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RADIATION INDUCED ACRYLAMIDE/CITRIC ACID HYDROGELS AND THEIR SWELLING BEHAVIORS

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ABSTRACT

Citric acid (CAc) moieties containing acrylamide (AAm) hydrogels were prepared by gamma irradiation of their aqueous solutions. A possible polymerization and crosslinking mechanism for acrylamide/citric acid (AAm/CAc) hydrogels is proposed. The effects of irradiation dose and citric acid content on swelling behavior were investigated. Swelling took place in water at 25°C and was followed gravimetrically. Incorporation of a relatively low amount of citric acid to acrylamide hydrogel increased its swelling up to 950% from 700%. The diffusion of water into AAm/CAc hydrogels was found to be a *non-Fickian* type. Diffusion coefficients of AAm/CAc hydrogels found as 5×10^{-7}– 10×10^{-7} cm^2 sec^{-1}. It has also been found that the number average molar mass between crosslinks is increased with the CAc content and decreased with irradiation dose.

Key Words: Acrylamide; Citric acid; Hydrogel; Gamma radiation; Swelling; Polymer

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INTRODUCTION

Hydrogels are three-dimensional crosslinked polymeric network, which swell significantly on contact with water. Most hydrogels are formed by polymerization of vinyl monomers containing hydrophilic groups with multifunctional vinyl monomers or by crosslinking reactive functional groups of hydrophilic polymers. By manipulating the chemistry of the hydrophilic segments in the polymers and degree of crosslinking, hydrogels may be tailored to exhibit specific properties [1]. Hydrogels have found enormous applications in bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology, and many others [2].

Hydrogels are synthesized using either chemical methods or a irradiation technique. In recent years, considerable research has been done on the characterization and swelling behavior of the hydrogels prepared by simultaneous free-radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent [3, 4].

Hydrogels can also be synthesized by γ-irradiation [5-9]. However, little work is done on the characterization of the hydrogels prepared by crosslinking of a homopolymer or copolymer in solution with γ-irradiation [10, 11]. It is very well known that the presence of an initiator and a crosslinking agent affects the macromolecular structure and phase behavior of hydrophilic polymers in solution and contributes to inhomogenity of the network structure. It is important to note that more homogeneous network structures can be synthesized, if crosslinking is accomplished with γ-irradiation in the absence of an initiator and a crosslinking agent. The structural homogeneity of the network affects the swelling behavior and mechanical properties.

In our previous study, the copolymeric hydrogels of acrylamide with crotonic, maleic, itaconic, tartaric, and succinic acid [5-9] were prepared and used in separation and adsorptions of some ions and molecules [12-14], and used in biocompatibility studies [15-17]. To increase water absorption capability of AAm hydrogels, incorporation of none vinyl group containing carboxylic acid such as citric acid is proposed. Here, aqueous solutions of acrylamide and citric acid were irradiated with γ-rays at various doses. Swelling properties, diffusion parameters and network properties of hydrogels were investigated.

EXPERIMENTAL

In order to prepare hydrogel systems, acrylamide (AAm) (BDH, Poole: UK) weighing 1 g was dissolved in 1 mL aqueous solutions of 0, 20, 40, and 60 mg citric acid (CAc) (BDH, Poole, UK). The solutions were placed in PVC straws of 3 mm diameter and irradiated to 2.60, 3.73, 4.65, and 5.20 kGy in air at ambient temperature in a ^{60}Co Gammacell 220 type γ irradiator at a fixed dose rate of 0.72 kGy hr^{-1}. The dose rate was determined by the conventional Fricke dosimeter.

Freshly obtained long cylindrical shaped hydrogels were cut into pieces of 3-4 mm in length. They were washed and thoroughly rinsed with distilled water, blot dried with filter paper, dried in air and vacuum, and stored for swelling studies.

Radiation crosslinked dried copolymeric hydrogels were accurately weighed, and transferred into water. Water uptake with respect to time was obtained by periodically removing samples from water, quickly blot drying, and reweighing. The measurements were conducted at 25 ± 0.1°C in a water bath.

