Incorporation of malonic acid into acrylamide hydrogel by radiation technique and its effect on swelling behavior

D. SARAYDIN*
Department of Chemistry, Hydrogel Res. Lab., Cumhuriyet University, 58140 Sivas, Turkey
E-mail: saraydin@cumhuriyet.edu.tr

E. KARADAĞ
Department of Chemistry, Adnan Menderes University, 09010 Aydin, Turkey

N. SAHINER, O. GÜVEN
Department of Chemistry, Hacettepe University, Beytepe, 06532 Ankara, Turkey

Different amounts of malonic acid (MAc) containing acrylamide (AAm) hydrogels were obtained in the form of rods via a radiation technique. Swelling experiments were performed in water at 25°C, gravimetrically. The influence of absorbed dose and malonic acid content of the hydrogels on swelling properties were examined. Diffusion behaviour and network parameters were investigated. Swelling of AAm/MAc hydrogels is increased up to ca. 900%, while pure AAm hydrogels swelled up to ca. 700%. Water diffusion into hydrogels was found to be *non-Fickian* in character. Diffusion coefficients of AAm/MAc hydrogels were calculated by the short time approximation and found to be 6.4×10^{-7}–10.4×10^{-7} cm^2 sec^{-1}. A possible mechanism for AAm/MAc hydrogels was also suggested. © *2002 Kluwer Academic Publishers*

1. Introduction

Hydrogels are three dimensional networks of crosslinked polymeric structures which are able to swell in aqueous media. Hydrogels are used extensively in medicine and pharmacy as drug delivery system, contact lenses, catheters, wound dressings, and biosensors [1]. One of the most powerful applications of hydrogels is in controlled release system for targeting delivery to specific areas of the body. More specifically, ionic hydrogels are used to immobilize a drug delivery device on a specific site for targeted release and optimal drug delivery due to the intimacy and extended duration of contact [1, 2]. After intimate contact is established, the rate and duration of drug release depends on the swelling behavior of the hydrogel [1, 3]. Because of the presence of carboxylic acid side groups, the swelling behavior of copolymeric acrylamide hydrogels is highly dependent on the surrounding medium [4–9].

Hydrogels can be prepared by simultaneous copolymerization and crosslinking of one or more monofunctional and one multifunctional monomer or by crosslinking of a homopolymer or copolymer in solution [10]. Hydrogels are synthesized using either chemical reagents or irradiation. In recent years, considerable research has been done on the characterization and swelling behavior of hydrogels prepared by simultaneous free-radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent.

Hydrogels can also be synthesized by crosslinking via γ-irradiation [4–9]. However, little work is done on the characterization of hydrogels prepared by crosslinking of a homopolymer or copolymer in solution with γ-irradiation [11, 12]. It is 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 argued 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 homogenity of the network affects the swelling behavior and mechanical properties.

In our previous study, copolymeric hydrogels of acrylamide with crotonic, maleic, itaconic, and also non-vinyl group containing acids such as tartaric, succinic and citric acid [4–9] were prepared and used in separation and adsorption of some ions and molecules [13–16], and biocompatibility studies [17–19]. It was of interest to increase the water absorption capacity of AAm hydrogels with non-vinyl functional groups containing chemical reagents such as malonic acid via the radiation method. Here, aqueous solutions of acrylamide and malonic acid were irradiated under γ-rays

---

*Author to whom all correspondence should be addressed.

at various doses. Swelling properties, diffusional parameters and network properties of these hydrogels were studied.

2. Experimental

To prepare hydrogel systems, acrylamide (AAm) (BDH, Poole-UK) weighing 1 g was dissolved in 1 mL aqueous solutions containing 0, 20, 40 and 60 mg malonic acid (MAc) (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. Fresh hydrogels obtained in long cylindrical shapes 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 weighted and transferred into water. Water uptake with respect to time was obtained by periodically removing the samples from water, quickly blot drying, and reweighing. The measurements were conducted at $25 \pm 0.1°C$ in a water bath.

3. Results and discussion

A network is obtained by permanently linking polymeric chains together in the form of a three-dimensional structure by high energy radiation (e, γ, UV), peroxide cures and sulphur cures. The processes are known as crosslinking, curing and vulcanization, respectively. Crosslinking can be brought about by either chemical reactions that form covalent bonds between chains or by physical aggregation of units from two or more chains. To crosslink a polymeric system, high-energy radiation

(or ionizing radiation), such as electrons (e), gamma rays (γ) and ultraviolet (UV) light can also be used [1].

