm/AAc)3 is 414°C and  $T_{1/2}$  is 380°C.

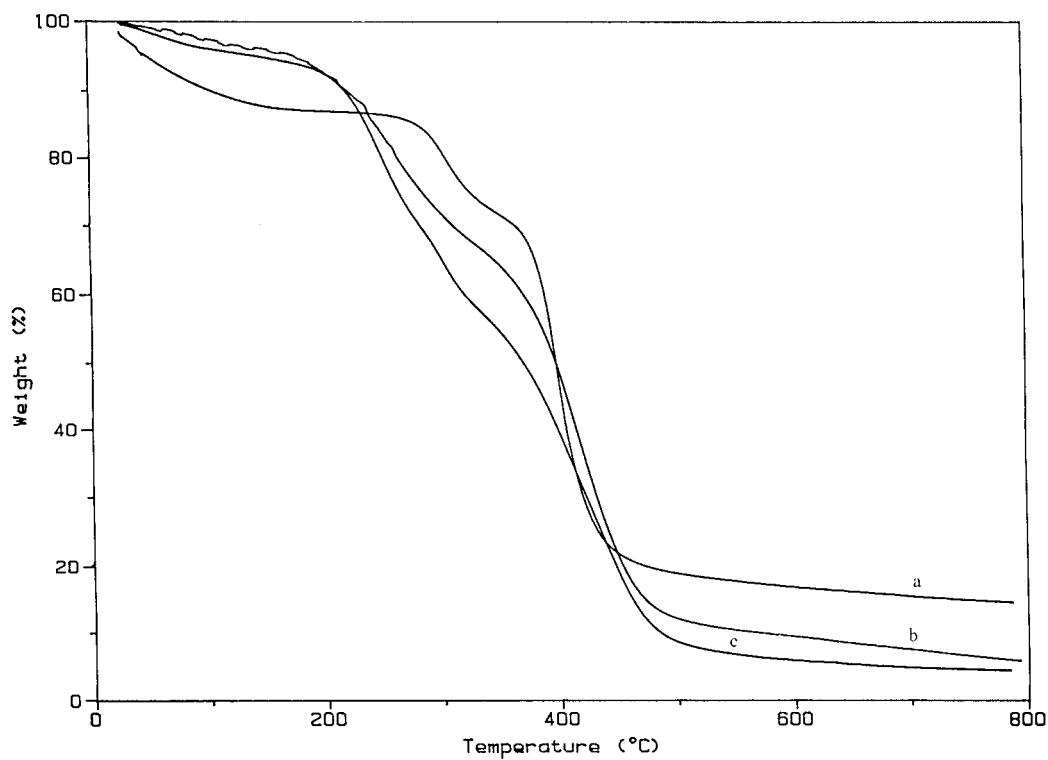
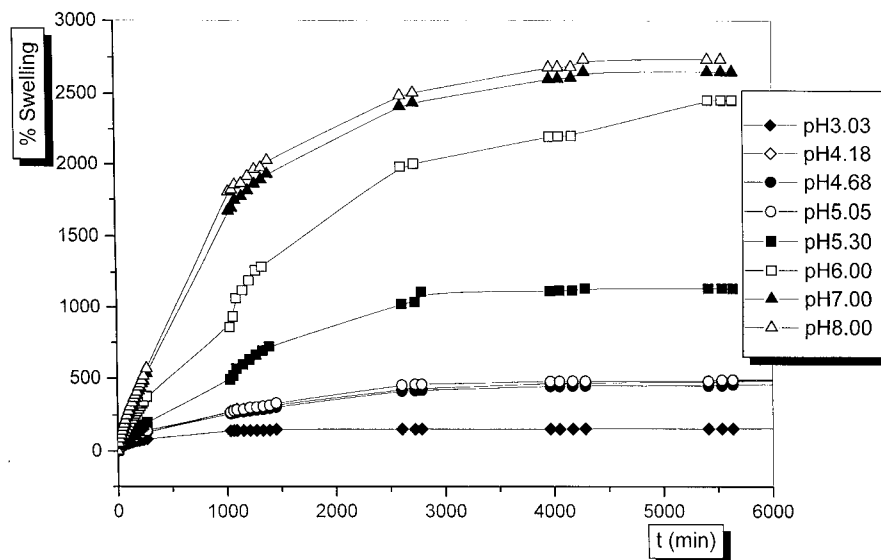


Figure 5 Thermogram of poly(AAm)(a), poly(AAm/AAc)3(b), and poly(AAc)(c).