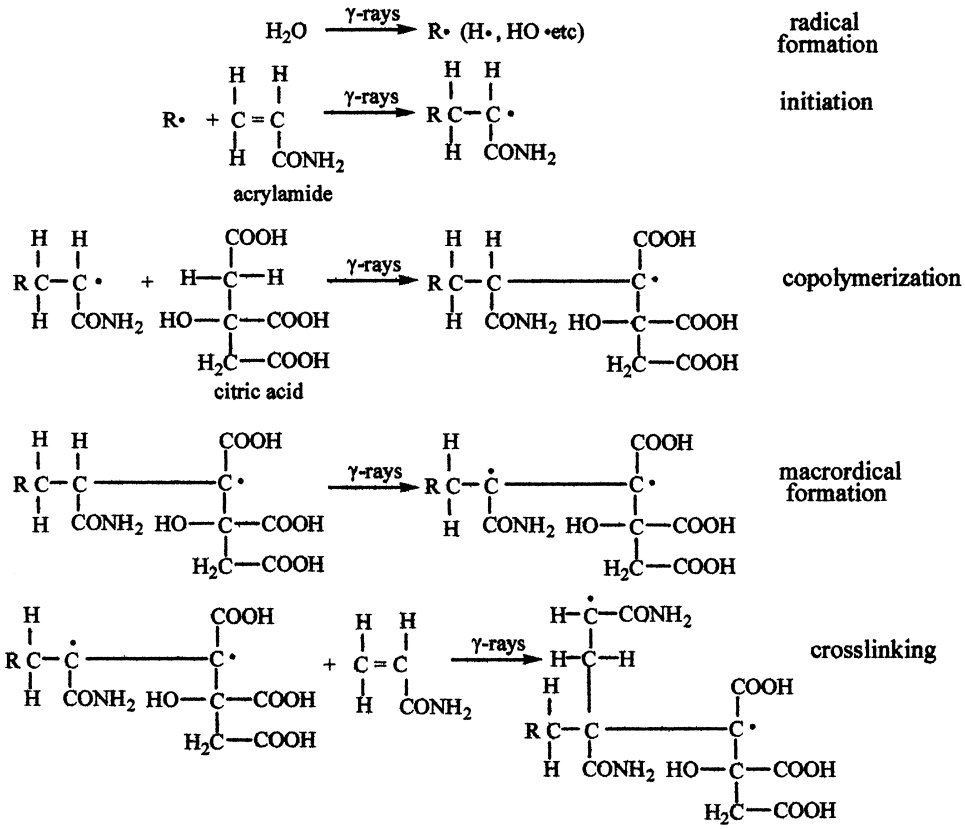
RESULTS AND DISCUSSION

In spite of the availability of the huge number and variety of synthetic vinyl monomers, there are just a few hydrophilic monomers from which hydrogels can be prepared. Among them 2-hydroxyethyl methacrylate, acrylamide and N-vinyl 2-pyrrolidone comprise the three most frequently used. Polyethylene oxide and poly vinyl alcohol are two polymers preferred in the synthesis of hydrogels [11]. For incorporation of some sensitivity properties to the hydrogels for specific purposes, the above mentioned monomers or polymers can be used for radiation copolymerization and/or grafting with monomers carrying appropriate functionalities. However, it is a challenge to obtain hydrogels from non-vinyl groups containing monomers. This problem can be overcome by a radiation method, which makes possible the incorporation of such moieties in the hydrogels network structure. To prepare such a system, high-energy radiation (or ionizing radiation), such as gamma rays, electron beams, and ultraviolet light can also be used.

Radiation technique seems viable for the preparation of hydrogels since monomers or a polymer in aqueous solution or water-swollen state readily undergoes crosslinking on irradiation to yield a gel-like material. As this hydrogel is not contaminated with foreign additives, crosslinks must be composed of stable C-C bonds, and it is of interest to study the preparation of hydrogels by irradiation [18, 19].

Preparation of Radiation Induced Hydrogels

A radiation technique was used to prepare AAm and AAm/CAc hydrogels. When monomers of AAm and CAc are irradiated together with ionizing rays, γ rays, one double bond of –C=C– on AAm and one or two of C-H bonds of CAc were broken by ionization irradiation and free radicals are generated. These free radicals react with each other, and a copolymeric AAm/CAc hydrogel is produced. For the polymerization and crosslinking of poly(AAm/CAc) by γ rays irradiation, a possible mechanism is proposed in Scheme 1. During the irradiation of AAm, CAc, and water ternary mixtures, the polymer chains crosslink and gel is obtained. It is reported that complete gelation of AAm is 2.00 kGy dose of γ rays irradiation at ambient temperature [20]. So, a minimum dose of 2.60 kGy of γ rays is used for preparation of AAm/CAc hydrogels.



Scheme 1. Possible copolymerization and crosslinking mechanism of acrylamide and citric acid.

Dried AAm/CAc copolymers are a glassy form and very hard, but swollen gels are very soft. The crosslinked copolymers are obtained in the form of cylindrical rods. Upon swelling, the hydrogels were strong enough to retain their shape.