The radiation technique seems promising for the preparation of hydrogels because a polymer in aqueous solution or a monomer dissolved in water undergo crosslinking on irradiation to yield a gel-like material. Since these hydrogels are not contaminated with foreign additives and crosslinks are composed of stable C—C bonds, it is of interest to study the preparation of hydrogels by irradiation [20, 21]. There are many works in the literature concerning radiation synthesis of hydrogels with vinyl monomers (acrylamide/crotonic acid [4], acrylamide/maleic acid [5], acrylamide/itaconic acid [6], vinyl imidazole/acrylonitrile [22], vinyl pyrrolidone/ acrylonitrile [23] etc.). Although it is possible to find much work on the grafting of vinyl monomers onto polymeric materials, there are very few works done on the incorporation of non-vinyl chemical reagents to polymeric networks via radiation [24]. Here, in this work we investigated the incorporation of a non-vinyl chemical such as malonic acid into acrylamide hydrogel during radiation synthesis. A mechanism for the polymerization and simultaneous crosslinking was suggested.

3.1. Preparation

Ionizing radiation was used for preparation of AAm and AAm/MAc hydrogels. When monomers of AAm and MAc are irradiated with ionization rays such as γ rays, one double bond of —C=C— on AAm and one or two of C—H bonds of MAc were broken by ionization irradiation and free radicals are generated. These free radicals react with each other, and a copolymer of AAm/MAc is produced. A possible free radical polymerization of poly(AAm/MAc) by γ rays irradiation is suggested in Scheme-1. When AAm, MAc, and water
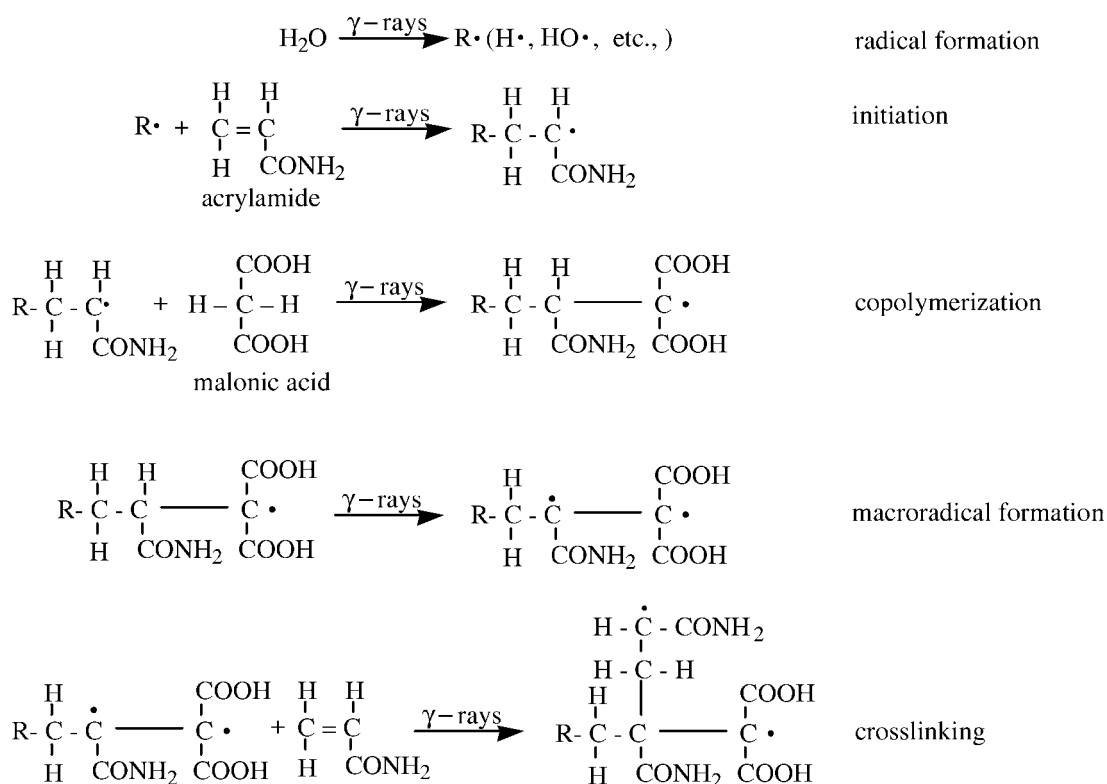
Scheme 1. Possible copolymerization and crosslinking mechanisms of acrylamide and malonic acid.

ternary mixtures were irradiated, polymerization and crosslinking occur simultaneously. It is reported that the dose for complete gelation of AAm is 2.00 kGy of γ ray irradiation at ambient temperature [25]. So, a minimum dose of 2.60 kGy of γ rays is used for the preparation of AAm/MAc hydrogels.