**Figure 6** Effect of pH on swelling behavior poly(AAm/AAC)3 hydrogel at 25°C. Initial mol ratio of AAm/AAC: 15/85 for poly(AAm/AAC)3.  $I$ : 0.1.

### Swelling studies

A fundamental relationship exists between the swelling of a crosslinked polymer in a solvent and the nature of the polymer and the solvent. Swelling of the three-dimensional network structure in a suitable solvent is the most important parameter (especially one of the most important parameters is mass swelling) for swelling measurements. The measurements were continued until a constant weight was reached for each sample. The percent swelling of each hydrogel was calculated from the following relation:

$$\%S \text{ (swelling)} = [(m_t - m_0)/m_0] \times 100 \quad (1)$$

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

The equilibrium swelling of the poly(AAm) and poly(AAm/AAC) hydrogels was investigated as a function of pH at 25°C and 0.1M ionic strength. Swelling curves of the poly(AAm/AAC)3 hydrogel at various pH values are shown in Figure 6. The water intake of initially dry hydrogels was followed for a long period of time. All the hydrogels showed a similar swelling behavior. Swelling of the hydrogels was found to increase with the pH and time. The measurements were continued until a constant weight was reached for each sample. This constant weight is the equilibrium swelling of a polymer in a given gel sample swollen to equilibrium in water.

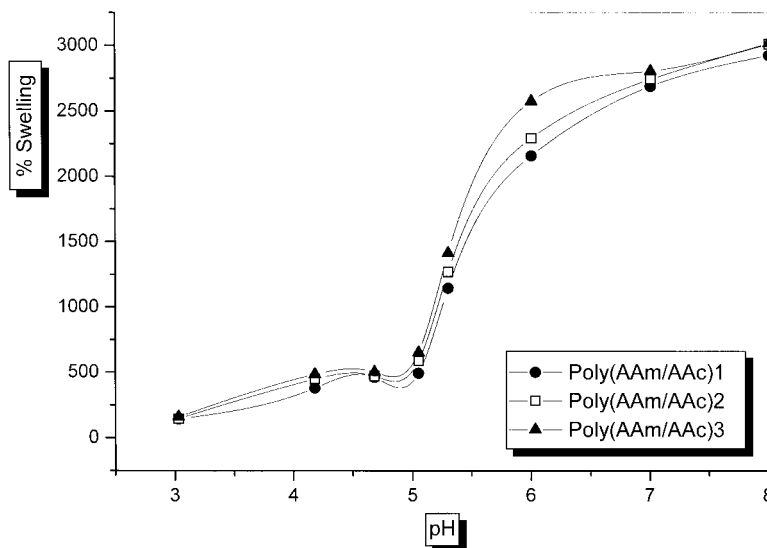
In the case of copolymerization of AAm with an ionic monomer such as AAC, pH-sensitive copolymers can be prepared. Charged groups attached to the polymeric network structure have played an essential role in the swelling properties. At low pH values, the water uptake of poly(AAm/AAC) hydrogels is lower

than that of poly(AAm). Consistent with the polyelectrolytic behavior, the swelling of hydrogels was found to increase with the pH. At higher pH values, carboxylic acid groups of AAC become ionized and hydrogen bonds break down.<sup>8</sup> As a result, hydrogels swell to a higher degree compared to poly(AAm) because of the electrostatic repulsions produced within the matrix.<sup>9</sup>

The variation of equilibrium swelling of poly(AAm/AAC) hydrogels as a function of pH at 25°C and 0.1M ionic strength are given in Figure 7. The equilibrium swelling was reached a maximum value at pH 8.0 for three different compositions of the poly(AAm/AAC) hydrogel, this being due to the complete dissociation of acidic groups of AAC at this pH value. It is quite well known that the  $pK_a$  value of poly(AAC) is about 4.25.<sup>10</sup> An experimental  $pK_a$  was calculated by having the first derivative of the percent swelling with time ( $d\% \text{ swelling}/dt$ ) with the first derivative of pH with time ( $dpH/dt$ ). These values are valid for pH values higher than 5.30. The equilibrium swelling of poly(AAm/AAC) hydrogels increases with the pH. Since the  $pK_a$  of AAC is 4.25, the swelling behavior of poly(AAm/AAC) depends on the ionization degree with the pH. All poly(AAm/AAC) hydrogels at three different compositions showed a similar swelling transition region between pH 3.0 and pH 8.0.

