

Swelling Behavior of Acrylamide-2-Hydroxyethyl Methacrylate Hydrogels

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Received 03.11.1998

In this study, hydrogels of poly(acrylamide-co-2-hydroxyethyl methacrylate) having different properties were prepared by a redox polymerization method. Poly(ethylene glycol), PEG 4000 was included in the polymerization recipe to increase the microporosity of the resultant polymeric structures. AAm/HEMA hydrogels with different properties were obtained by changing initial AAm/HEMA mole ratio, total monomer, PEG 4000 and crosslinker concentrations.

Key Words: Acrylamide, 2-hydroxyethyl methacrylate, hydrogel, crosslinking, swelling, diffusion.

Introduction

Hydrogels which are water swollen polymer and copolymer networks, have been used in bioengineering, biotechnology, medicine, pharmacy, agriculture, food industry, photographic technology and other fields. 2-hydroxyethyl methacrylate (HEMA) and acrylamide (AAm) based hydrogels can be polymerized easily and they are biocompatible. Poly(acrylamide) and its derivatives the most preferred members of this family in these fields¹⁻⁷. In recent studies, the copolymers of AAm with the diprotic acids were tested as adsorbent in the adsorption of some cationic dyes⁸⁻¹⁰, uranyl ions and some heavy metal ions^{11,12}, the biocompatibility of blood¹³, and the adsorption of Bovine Serum Albumin (BSA)¹⁴. The other widely used hydrogel is water swollen, crosslinked poly(2-hydroxyethyl methacrylate), p(HEMA). p(HEMA) is inert to normal biological processes, shows resistance to degradation, is not absorbed by the body and can be prepared in a variety of shapes and forms. The properties of p(HEMA) hydrogels are dependent upon their method of preparation, polymer volume fraction, degree of crosslinking, temperature and swelling agent¹⁵⁻²⁰.

In this study, crosslinked poly(acrylamide-co-2-hydroxyethyl methacrylate) hydrogels in rod form were prepared by a redox copolymerization method. The influence of initial AAm/HEMA mole ratio, total monomer, PEG 4000 and crosslinker concentrations on the swelling properties and diffusional behavior of water were investigated at the end of the swelling tests.

Experimental

Materials

Acrylamide (AAm) and the comonomer, 2-hydroxyethyl methacrylate (HEMA) supplied by from BDH Chemicals Ltd. (Poole, UK). HEMA stabilized with 0.12% (w/v) methoxyethyl hydroquinone, was vacuum distilled to remove the polymerization inhibitor.

Potassium persulphate (KPS, BDH Chemicals Ltd., Poole, UK) and tetramethylene diamine (TEMED, Merck, Darmstadt, Germany) were used as the redox initiator pair.

Poly(ethylene glycol), (PEG 4000, $M_r=4000$, BDH Chemicals Ltd., Poole, UK) and N-N'-methylene-bisacrylamide (MBAAm, BDH Chemicals Ltd., Poole, UK) were used as a diluent and as a crosslinker, respectively. Distilled water was used in the copolymerizations and swelling studies.

Copolymer Preparation

Acrylamide/2-hydroxyethyl methacrylate hydrogels were prepared by redox polymerization. A typical procedure for the copolymerization can be described as follows: AAm, 1.0 g, and HEMA 0.1 mL and PEG 4000, 0.11 g were dissolved in 1.0 mL of distilled water. 0.11 mL MBAAm (50 mg/mL), KPS (50 mg/mL) and TEMED (50 mg/1.5 mL) solutions were added to the solution mixture, respectively. The poly(vinyl chloride) straws of 4 mm diameter were used as the polymerization reactors. The polymerization medium was purged in these straws and the copolymerization was performed for 10 minutes at room temperature. The copolymer blocks obtained in the form of long cylinders then were cut and washed within distilled water at room temperature for 24 hours to remove any unreacted monomers and physically entrapped PEG 4000 within the copolymer matrix and dried in air and in a vacuum. In the copolymer preparation, the total monomer concentration, AAm/HEMA mole ratio, total monomer, PEG 4000 and crosslinker concentrations were changed. The conditions for the production of hydrogels are summarized in Table 1. At these conditions, the conversion of monomers was checked by gravimetric determination. These samples were used in experiments of swelling and diffusion.