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

3.2. Swelling

A fundamental relationship exists 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:

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

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

The water intake of initially dry hydrogels was followed for a period of time, gravimetrically. Swelling curves of the hydrogels were constructed and representative swelling curves are shown in Figs 1 and 2.

Figs 1 and 2 show that swelling increases with time up to certain level, then levels off. This value of swelling may be called the equilibrium swelling percentage
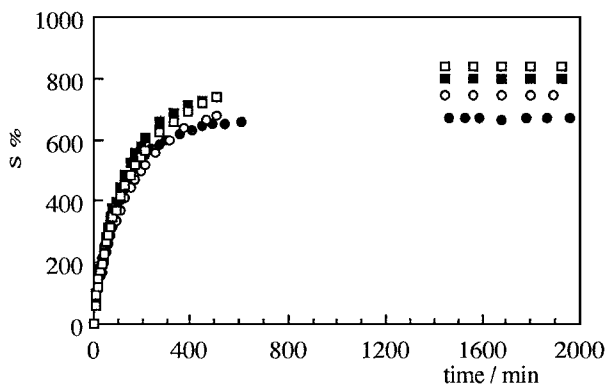

Figure 1 Combined effects of water and malonic acid on the swelling of AAm/MAc copolymers. Total dose given 4.65 kGy, -●-; 0 mg MAc, -○-; 20 mg MAc, -■-; 40 mg MAc, -□-; 60 mg MAc.
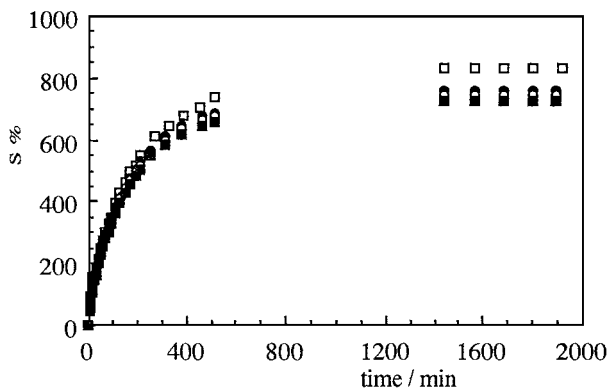

Figure 2 Combined effects of water and irradiation dose on the swelling of AAm/MAc copolymers containing 20 mg malonic acid, -□-; 2.60 kGy, -●-; 3.73 kGy, -○-; 4.65 kGy, -■-; 5.20 kGy.

TABLE I The values of $S_{eq}\%$ of AAm/MAc hydrogels

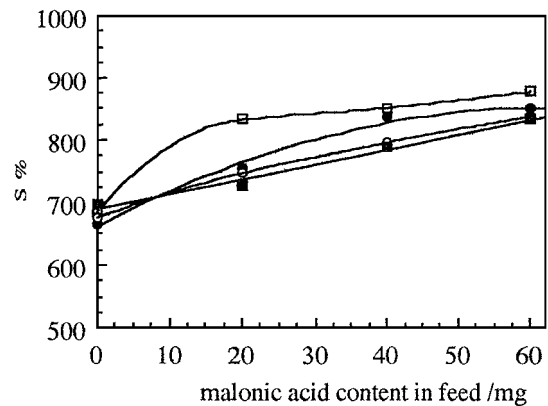| Dose	2.60 kGy	3.73 kGy	4.65 kGy	5.20 kGy
0 mg	685	665	675	695
20 mg	835	755	745	726
40 mg	850	835	796	789
60 mg	880	850	838	833