Figure 8 shows the kinetics and reversibility of the hydrogels between pH 8.0 and 3.0. This procedure was repeated three times and the equilibrium swelling value was measured as a function of time. The swelling of the hydrogels was shown to be reversible. Swelling is slower than is deswelling during the swelling and deswelling cycles.

The percent swelling of the poly(AAm/AAC)3 hydrogel which contains 15% AAm as a function of ionic



**Figure 7** Effect of pH on swelling behavior of poly(AAm/AAc) hydrogels at 25°C. Initial mol ratios of AAm/AAc are 30/70, 20/80, and 15/85 for poly(AAm/AAc)1, poly(AAm/AAc)2, and poly(AAm/AAc)3, respectively. *I*: 0.1.

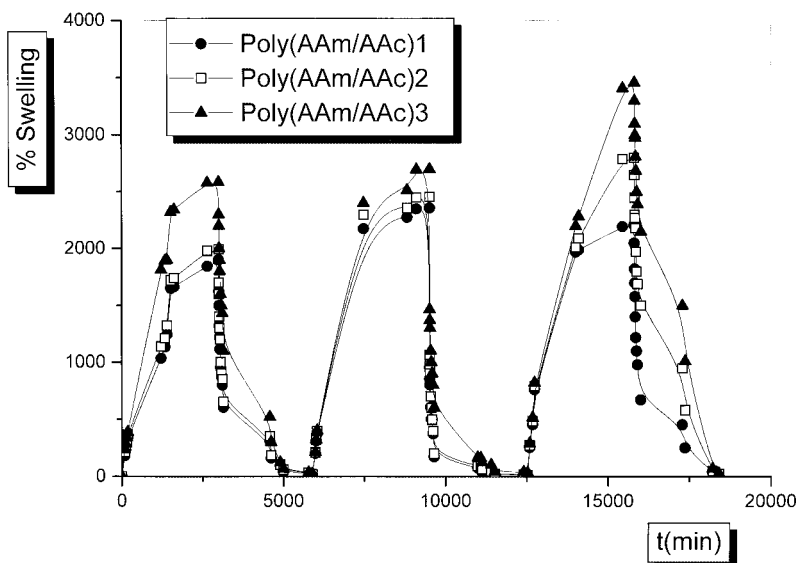
strength at 25°C and at pH 8.0 is shown in Figure 9. As ionic strength increases, the percent swelling decreases due to the increased counterion concentration, shielding of charges on the polymer chain, and high ion concentration outside the gel. As the concentration of ions outside the gel increases, the concentration of ions inside and outside the hydrogel will become equal and osmotic pressure inside the hydrogel will decrease.

#### Diffusion studies

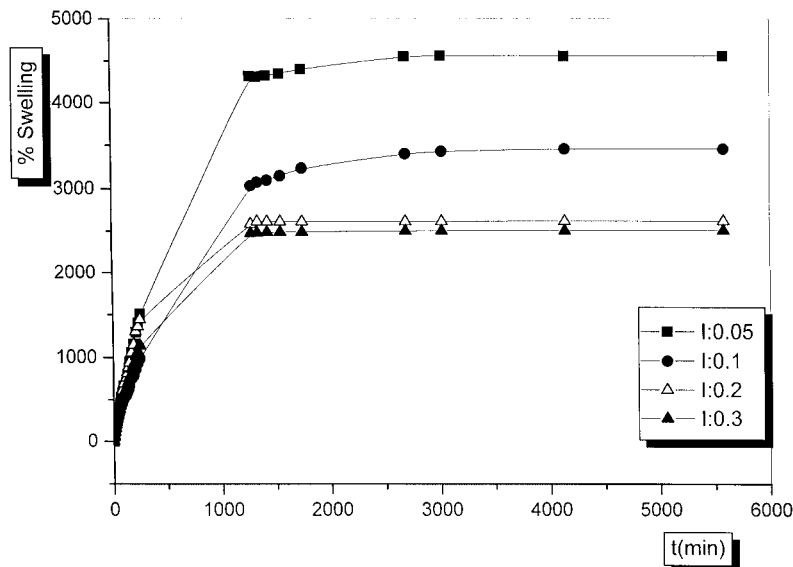
When a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the hydro-

gel swells. Diffusion involves migration of water into preexisting or dynamically formed spaces between hydrogel chains. Swelling of the hydrogel involves larger-scale segmental motion, resulting, ultimately, in an increased distance of separation between hydrogel chains.<sup>9</sup>