Experiments of Swelling and Diffusion

In order to determine the swelling behavior of hydrogels, initially dry gels were placed in distilled water and kept at room temperature. Swollen gels periodically removed from the water bath were dried with filter paper and weighed by an electronic balance (Shimadzu, Japan, EB. 280+1x10⁻³g) 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.

Results and Discussions

Swelling Behaviors of Hydrogels

Swelling behaviors of hydrogels were observed gravimetrically. The water content of swollen gels was calculated from the following expression¹⁰:

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

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

Table 1. The production condition of AAm and AAm/HEMA hydrogels and the values of equilibrium mass swelling [%S(m)] and equilibrium volume swelling [%S(v)] of the same hydrogels.

Sample No	AAm(g)	HEMA(mL)	MBAAm(%)	PEG 4000(g)	Water(mL)	%S(m)	%S(v)
0	1.0	-	-	-	1.0	1122	1589
2	1.0	0.10	7.7	-	1.0	660	862
8	1.0	0.10	8.3	-	1.0	606	792
9	1.0	0.10	9.0	-	1.0	586	765
10	1.0	0.10	9.6	-	1.0	577	754
11	1.0	0.10	10.2	-	1.0	565	738
1	1.0	-	7.7	-	1.0	665	868
2	1.0	0.10	7.7	-	1.0	660	862
3	1.0	0.20	7.7	-	1.0	611	797
4	1.0	0.30	7.7	-	1.0	575	720
5	1.0	0.40	7.7	-	1.0	513	671
6T	1.0	0.10	7.7	0.11	1.0	704	920
1E	1.0	0.20	7.7	0.11	1.0	628	820
2E	1.0	0.30	7.7	0.11	1.0	593	774
3E	1.0	0.40	7.7	0.11	1.0	550	719
2	1.0	0.10	7.7	-	1.0	660	862
6T	1.0	0.10	7.7	0.11	1.0	704	920
7T	1.0	0.10	7.7	0.22	1.0	730	954
1	1.0	-	7.7	-	1.0	665	868
7E	0.5	0.05	7.7	-	1.0	728	951
2	1.0	0.10	7.7	-	1.0	660	862
6E	1.5	0.15	7.7	-	1.0	686	896
4E	0.5	0.05	7.7	0.11	1.0	988	1636
6T	1.0	0.10	7.7	0.11	1.0	704	920
5E	1.5	0.15	7.7	0.11	1.0	715	934

Effect of AAm/HEMA Mole Ratio

The effect of AAm/HEMA mole ratio on the swelling curve of produced hydrogels was studied by varying this ratio between 100/0 and 81.1/18.9. AAm concentration in the polymerization medium was fixed to 1.0 g/mL. Swelling behavior of hydrogels obtained with various AAm/HEMA mole ratios is given in Figure 1. As seen in this figure, the percentage swelling increased with time but after a while constant percentage swelling is observed. This value of swelling percentage may be called equilibrium mass swelling. The values of equilibrium mass swelling of AAm hydrogels range from 665% to 1122%, and the values of equilibrium mass swelling of AAm/HEMA hydrogels are range from 513% to 660%. Table 1 shows that lower equilibrium percentage mass swelling was obtained at constant temperature by increasing the HEMA content of the copolymer structure. Poly(AAm) gel exhibited the highest equilibrium percentage mass swelling. Therefore, the equilibrium percentage mass swelling of copolymers decreased with increasing HEMA content. In the HEMA-rich gels, the percentage swelling was possibly controlled by the HEMA part of copolymer. The reason for this is probably the intermolecular hydrogen bonding between hydroxyl and amide groups and intramolecular hydrogen bonding between amide groups, so the hydrophilic group numbers of copolymers decrease. The hydrophilic group numbers of AAm/HEMA gels are lower than those of AAm, so the

equilibrium swelling of AAm/HEMA copolymers are lower. The fewer hydrophilic groups there are in copolymers, the lower the swelling capacity is in AAm/HEMA hydrogels.