Swelling of Hydrogels

There exists a fundamental relationship between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. The swelling [S%] of the hydrogels in distilled water was calculated from the following relation:

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

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

The water intake of initially dry hydrogels was followed for a period of time, up to a maximum swelling achieved. Swelling curves of the hydrogels were plotted and representative swelling curves are shown in Figures 1 and 2.

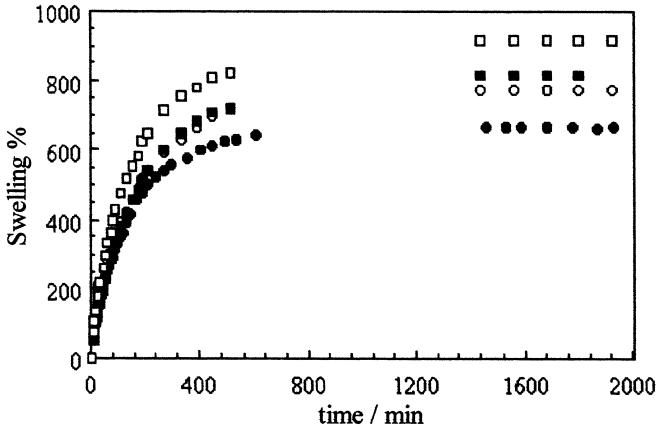


Figure 1. The effect of citric acid on the swelling of AAm/CAc copolymers. Total dose given 3.73kGy. ○, 0 mg Cac; ●, 20 mg Cac; □, 40 mg Cac; ■, 60 mg CAc.

Figures 1 and 2 show that swelling is increased with time, but after some time, it levels off. This value of swelling may be named equilibrium swelling percentage (S_{eq}%). The values of S_{eq}% of AAm/CAc copolymers are used for the calculation of some network characterization parameters. S_{eq}% values of AAm/CAc copolymers are given in Table 1.

Table 1 shows that S_{eq}% values of AAm are 665%–695%, while S_{eq}% values of AAm/CAc hydrogels are 740–955%. Since the hydrophilic groups of AAm/CAc copolymers are greater than those of AAm, the swelling of AAm/CAc copolymers is greater than the swelling of AAm hydrogels.

To understand the effect of the content of CAc in the hydrogels, and γ rays dose on the swelling behavior, S_{eq}% of the radiation induced hydrogels versus the content of CAc and γ rays dose are plotted in Figures 3 and 4.

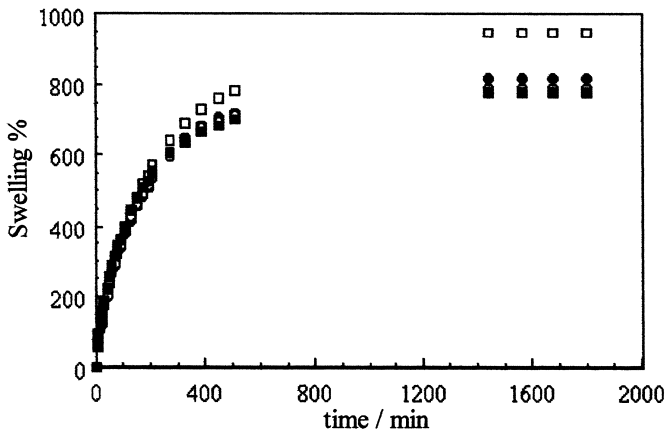


Figure 2. The effect of irradiation dose on the swelling of AAm/CAc copolymers containing 40 mg CAc. □, 2.60 kGy; ●, 3.73 kGy; ○, 4.65 kGy; ■, 5.20 kGy.

Table 1. Variation of S_{eq}% of AAm/CAc Hydrogels with CAc Content and Irradiation Dose

Dose	2.60 kGy	3.73 kGy	4.65 kGy	5.20 kGy
0 mg	685	665	675	695
20 mg	865	775	770	740
40 mg	945	815	790	780
60 mg	955	915	840	780

From Figure 3, it can be seen that S_{eq}% are decreased with the increase of irradiation dose, while increasing with CAc content. Again, from Figure 4, S_{eq}% of CAc containing hydrogels reduced more dominantly than non-CAc containing AAm gel with irradiation dose. As can be deduced easily, the increase in the extent of hydrophilic groups in the structure raises the S_{eq}%, while the total absorbed dose reducing the S_{eq}%.

The increase in the amount of absorbed dose lessens the number of small chains. Thus, hydrogels exposed higher doses has higher crosslink density than hydrogel exposed lower doses. This means that a high amount adsorbed dose decrease the number average molar mass between crosslinks while a low amount of adsorbed dose increase the number average molar mass between crosslinks.