Analysis of the mechanism of water diffusion in a swellable polymeric system has received considerable attention in recent years because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering fields.<sup>11</sup> The study of the diffusion phenomena in a hydrogel and water is of importance as it clarifies the polymer behavior. The swelling curves of poly(AAm/



**Figure 8** Equilibrium swelling of poly(AAm/AAc) hydrogels as a function of time at 25°C under repeated abrupt changes of pH between 3.0 and 8.0. Initial mol ratios of AAm/AAc are 30/70, 20/80, and 15/85 for poly(AAm/AAc)1, poly(AAm/AAc)2, and poly(AAm/AAc)3, respectively. *I*: 0.1.



**Figure 9** Equilibrium swelling of poly(AAm/AAc)3 hydrogel as a function of ionic strength at 25°C. Initial mol ratio of AAm/AAc is 15/85 for poly(AAm/AAc)3. pH: 8.0.

AAc) hydrogels were used for the calculation of the swelling behavior and diffusional properties. The following equation was used to determine the nature of the diffusion of water into hydrogels:

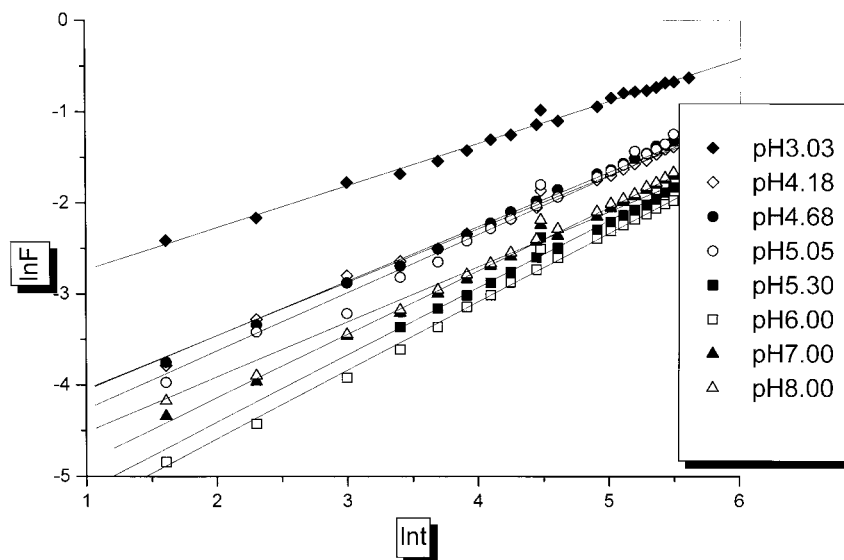
$$F = kt^n \tag{2}$$

where  $F$  denotes the amount of the solvent fraction at time  $t$ ,  $k$  is a constant related to the structure of the network, and the exponential  $n$  is a number used to determine the type of diffusion. This equation was applied to the initial stages of swelling. Plots of  $\ln(F)$  versus  $\ln(t)$  are shown for the poly(AAm/AAc)3 hydrogel in

Figure 10 The exponents  $n$  and  $k$  were calculated from the slope and intercept of the lines and the results are given for three different hydrogels in Table III.

For hydrogel characterization, the diffusion coefficient can be calculated by various methods. The short-time approximation method is used for calculation of the diffusion coefficients of the poly(AAm/AAc) hydrogels. The short-time approximation is valid for the first 60% of the swelling. The diffusion coefficients of the cylindrical poly(AAm/AAc) hydrogels are calculated from the following relations<sup>12,13</sup>:

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



**Figure 10** Plots of  $\ln(F)$  versus  $\ln(t)$  of poly(AAm/AAc) hydrogels at various pH's and 25°C. Initial mol ratio of AAm/AAc is 15/85 for poly(AAm/AAc)3. I: 0.1.