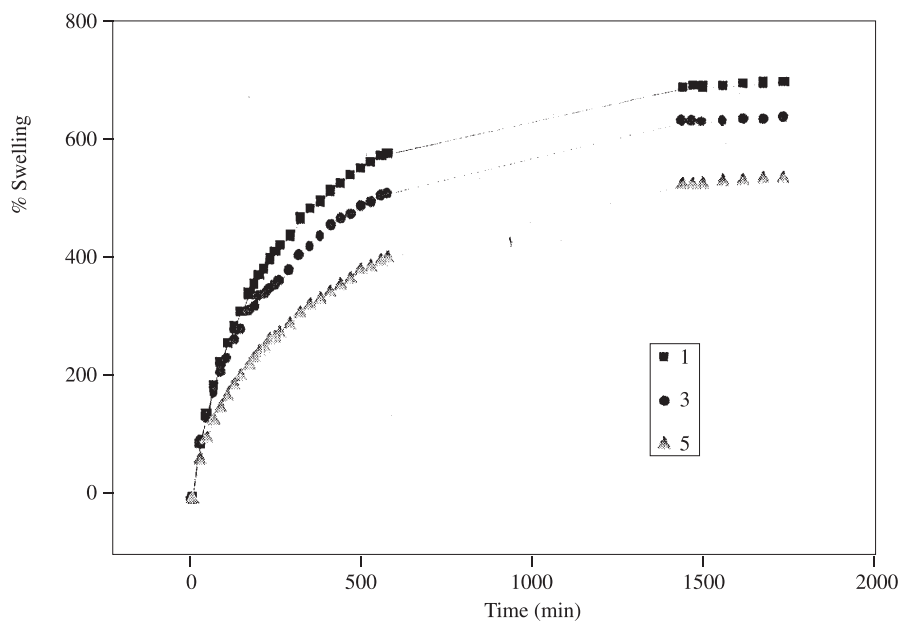


Figure 1. Swelling curves of AAm/HEMA hydrogels produced by different AAm/HEMA mole ratios. AAm concentration: 1.0 g/mL.

Effect of Total Monomer Concentration

In the swelling experiments, the total monomer concentration was varied between 0.55 and 1.66 g/mL by fixing the initial AAm/HEMA mole ratio to 94.5/5.5. The crosslinking was achieved by 7.7% MBAAm. The variation of equilibrium mass swelling of the produced hydrogels is given in Figure 2. The swelling curve of hydrogel produced with a total monomer concentration of 1.11 g/mL was placed between the swelling curves of obtained with a total monomer concentration of 0.55 and 1.66 g/mL, respectively. As seen here, the hydrogels produced with lower total monomer concentration exhibited higher swelling percentage, and the equilibrium mass swelling of the hydrogels decreased with increasing total monomer concentration. 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.

Effect of PEG 4000 Concentration

To increase the equilibrium mass swelling of produced hydrogels by creating an additional degree of dilution within the gel matrix, PEG 4000 was tried since it was soluble in the initial polymerization medium and its molecular weight was sufficiently low to remove it from the gel after copolymerization. The effect of PEG 4000 on the swelling behavior of hydrogel at constant total monomer concentration and at constant monomer composition was studied by varying PEG 4000 concentration between 0 and 0.22 g/mL. The total monomer concentration and AAm/HEMA mole ratio were fixed to 1.11 g/mL and 94.5/5.5. The variation of equilibrium mass swelling of the hydrogels produced with different PEG 4000 concentration is given in Figure 3. As seen here, the use of PEG 4000 caused an increase in the percentage swelling. This result may

be explained by the formation of an additional degree of dilution within the gel matrix by the increase in PEG 4000 concentration.