To impart pH sensitivity to neutral AAm hydrogels, CAc groups are incorporated in the network of AAm hydrogels. The variation of S_{eq}% with pH of solution is important property for the pH sensitive hydrogels. As is well known, poly(acrylamide) starts to hydrolyze about pH 10 to give corresponding carboxylic acid such as poly(acrylic acid). Figure 5 illustrates the S_{eq}% of AAm and 60 mg CAc containing hydrogels irradiated to 2.6 kGy in universal buffer solutions (0.04 M H_3BO_3 + 0.04 M CH_3COOH+ 0.04 M H_3PO_4 and 0.2 M NaOH)

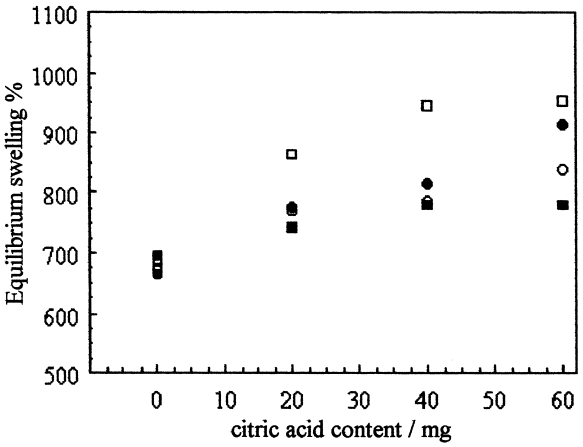


Figure 3. Variation of S_{eq}% of AAm/CAc copolymers with CAc content in hydrogels. □, 2.60 kGy; ●, 3.73 kGy; ○, 4.65 kGy; ■, 5.20 kGy.

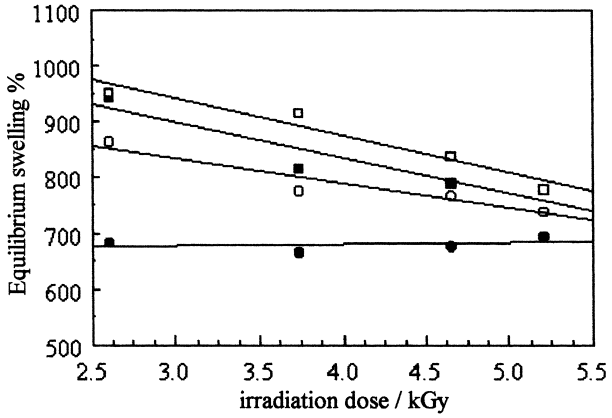


Figure 4. Variation of S_{eq}% of AAm/CAc copolymers with the irradiation dose. □, 2.60 kGy; ●, 3.73 kGy; ○, 4.65 kGy; ■, 5.20 kGy.

from pH 1.5 to 10. As can be seen from Figure 5, the values S_{eq}% of neutral AAm hydrogels increased significantly with the incorporation of ionizable citric acid. It is well known that CAc is a polytropic acid with the dissociation constants $pK_{a,1}$=3.14, $pK_{a,2}$=4.77, and $pK_{a,3}$ 6.39; and can be said that the swelling takes place more or less in a stepwise manner around pK_a values of citric acid. A sharp increase could be expected in S_{eq}% values around these pK_a value, however it should be forgotten that the amount of used citric acid is very low when compared to overall composition of hydrogels. Hence, the ionization of all carboxylic groups in citric acid increases the S_{eq}% of AAm/CAc hydrogel in the basic media as shown in Figure 5.

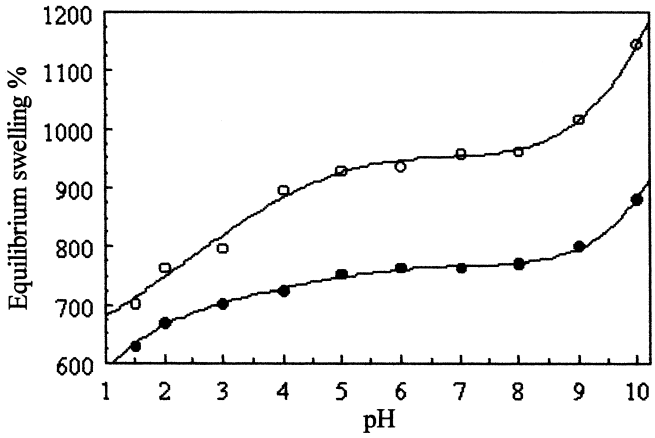


Figure 5. Variation of S_{eq}% of AAm/CAc copolymers with pH. Total dose given 2.6 kGy. ●, AAm; ○, AAm/CA containing 60 mg CAc.