TABLE III  
Swelling and Diffusion Parameters of Poly(AAm/AAc) Hydrogels in Water at Various pH and 25°C

| pH   | Poly(AAm/AAc)1  |      |                 | Poly(AAm/AAc)2  |      |                 | Poly(AAm/AAc)3  |      |                 |
|------|-----------------|------|-----------------|-----------------|------|-----------------|-----------------|------|-----------------|
|      | $k \times 10^2$ | $n$  | $D \times 10^5$ | $k \times 10^2$ | $n$  | $D \times 10^5$ | $k \times 10^2$ | $n$  | $D \times 10^5$ |
| 3.03 | 3.81            | 0.46 | 1.42            | 3.72            | 0.46 | 1.57            | 4.06            | 0.46 | 1.96            |
| 4.18 | 1.10            | 0.57 | 0.80            | 1.10            | 0.57 | 0.79            | 0.96            | 0.59 | 0.93            |
| 4.68 | 0.84            | 0.61 | 0.94            | 0.85            | 0.60 | 0.85            | 0.86            | 0.60 | 0.89            |
| 5.05 | 0.60            | 0.65 | 1.04            | 0.69            | 0.63 | 0.90            | 0.79            | 0.67 | 0.93            |
| 5.30 | 0.39            | 0.69 | 0.95            | 0.34            | 0.70 | 0.95            | 0.37            | 0.69 | 0.86            |
| 6.00 | 0.24            | 0.76 | 1.24            | 0.23            | 0.76 | 1.16            | 0.22            | 0.75 | 1.06            |
| 7.00 | 0.35            | 0.76 | 2.48            | 0.40            | 0.76 | 1.22            | 0.39            | 0.76 | 1.05            |
| 8.00 | 0.50            | 0.79 | 2.78            | 0.46            | 0.78 | 1.52            | 0.45            | 0.78 | 1.36            |

$D$ :  $\text{cm}^2 \text{min}^{-1}$ .

Initial mol ratios of AAm/AAc are 30/70, 20/80, and 15/85 for poly(AAm/AAc)1, poly(AAm/AAc)2, and poly(AAm/AAc)3, respectively.  $I$ : 0.1.

where  $D$  is in  $\text{cm}^2 \text{min}^{-1}$ ,  $t$  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 cylindrical sample. A graphical comparison of eqs. (2) and (3) shows the semiempirical eq. (2) and  $k = 4(D/\pi r^2)^{1/2}$  and  $D = 0.049/(t/4r^2)^{1/2}$ . For the poly(AAm/AAc)3 hydrogel,  $F$  versus  $t^{1/2}$  curves are given in Figure 11. Slopes of the lines of  $F$  versus  $t^{1/2}$  give the diffusion coefficients. Diffusion coefficients are also listed for three different hydrogels in Table III.

In Table III, it is clearly seen that the numbers used to determine the type of diffusion ( $n$ ) were found to be between 0.46 and 0.76 and over 0.50 for the diffusion of water. Hence, the diffusion of water into poly(AAm/AAc) hydrogels was taken to be non-Fickian. This is generally explained as a consequence of the slow relaxation rate of the polymer matrix or that relaxation and diffusion have the same properties, simultaneously, on the swelling of these hydrogels.<sup>14</sup>

At higher pH values, the transport of water into the hydrogels is more non-Fickian. The diffusion coefficients of poly(AAm/AAc) hydrogels varied from  $0.79 \times 10^{-5}$  to  $2.78 \times 10^{-5} \text{cm}^2 \text{min}^{-1}$ . We can say that the diffusion coefficient is highly affected by the pH of the buffer solution. Penetration of the solvent into the poly(AAm/AAc) hydrogel is easier and the diffusion rate is fast in an aqueous solution of pH 3.0, because there is a hydrophilic interaction between the hydrogel and water. The rate of diffusion and the diffusion coefficient decreased at pH 4.18. They increased again from pH 4.18 to a basic medium because of the decomposing of the COOH group in the hydrogel at the basic medium.