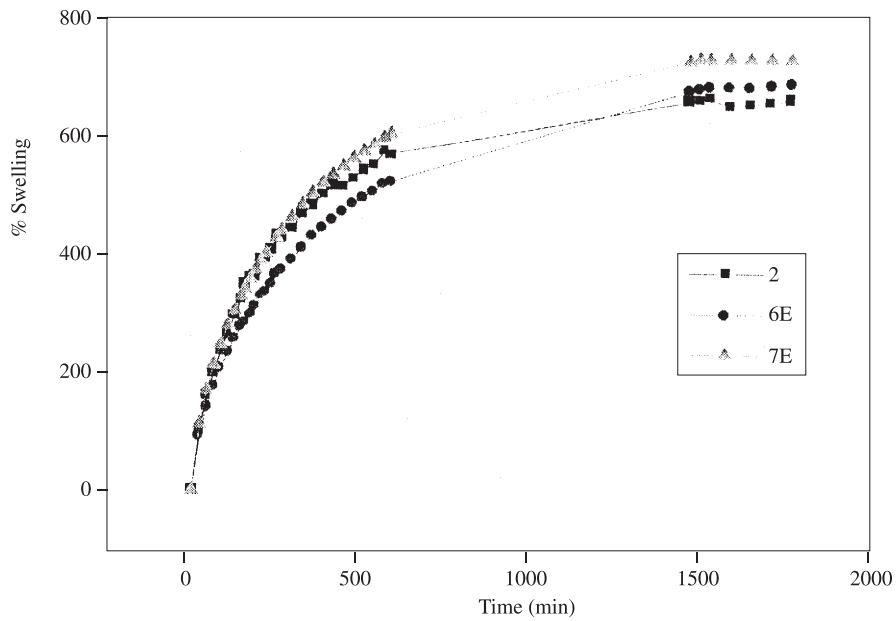


Figure 2. Swelling curves of AAm/HEMA hydrogels produced by changing total monomer concentration. AAm/HEMA mole ratio: 94.5/5.5.

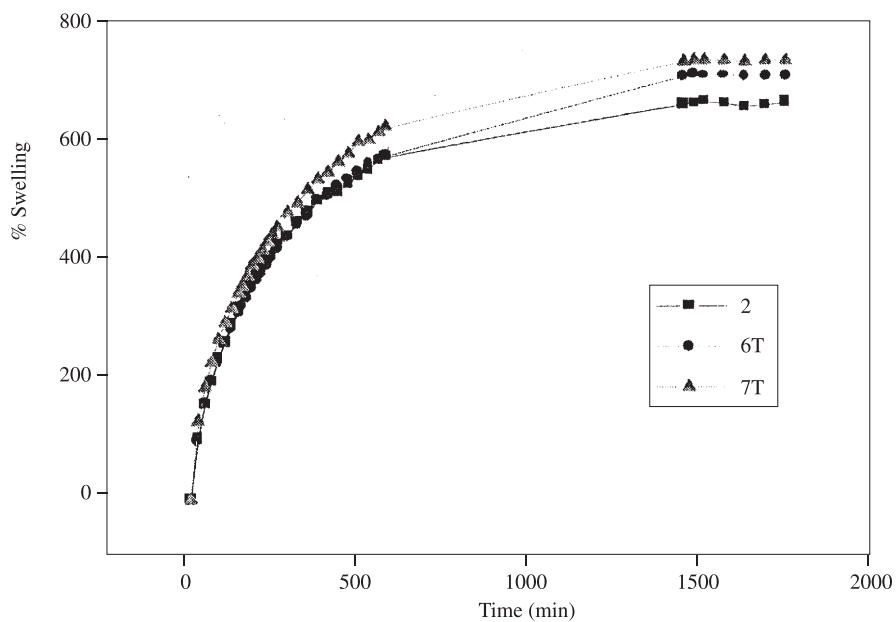


Figure 3. Effect of PEG 4000 concentration on the swelling of AAm/HEMA hydrogels. Total monomer concentration: 1.11 g/mL, AAm/HEMA mole ratio: 94.5/5.5.

To have copolymeric structures with better swelling properties relative to those produced without any diluent, the total monomer concentration and AAm/HEMA mole ratio were changed again by including a constant amount of the diluent in the copolymerization recipe, and the copolymer behaviors obtained with

PEG 4000 were compared with the those produced in the absence of the diluent. The effect of total monomer concentration on the swelling behavior of hydrogels produced in the presence of PEG 4000 is given in Figure 4. PEG 4000 concentration was fixed to 0.11 g/mL and the total monomer concentration was varied between 0.55 and 1.66 g/mL. When the swelling behaviors given in Figure 4 were compared with the results in Figure 2, it was seen that the use of PEG 4000 caused an increase in the swelling rate of hydrogel produced with the total monomer concentration to 0.55 g/mL.