Swelling Kinetics

To investigate the controlling mechanism of the swelling processes, several kinetic models are used to test experimental data. The large number and array of different chemical groups on the AAm/CAc chains (e.g., amine, amide, carbonyl, carboxyl or hydroxyl) imply that there are many types of polymer-solvent interactions. It is probable that any kinetic is likely to be global. From a system design viewpoint, a lumped analysis of adsorption rates is thus sufficient for the practical application.

A simple kinetic analysis is the first order equation in the form:

$$\frac{dS}{dt} = k_{1,s}(S_{max} - S) \tag{2}$$

where $k_{1,s}$ is the rate constant of first order swelling and S_{max} denotes of the degree of swelling at equilibrium. After definite integration by applying the initial conditions S=0 at t=0 and S=S at t=t, Equation 2 becomes:

$$\ln W = k_{1,s}\, t \tag{3}$$

where $W = S_{max}/(S_{max}-S)$.

Also, a second order equation based on swelling equilibrium degree may be expressed in the form:

$$\frac{dS}{dt} = k_{2,s}(S_{max} - S)^2 \tag{4}$$

where $k_{2,s}$ is the rate constant of second order swelling. Integrating equation (4) and applying the initial conditions, we have

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

where A is reciprocal of initial swelling rate r_O or $1/k_{2,s}S_{max}^2$ and B is inverse of the degree swelling equilibrium. If second order kinetics are applicable, the plot of t/s against t of Equation 5 should give a liner relationship, from which S_{max}, $k_{2,s}$ and r_o can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

To test kinetics models, ln W vs. t and t/S vs. t graphs is plotted and representative graphs are shown in Figures 6 and 7. Calculated kinetic parameters are tabulated in Tables 2 and 3.

As seen from Table 2, the swelling rate constants of first order equation are higher than the second order swelling rate constants. However, as shown in Figures 5 and 6, the second order swelling equation seems to fit better than the first order swelling equation.

Table 3 presents the initial swelling rates and equilibrium swelling degrees calculated according to second order swelling equation. Although an increased amount of CAc content of AAm/CAc copolymeric hydrogels are expected to swell

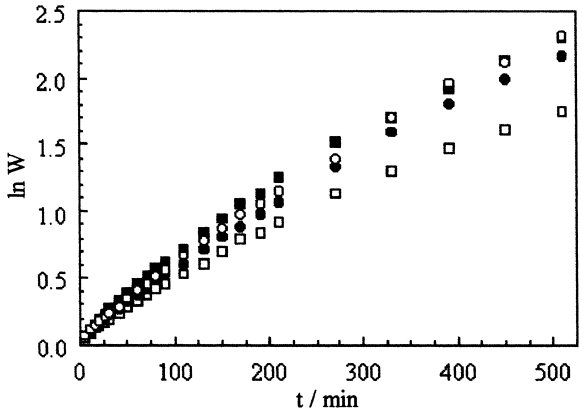


Figure 6. First order swelling kinetics for AAm/CAc copolymers containing 40 mg CAc. □, 2.60 kGy; ●, 3.73 kGy; ○, 4.65 kGy; ■, 5.20 kGy.

faster than a lower amount CAc containing hydrogels due to the increased extent of hydrophilicity, there could not be any proportionality between them. Because the swelling degree and rate largely depend on ionization of carboxyl groups of CAc as well as the hydrophilic nature of amide groups on Aam, and also ionization of carboxyl groups somehow differs in the hydrogel than that of pure citric acid.

Diffusion

Due to its hydrophilic nature, when a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the hydrogel swells. Diffusion involves migration of water into pre-existing or dynamically formed

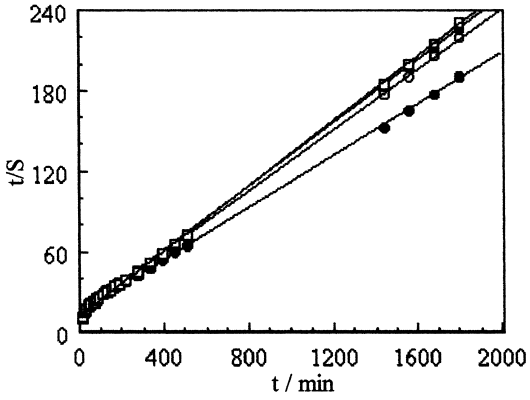


Figure 7. Second order swelling kinetics for AAm/CAc copolymers containing 40 mg CAc. □, 2.60 kGy; ●, 3.73 kGy; ○, 4.65 kGy; ■, 5.20 kGy.