For extensive swelling of poly(AAm/AAc) hydrogels, the following equation can be written<sup>14</sup>:

$$t/S = A + Bt \quad (4)$$

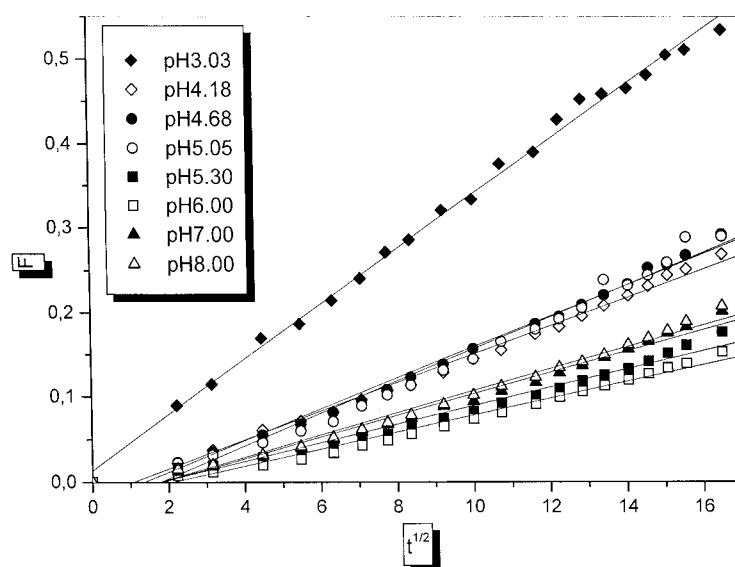
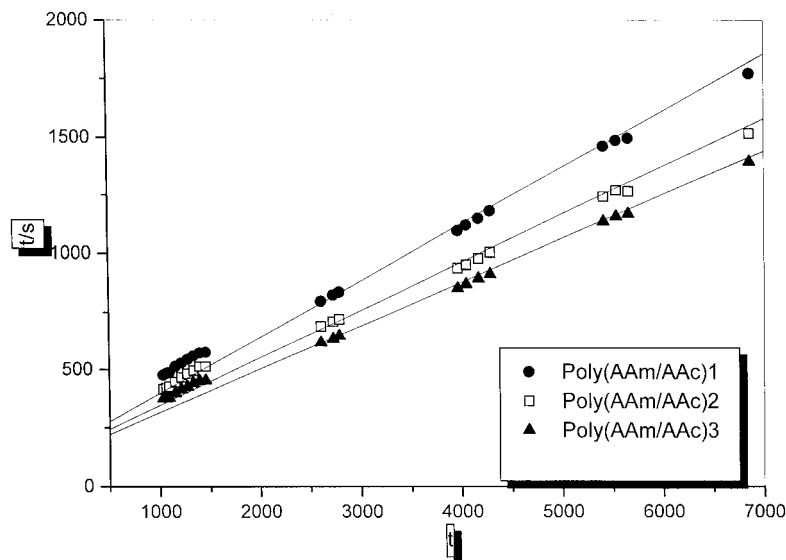


Figure 11 Plots of  $F$  versus  $t^{1/2}$  of poly(AAm/AAc)3 hydrogel at various pH's and 25°C. Initial mol ratio of AAm/AAc is 15/85 for poly(AAm/AAc)3.  $I$ : 0.1.



**Figure 12** Swelling kinetics curves of poly(AAm/AAC) hydrogels in water at pH 8.0 and 25°C. Initial mol ratio of AAm/AAC is 30/70, 20/80, and 15/85 for poly(AAm/AAC)1, poly(AAm/AAC)2, and poly(AAm/AAC)3.  $I$ : 0.1.

where  $B = 1/S_{eq}$  is the inverse 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.<sup>14</sup> Figure 12 shows the linear regression of the swelling curves obtained using eq. (4) for the poly(AAm/AAC) hydrogels. The initial swelling rate ( $r_i$ ), swelling rate constant ( $k_s$ ), and theoretical equilibrium swelling ( $S_{eq}$ ) of poly(AAm/AAC) hydrogels were calculated from the slope and interaction of the lines and are 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 the equilibrium swelling of the poly(AAm/AAC) hydrogels (Fig. 6). The swelling rate of poly(AAm/AAC) hydrogels in a basic solution is higher than in an acidic solution. We found that swelling of the hydrogels has the highest value in

a basic medium. At higher pH values, carboxylic acid groups of AAC become ionized and electrostatic repulsion occurred. The initial rate decreased with an increasing AAC content in the hydrogel, but rate constants did not change in the basic medium. The initial rate increased with an increasing AAC content in the hydrogel in an acidic medium. More COOH groups are in the poly(AAm/AAC)3 hydrogel than in the other hydrogels.