Figure 3 Variation of $S_{eq}\%$ of AAm/MAc copolymers with MAc content in feed, -□-; 2.60 kGy, -●-; 3.73 kGy, -○-; 4.65 kGy, -■-; 5.20 kGy.
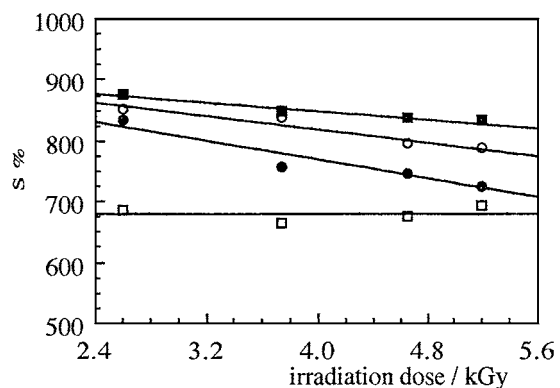

Figure 4 Variation of $S\%$ of AAm/MAc copolymers with the irradiation dose, -□-; 0 mg MAc, -●-; 20 mg MAc, -○-; 40 mg MAc, -■-; 60 mg MAc.

($S_{eq}\%$). $S_{eq}\%$ of AAm/MAc copolymers are used for the calculation of network characterization parameters. $S_{eq}\%$ of AAm/MAc copolymers are given Table I.

Table I shows that $S_{eq}\%$ of AAm are 660%–695%, but $S_{eq}\%$ of AAm/MAc hydrogels are 725–875% with the incorporation of malonic acid groups into polyacrylamide hydrogels. Hydrophilicity of AAm/MAc copolymers becomes greater than that of AAm, so, the swelling of AAm/MAc copolymers is greater than the swelling of AAm hydrogels.

For understanding the effect of MAc content, and irradiation dose on the swelling behavior, $S_{eq}\%$ of the radiation induced hydrogels versus the content of MAc and irradiation dose are plotted in Figs 3 and 4.

In Figs 3 and 4, $S_{eq}\%$ of the hydrogels decreased with the increase in the irradiation dose and, increased with the MAc content in the copolymers. $S_{eq}\%$ of AAm/MAc hydrogels is higher than $S_{eq}\%$ of pure AAm hydrogels. The reason of this is the hydrophilic groups on the MAc. The more hydrophilic groups in the AAm/MAc get the more the swelling of the AAm/MAc hydrogels.

The increase in 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 high amount adsorbed dose decrease the number average molar mass between crosslinks while low amount of adsorbed dose increase the number average molar mass between crosslinks.

3.3. Swelling kinetics

In order to examine 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/MAc chains (e.g., amine, amide, carbonyl, carboxyl or hydroxyl) imply that there are many types of polymer-solvent interactions. It is probable that any kinetics is likely to be global. From a system design viewpoint, a lumped analysis of swelling rates is thus sufficient to the practical operation.

A simple kinetic analysis is a second order equation in the form of

$$\frac{dS}{dt} = k_{2,s}(S_{eq} - S)^2 \qquad (2)$$

where $k_{2,S}$ is the rate constant of swelling and S_{eq} denotes 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

$$\frac{t}{S} = A + Bt \qquad (3)$$

where A is reciprocal of initial swelling rate r_0 or $1/k_{2,S}S_{eq}^2$ and B is inverse of the degree of swelling at equilibrium.

To test the kinetics model, t/S vs. t graphs are plotted and representative graphs are illustrated in Fig. 5. The calculated kinetic parameters are tabulated in Table II.

As can be seen from Table II, kinetics model is agreement with swelling experiments, since, as depicted in Table II, S_{eq} is increased with MAc content and decreased with irradiation doses. Again, the initial swelling rate is increased with MAc content and decreased with irradiation doses. This is plausible since the hydrophilicity of the network is enhanced with the extent of MAc groups in structure, initial swelling rate
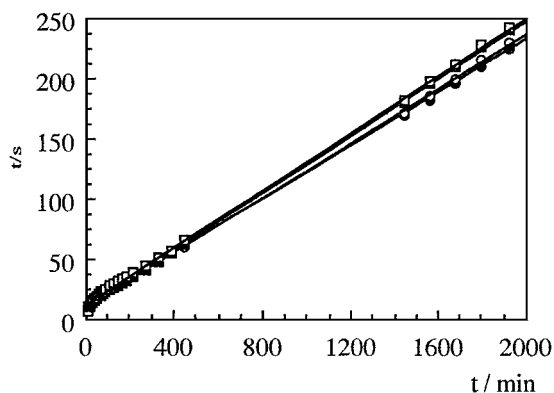

Figure 5 Plots of swelling rate for AAm/MAc copolymers containing 40 mg malonic acid, -□-; 2.60 kGy, -●-; 3.73 kGy, -○-; 4.65 kGy, -■-; 5.20 kGy.