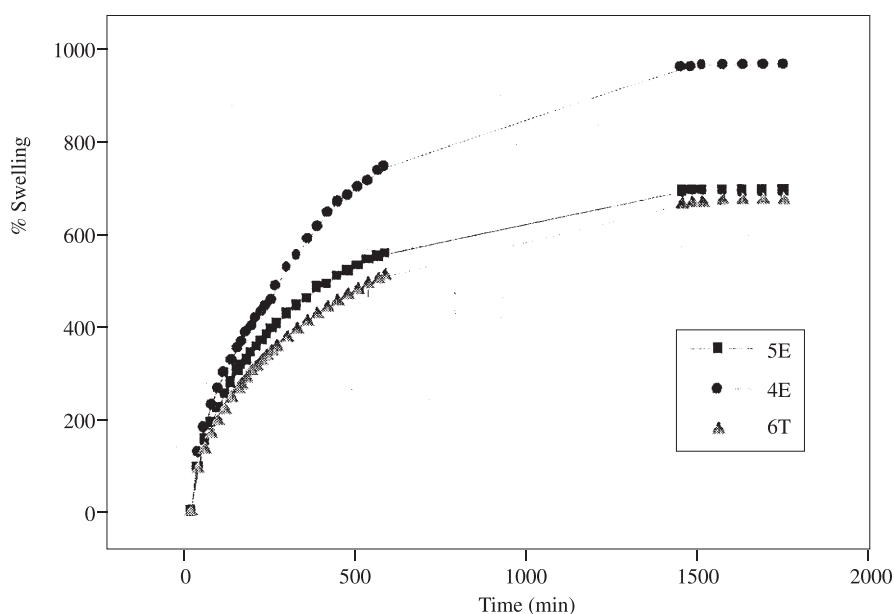


Figure 4. Swelling curves of AAm/HEMA hydrogels produced by changing total monomer concentration in the presence of PEG 4000 as a diluent. PEG 4000 concentration: 0.11 g/mL and AAm/HEMA mole ratio: 94.5/5.5.

Effect of Crosslinker Concentration

The effect of crosslinker concentration on the swelling behavior of hydrogel is given in Figure 6. In these experiments, crosslinker concentration was varied between 7% and 10.2%. The total monomer concentration and AAm/HEMA mole ratio were fixed to 1.11 g/mL and 94.5/5.5. Generally, when a crosslinker is added to a hydrogel, it is known that there is a decrease in the swelling percentage 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 percentage is in the hydrogel systems.

To determine the percentage of volume swelling equilibrium, it is necessary to know density of the solvent which is used in the swelling experiments of the polymer. The volume swelling, % $S(v)$, is given by

$$\%S(v) = [(m_t - m_0)/d_s / (m_0/d_p)] \times 100 \quad (2)$$

where m_0 and m_t are the mass of the dry gel at time 0 and the mass of the swollen gel at time t , and d_s and d_p are the water density and polymer density, respectively²¹. The conditions for the production of poly(AAm-co-HEMA) and the values of percentage equilibrium mass and volume swelling of the hydrogels are summarized in Table 1.