## CONCLUSIONS

1. Poly(AAm/AAC) hydrogels were prepared at three different mol percentages and irradiated in a  $^{60}\text{Co}$ - $\gamma$  source at different doses.
2. The percentage of gelation of the hydrogels was decreased with an increasing irradiation dose.

**TABLE IV**  
Swelling Characteristic of Poly(AAm/AAC) Hydrogels in Water at Various pH and 25°C

| pH   | Poly(AAm/AAC)1    |                   |          | Poly(AAm/AAC)2    |                   |          | Poly(AAm/AAC)3    |                   |          |
|------|-------------------|-------------------|----------|-------------------|-------------------|----------|-------------------|-------------------|----------|
|      | $k_s \times 10^3$ | $r_i \times 10^2$ | $S_{eq}$ | $k_s \times 10^3$ | $r_i \times 10^2$ | $S_{eq}$ | $k_s \times 10^3$ | $r_i \times 10^2$ | $S_{eq}$ |
| 3.03 | 3.25              | 0.71              | 1.48     | 3.19              | 0.73              | 1.51     | 3.54              | 0.95              | 1.64     |
| 4.18 | 0.37              | 0.63              | 4.14     | 0.29              | 0.68              | 4.89     | 0.26              | 0.76              | 5.37     |
| 4.68 | 0.25              | 0.77              | 5.59     | 0.25              | 0.68              | 5.25     | 0.29              | 0.75              | 5.09     |
| 5.05 | 0.15              | 0.86              | 7.50     | 0.17              | 0.77              | 6.68     | 0.26              | 0.78              | 5.50     |
| 5.30 | 0.05              | 1.25              | 16.00    | 0.04              | 1.25              | 18.44    | 0.05              | 1.03              | 14.98    |
| 6.00 | 0.02              | 1.92              | 29.87    | 0.02              | 1.83              | 30.02    | 0.02              | 1.18              | 31.58    |
| 7.00 | 0.03              | 3.33              | 32.14    | 0.03              | 3.05              | 33.06    | 0.03              | 3.02              | 34.04    |
| 8.00 | 0.03              | 3.77              | 32.81    | 0.03              | 3.45              | 34.02    | 0.03              | 3.27              | 34.58    |

Initial mol ratios of AAm/AAC are 30/70, 20/80, and 15/85 for poly(AAm/AAC)1, poly(AAm/AAC)2, and poly(AAm/AAC)3, respectively.  $I$ : 0.1.

$r_i$ : (g water/g hydrogel)/min;

$k_s$ : (g hydrogel/g water)/min;

$S_{eq}$ : g water/g hydrogel.

Approximately 100% conversion of monomers into hydrogels was achieved at an 8.0-kGy dose.

3. For the FTIR spectra of poly(AAm/AAC) hydrogels obtained by using FTIR, the polymerization reaction of AAm and AAC were carried on their double bonds.
4. DSC thermograms showed that the glass transition temperature of the poly(AAm/AAC) hydrogel was between those of poly(AAm) and poly(AAC).
5. The poly(AAm/AAC) hydrogel that contains more AAC was swelled between 1000 and 3000%, while poly(AAm) hydrogels swelled between 450 and 650%.
6. The diffusion of water into the hydrogels was found to be of a non-Fickian character.
7. Diffusion coefficients were found for the poly(AAm/AAC) hydrogels in water between  $0.79 \times 10^{-5}$  and  $2.78 \times 10^{-5} \text{ cm}^2 \text{ min}^{-1}$ .
8. The swelling kinetics of the poly(AAm/AAC) hydrogel in water was determined to be second order.
9. The initial swelling rate increased with an increasing pH and AAC content in the hydrogels.
10. It was found that poly(AAm/AAC) hydrogels are pH-sensitive because of their swelling in a

basic medium and collapsing in an acidic medium.

As a result of this study, we can say that poly(AAm/AAC) hydrogels can be used as super water retainers for carrying substances in biomedical, agricultural, and environmental applications.

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