TABLE II The values of initial swelling rate (r_0/g water (g gel min)$^{-1}$) and equilibrium swelling (S_{eq}/g water (g gel)$^{-1}$) of AAm/MAc hydrogels

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy	
MAc	$r_0 \times 10^2$	S_{eq}	$r_0 \times 10^2$	S_{eq}	$r_0 \times 10^2$	S_{eq}	$r_0 \times 10^2$	S_{eq}
0 mg	7.45	7.24	7.88	7.00	11.00	6.98	10.86	7.23
20 mg	7.26	8.93	7.56	8.05	7.36	7.95	7.11	7.74
40 mg	8.02	9.09	8.96	8.85	9.68	8.37	7.85	8.38
60 mg	9.32	9.31	9.35	8.97	7.90	8.92	9.53	8.78

should be higher. However, the increase in the absorbed dose makes the structure tighter for water to diffuse, in spite of its high hydrophilic content. So it is important to note that extent of irradiation dose determines the swelling rate by increasing hydrophilicity, but reduced the molar mass between crosslinks. So, these two phenomena compete to determining the rate of swelling.

3.4. Diffusion

When a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the network expands resulting in swelling of the hydrogel. Diffusion involves migration of water into pre-existing or dynamically formed 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 into swellable polymeric systems has received considerable attention in recent years, because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering [10].

The following equation is used to determine the nature of diffusion of water into hydrogels.

$$F = kt^n \qquad (4)$$

where F is the fractional uptake at time t, k is a constant incorporating characteristic of the macromolecular network system and the penetrant, and n is the diffusional exponent, which is indicative of the transport mechanism. Equation 4 is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by n values of 0.5 and 1, respectively. Anomalous transport behaviour (non-Fickian diffusion) is intermediate between Fickian and Case II. That is reflected by n between 1/2 and 1 [26].

For radiation induced hydrogels, $\ln F$ vs. $\ln t$ graphs are plotted and representative results are shown in Fig. 6. n exponents and k parameters are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table III.

TABLE III The values of n and k of AAm/MAc hydrogels

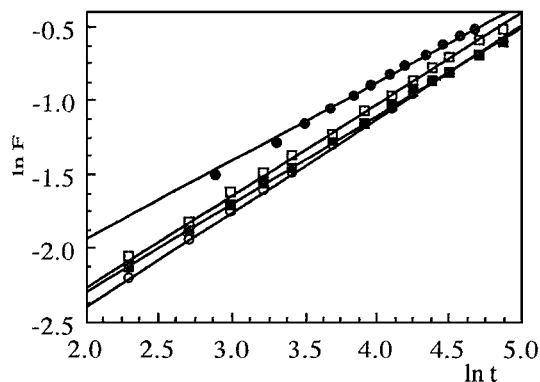| Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy	
MAc	$k \times 10^2$	n	$k \times 10^2$	n	$k \times 10^2$	n	$k \times 10^2$	n
0 mg	2.62	0.64	3.39	0.56	4.99	0.53	5.04	0.53
20 mg	2.71	0.61	2.90	0.61	2.88	0.61	2.55	0.64
40 mg	2.83	0.61	3.18	0.60	3.10	0.62	3.04	0.60
60 mg	2.95	0.61	3.32	0.59	2.81	0.61	2.97	0.62

Figure 6 Plots of ln F vs. ln t for AAm/MAc copolymers. Total dose given 4.65 kGy, -●-; 0 mg MAc, -○-; 20 mg MAc, -■-; 40 mg MAc, -□-; 60 mg MAc.

Table III shows that the number determining the type of diffusion (n) is over 0.50. Hence the diffusion of water into the super water-retainer hydrogels is generally found to have a *non-Fickian* character [26]. When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. As solvent diffuses into the hydrogel, rearrangement of chains does not occur immediately.

The study of diffusion phenomena of water in hydrogels is of value in that it clarifies polymer behavior. For hydrogel characterization, the diffusion coefficients can be calculated by various methods. The short time approximation method is used for the calculation of diffusion coefficients of AAm/MAc hydrogels. The short time approximation is valid for the first 60% of initial swelling [27].