Table 2. Variation of First Order ($k_{1,s}$/min^{-1}) and Second Order $k_{2,s}$/g gel (g water min)$^{-1}$ Swelling Rate Constants of AAm/CAc Hydrogels with CAc Content and Irradiation Dose

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy	
CAc	$k_{1,s}\times10^3$	$k_{2,s}\times10^3$	$k_{1,s}\times10^3$	$k_{2,s}\times10^3$	$k_{1,s}\times10^3$	$k_{2,s}\times10^3$	$k_{1,s}\times10^3$	$k_{2,s}\times10^3$
0 mg	39.4	1.4	37.6	1.7	40.7	2.3	41.3	2.1
20 mg	4.41	0.9	2.72	1.2	2.93	1.1	3.54	1.2
40 mg	3.43	0.6	4.40	0.9	4.55	1.0	4.70	1.2
60 mg	3.93	0.7	4.68	1.0	4.06	0.9	4.83	1.3

spaces between hydrogel chains. Swelling of the hydrogel involves larger segmental motion resulting, ultimately, in increased separation between hydrogel chains.

Analysis of the mechanisms of water diffusion in swellable polymeric systems has received considerable attention in recent years due to the important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering [3].

The following equations are used to determine the nature of diffusion of solvent, water, in this case into hydrogels.

$$F=kt^n \tag{6}$$

where F is the fractional uptake at time t, and k is a constant incorporating characteristic of the macromolecular network system and the penetrant. n is the diffusional exponent, which is indicative of the transport mechanism. Equation 6 is valid for the first 60% of the fractional uptake. Fickian diffusion, and Case II transport are defined by n that are equal to 1/2 and 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. This is reflected on n between 1/2 and 1 [21].

For radiation induced hydrogels, ln F vs. ln t graphs is plotted and representative graphs are shown in Figure 8. n exponents and k parameters are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table 4.

Table 3. Variation of Initial Swelling Rate (r_o/g water (g gel min)$^{-1}$) and Equilibrium Swelling (Smax/g water (g gel)$^{-1}$) of AAm/CAc Hydrogels with CAc Content and Irradiation Dose

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy	
CAc	$r_o\times10^2$	S_{max}	$r_o\times10^2$	S_{max}	$r_o\times10^2$	S_{max}	$r_o\times10^2$	S_{max}
0 mg	7.45	7.24	7.88	7.00	11.00	6.98	10.86	7.23
20 mg	7.81	9.24	8.05	8.18	7.54	8.14	7.38	7.86
40 mg	6.66	10.33	6.96	8.80	7.43	8.44	8.40	8.28
60 mg	7.03	10.35	9.62	8.70	7.04	8.01	8.48	9.23

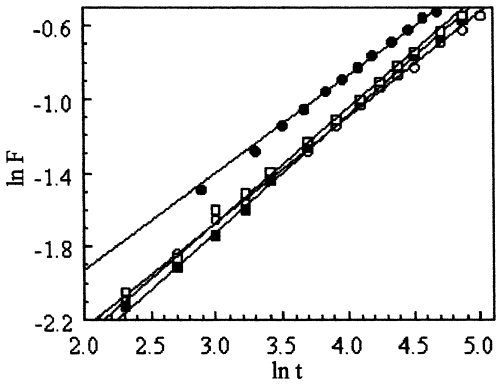


Figure 8. Plots of ln F vs. ln t for AAm/CAc copolymers. Total dose given 5.2 kGy. □, 2.60 kGy; ●, 3.73 kGy; ○, 4.65 kGy; ■, 5.20 kGy.

Table 4 shows the number determining type of diffusion (n) is over 1/2. Hence, the diffusion of water into the super water-retainer hydrogels is taken as a *non-Fickian* in character. In anomalous diffusion, solvent diffusion rate and polymer relaxation rate are about the same order of the magnitude [25].

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behavior. For hydrogel characterization, diffusion coefficient can be calculated by various methods. The short time approximation method is used for calculation of diffusion coefficients of AAm/CAc hydrogels. The short time approximation is valid for the first 60% of initial swelling.

The diffusion coefficients of the cylindrical AAm/CAc hydrogels are calculated from the following relations:

$$F = 4\left[\frac{Dt}{\pi r^2}\right]^{1/2} - \pi\left[\frac{Dt}{\pi r^2}\right] - \frac{\pi}{3}\left[\frac{Dt}{\pi r^2}\right]^{3/2} + \ldots \tag{7}$$

where D in $cm^2\ s^{-1}$, t in sec and r is the radius of cylindrical polymer sample. A graphical comparison of Equations 6 and 7 shows the semi-empirical Equation 6 with n = 0.5 and $k = 4\ (D / \pi r^2)^{1/2}$.