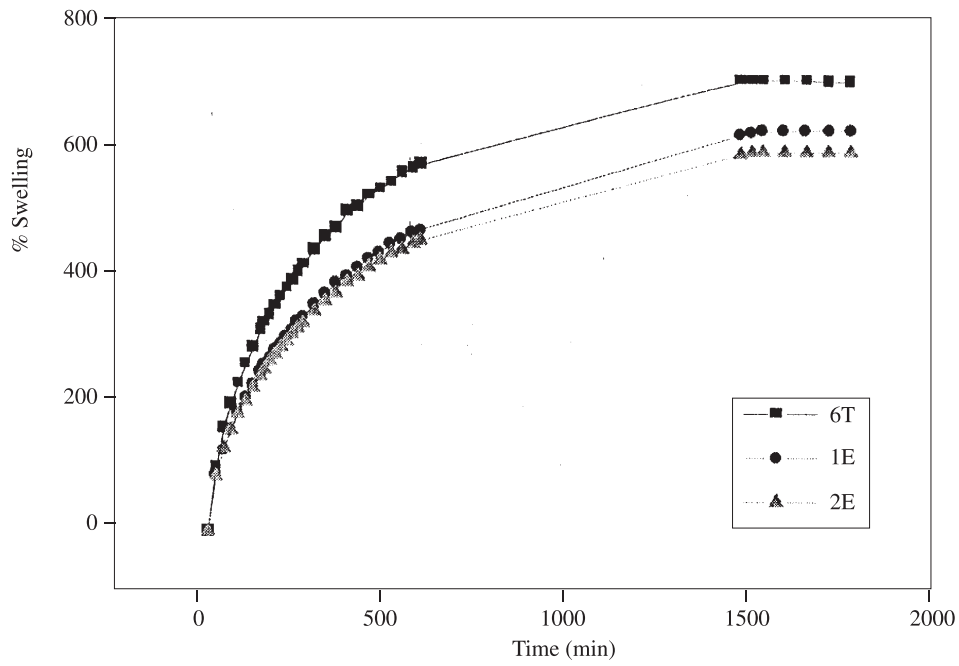


Figure 5. Swelling curves of AAm/HEMA hydrogels produced by different AAm/HEMA mole ratios in the presence of PEG 4000. PEG 4000 concentration: 0.11 g/mL and AAm concentration: 1.0 g/mL.

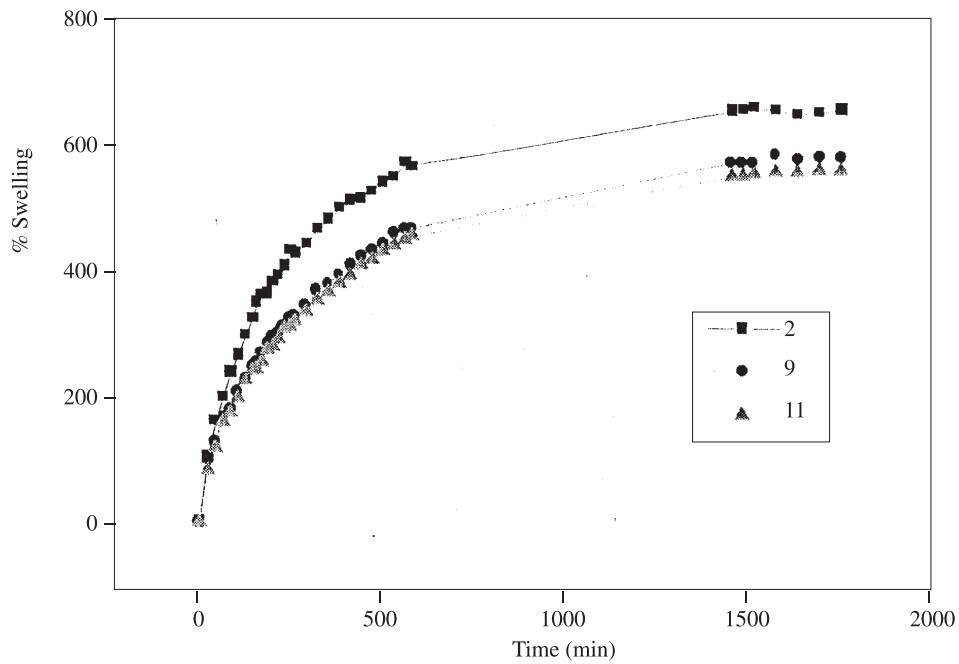


Figure 6. Effect of crosslinker concentration on swelling of AAm/HEMA hydrogels. AAm/HEMA mole ratio: 94.5/5.5.