Table 4. Variation of n and k of Aam/CAc Hydrogels with CAc Content and Irradiation Dose

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy	
CAc	$k\times10^2$	n	$k\times10^2$	n	$k\times10^2$	n	$k\times10^2$	n
0 mg	2.62	0.64	3.39	0.56	4.99	0.53	5.04	0.53
20 mg	2.70	0.61	3.34	0.58	3.00	0.60	3.40	0.57
40 mg	2.28	0.62	2.49	0.62	2.69	0.62	2.69	0.63
60 mg	2.01	0.65	3.13	0.60	2.42	0.63	2.97	0.62

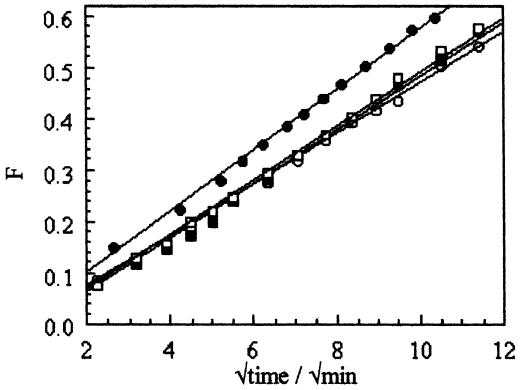


Figure 9. Plots of F vs. $t^{0.5}$ for AAm/CAc copolymers. Total dose given 5.2 kGy. ○, 0 mg CAc; ●, 20 mg CAc; □, 40 mg CAc; ■, 60 mg CAc.

For hydrogels, F vs. $t^{1/2}$ values is plotted and representative graphs are shown in Figure 9. The diffusion coefficients were calculated from the slope of the lines. The values of diffusion coefficient calculated for the hydrogels are listed in Table 5.

Table 5 shows that the values of the diffusion coefficient of the AAm/CAc hydrogels vary from 5×10^{-7} cm^2 s^{-1} to 10×10^{-7} cm^2 s^{-1}.

Network Studies

One of the most important structural parameters characterizing crosslinked polymers is M_c, the average molar mass between crosslinks that is directly related to the crosslink density. The magnitude of M_c significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine M_c. Early research by Flory and Rehner laid the foundations for analysis of equilibrium swelling. According to the theory of Flory and Rehner, for a network:

Table 5. Variation of the Diffusion Coefficient (D/cm^2 sec^{-1}) of AAm/CAc Hydrogels with CAc Content and Irradiation Dose

CAc	2.60 kGy	3.73 kGy	4.65 kGy	5.20 kGy
0 mg	8.0×10^{-7}	8.9×10^{-7}	10.0×10^{-7}	9.0×10^{-7}
20 mg	5.9×10^{-7}	5.7×10^{-7}	5.9×10^{-7}	5.5×10^{-7}
40 mg	4.9×10^{-7}	5.4×10^{-7}	6.3×10^{-7}	6.8×10^{-7}
60 mg	7.1×10^{-7}	6.5×10^{-7}	5.9×10^{-7}	6.7×10^{-7}

$$M_c = -V_1 d_p \frac{v_s^{1/3} - v_s/2}{\ln(1 - v_s) + v_s + \chi v_s^2} \tag{8}$$

where V_1 is the molar volume of solvent (mL mol^{-1}), d_p is the polymer density (g mL^{-1}), v_S is the volume fraction of polymer in the swollen gel, χ; is the Flory-Huggins interaction parameter between solvent and polymer [22].

The swelling ratio (Q) is equal to $1/v_s$. Here, the crosslink density, q, is defined as the mol fraction of crosslinked units [22].

$$q = \frac{M_o}{M_c} \tag{9}$$

where M_o is the molar mass of the repeating unit.

Since hydrogel is copolymeric structure, the molar mass of the polymer repeat unit, M_o, can be calculated with the following equation:

$$M_o = \frac{n_{AAm} \times M_{AAm} + n_{CAc} \times M_{CAc}}{n_{AAm} + n_{CAc}} \tag{10}$$

where n_{AAm} and n_{CAc} are the mol number of AAm and CAc (mol), and M_{AAm} and M_{CAc} are the molar mass of AAm and CAc (g mol^{-1}), respectively.

The polymer/solvent interaction parameter, χ, was taken to be 0.494, by analogy to those other acrylamide polymers. The density of the polymer was taken as 1.302 g cm^{-3}. Molar volume of water was taken as 18 cm^3 mol^{-1}. Finally, the swelling of AAm/CAc hydrogel was considered ideal [18]. M_c and q of AAm and AAm/CAc hydrogels are calculated and listed in Table 6.

Table 6 shows that the number-average molar mass between crosslinks of hydrogels increases with CAc content of AAm/CAc copolymeric hydrogels, while it decreases with increasing of the irradiation dose. Since AAm and CAc in hydrogels includes many hydrophilic moieties (nonionizable and ionizable), AAm/CAc hydrogels can swell significantly. Crosslink density is inverse due to the value of the number-average molar mass between crosslinks (Table 6).

Table 6. Variation of Number-Average Molar Mass Between Crosslinks (Mc/g mol^{-1}) and the Crosslink Density (q) in AAm/CAc Hydrogels with CAc Content and Irradiation Dose

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy	
CAc	M_c	$q \times 10^3$	M_c	$q \times 10^3$	M_c	$q \times 10^3$	M_c	$q \times 10^3$
0 mg	17 900	3.97	16 300	4.34	17 000	4.17	18 600	3.80
20 mg	33 700	2.14	25 200	2.86	24 500	2.94	22 100	3.25
40 mg	43 000	1.70	28 800	2.53	26 300	2.77	25 300	2.87
60 mg	43 700	1.69	39 200	1.88	31 000	2.38	25 300	2.91

Table 7. Variation of Number of Repeating Units Between Crosslinks (N) and Mesh Size (ξ/Å) of Aam/Cac Hydrogels with Cac Content and Irradiation Dose

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy	
CAc	N	ξ/Å	N	ξ/Å	N	ξ/Å	N	ξ/Å
0 mg	252	128	230	121	240	124	263	131
20 mg	468	188	350	118	340	154	308	145
40 mg	590	217	396	170	361	160	348	156
60 mg	593	218	532	204	421	176	344	156

Another important parameter of networks is gel pore size or mesh size (ξ) [23]. For determining this parameter, the end-to-end distance in the freely jointed state is determined as:

$$\bar{r}_f = l\sqrt{N} \tag{11}$$

where l=1.54 Å and the number of links, $N = \lambda M_c/M_o$ and $\lambda = 2$. The end-to-end distance in the unperturbed state is calculated through the characteristic ratio C_n=6.32:

$$\bar{r}_o^2 = C_n \bar{r}_f^2 \tag{12}$$

The end-to-end distance in the swollen state, equivalent to the mesh size, ξ, is:

$$\xi = v_s^{-1/3} r_o \tag{13}$$

The porosity (P%) of the hydrogels is:

$$P\% = \frac{V_d}{1 - V_d} \times 100 \tag{14}$$

here, V_d is the volume ratio of water imbibed to the gel phase in the equilibrium state.

The values of number of repeating units between crosslinks, N, the mesh size, ξ(Å) and porosity are shown in Tables 7 and 8.

As presented at Tables 7 and 8, the mesh size and P% increase with the CAc content of AAm/CAc hydrogels, and decrease with the increase in the irradiation

Table 8. Variation of the Percent Porosity (P%) of Aam/Cac Hydrogels with Cac Content and Irradiation Dose

CAc	2.60 kGy	3.73 kGy	4.65 kGy	5.20 kGy
0 mg	89.52	89.95	89.65	89.79
20 mg	91.86	91.02	90.94	90.63
40 mg	92.52	91.43	91.15	91.04
60 mg	92.56	92.28	91.63	91.04

doses. These are consistent with the results obtained from swelling experiments. Thus, with the ionization of the citric acid, the pores in the gel expand due to electrostatic repulsion of similarly charged groups. Accordingly, the more the ionizable groups in the gel, the more the expansion of network and the more the mesh size and porosity get.

CONCLUSION

AAm/CAc copolymeric hydrogels are prepared via the gamma irradiation method. Irradiation over maximum gelation dose (for complete gelation dose of PAAm hydrogel is 2.0 kGy) made it available to incorporate citric acid into the network. Although a relatively low amount of citric acid was used, the obtain hydrogel could show pH sensitivity. Thus, a neutral hydrogel such as pAAm can be made ionizable with the incorporation of an acid group such as citric acid by means of an irradiation technique. This study simply shows that this type of method can be used for the incorporation of desired functional group containing structure into the hydrogel network with a suitable monomer without taking into consideration the materials, and whether they have vinyl functionality or not. To impart pH sensitivity to a gel system, irradiation technique can be successfully used, and the parameters such as swelling degree, pore size, and molar mass between crosslinks can be regulated with the amount of irradiation dose.

The utilization of these types of hydrogels, in biomedicine, controlled drug delivery, pharmaceuticals, agriculture, adsorption, separation, purification, and enrichment of some species makes hydrogel more popular. Furthermore, the use of irradiation method for hydrogel synthesis is viable and very promising especially *in vivo* studies due to their innate sterility.

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