Diffusion of Water

The following equation was used to determine the type of diffusion of water into hydrogels^{21,22}

$$F = (M_t/M_i) = kt^n \quad (3)$$

where M_t and M_i represent to 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 the range of 0.45-0.50, diffusion is Fickian, while $0.50 < n < 1.0$ indicates that diffusion is of a non-Fickian type. Equation 3 is applied to the initial stages of swelling and plots of $\ln F$ versus $\ln t$ ²³. Figure 7 shows the typical curves of swelling kinetics of hydrogels. Then n and k values were calculated from the slopes and intercepts of the lines, respectively. The values of diffusion constants and diffusional exponents of AAm and AAm/HEMA hydrogels are listed in Table 2. In Table 2 it is clearly seen that the values of diffusional exponent range between 0.50 and 0.62, are and found to be over 0.50. Hence the diffusion of water into hydrogels was taken as a non-Fickian type²². This behavior is generally explained as a consequence of a slow relaxation rate of the polymer matrix.

Table 2. The values of n and k of the hydrogels.

Sample No	$k \times 10^2$	n
0	2.07	0.56
2	2.76	0.58
8	2.79	0.53
9	3.50	0.50
10	3.05	0.53
11	3.13	0.52
1	2.54	0.58
2	2.76	0.58
3	2.96	0.54
4	2.22	0.62
5	2.46	0.55
6T	2.90	0.55
1E	3.01	0.52
2E	3.20	0.50
2	2.76	0.58
6T	2.90	0.55
7T	3.54	0.50
1	2.54	0.58
7E	2.96	0.55
2	2.76	0.58
6E	3.35	0.50
4E	2.63	0.54
6T	2.90	0.55
5E	2.53	0.56

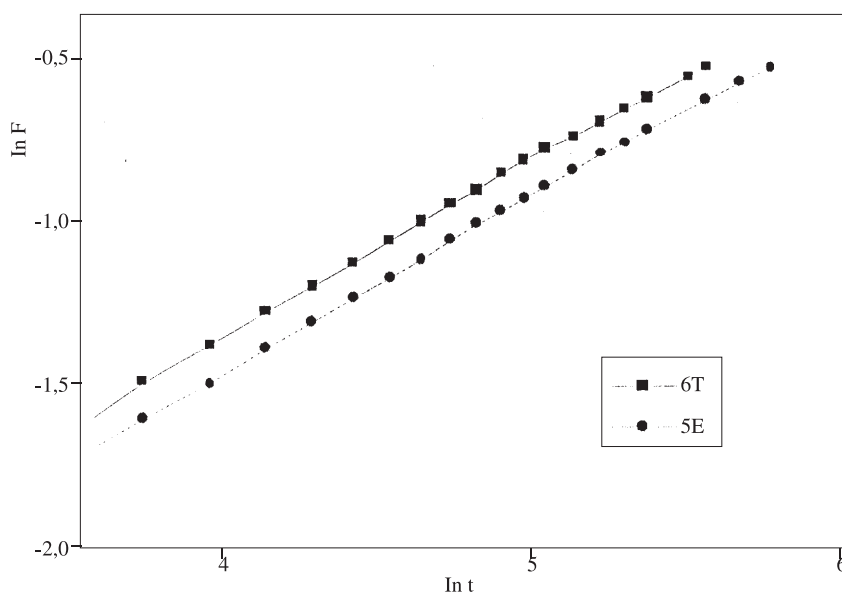


Figure 7. The typical curves of swelling kinetics of AAm/HEMA hydrogels.

Conclusion

In this study, poly(acrylamide-co-2-hydroxyethyl methacrylate) hydrogels were prepared by redox polymerization by changing the initial AAm/HEMA mole ratio; the total monomer, PEG 4000 and crosslinker concentrations on the swelling properties of hydrogels were examined. Hydrogels were prepared in water and swollen to equilibrium in water. Equilibrium swelling values were used for the determination of diffusional behavior of water of the hydrogel systems. The diffusion type of hydrogel systems was of non-Fickian diffusion character. It is seen that swelling of hydrogels decreased with the increasing total monomer, HEMA and crosslinker concentrations, and it increased with the increasing of content of PEG 4000 in hydrogels.

As a result, poly(AAm-co-HEMA) hydrogels with different properties can be used as a water retainer for carrying some substances in aquatic fields in pharmaceutical, agricultural, environmental and biomedical applications, or in the application of immobilized biologically active molecules.

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