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

$$F = 4\left[\frac{Dt}{\pi r^2}\right]^{1/2} - \pi\left[\frac{Dt}{\pi r^2}\right] - \frac{\pi}{3}\left[\frac{Dt}{\pi r^2}\right]^{3/2} + \cdots \quad (5)$$

where D is in cm^2 s^{-1}, t in sec and r is the radius of a cylindrical polymer sample. A comparison of Equations 4 and 5 shows the semi-empirical Equation 4 with $n = 0.5$ and $k = 4 (D/\pi r^2)^{1/2}$.

For hydrogels, F versus $t^{1/2}$ plots are constructed and representative results are shown in Fig. 7. The diffusion coefficients were calculated from the slope of the lines.
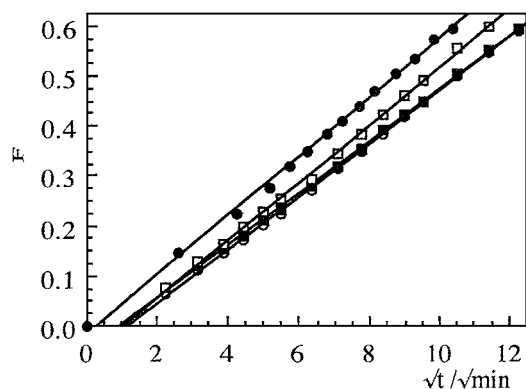

Figure 7 Plots of F vs. $\sqrt{t}$ for AAm/MAc copolymers. Total dose given 5.20 kGy, -●-; 0 mg MAc, -○-; 20 mg MAc, -■-; 40 mg MAc, -□-; 60 mg MAc.

TABLE IV The values of the diffusion coefficient (D/cm^2 sec^{-1}) of AAm/MAc hydrogels

MAc	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	8.2×10^{-7}	8.4×10^{-7}	7.7×10^{-7}	8.5×10^{-7}
40 mg	6.4×10^{-7}	8.5×10^{-7}	10.1×10^{-7}	10.4×10^{-7}
60 mg	8.8×10^{-7}	6.4×10^{-7}	5.9×10^{-7}	10.2×10^{-7}

The values of diffusion coefficient determined for the hydrogels are listed in Table IV.

Table IV shows that the values of the diffusion coefficient of the AAm/MAc hydrogels vary from 6.4×10^{-7} cm^2 s^{-1} to 10.4×10^{-7} cm^2 s^{-1}.

3.5. Network studies

An important structural parameter characterizing crosslinked polymers is M_c, the average molar mass between crosslinks which 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 the analysis of equilibrium swelling. According to the theory of Flory and Rehner, for a network:

$$M_c = -V_1 d_p \frac{v_s^{1/3} - v_s/2}{\ln(1 - v_s) + v_s + \chi v_s^2} \quad (6)$$

where V_1 is the molar volume (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[28].

The swelling ratio (Q) is equal to $1/v_s$. Here, the crosslink density, q, is defined as the mol fraction of crosslinked units [28].

$$q = \frac{M_o}{M_c} \quad (7)$$

where, M_o is the molar mass of the repeating unit.

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

$$M_o = \frac{n_{AAm} \times M_{AAm} + n_{MAc} \times M_{MAc}}{n_{AAm} + n_{MAc}} \quad (8)$$

where n_{AAm} and n_{MAc} are the mol numbers of AAm and MAc (mol) and, M_{AAm} and M_{MAc} are the molar mass of AAm and MAc (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/MAc hydrogel was considered ideal [20]. M_c and q of AAm and AAm/MAc hydrogels are calculated and listed in Table V.

Table V shows that the number-average molar mass between crosslinks of hydrogels increases with

TABLE V The values of number-average molar mass between crosslinks (M_c/g mol^{-1}) and the crosslink density (q) of AAm/MAc hydrogels

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy	
MAc	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	30 400	2.38	23 400	3.03	22 600	3.16	20 900	3.40
40 mg	32 300	2.20	30 700	2.33	26 800	3.67	26 200	2.73
60 mg	35 100	2.06	32 100	2.25	30 800	2.34	30 400	2.37

MAc content of AAm/MAc hydrogels, while it decreases with increasing irradiation dose. Since the MAc in the hydrogels includes many hydrophilic groups, AAm/MAc hydrogels can swell more than pure AAm hydrogels. For q, the results shown in Table V are conceivable, since crosslink density is inversely related to M_c.

Another important parameter of networks is gel pore size or mesh size (ξ) [26]. For determining this parameter, the end-to-end distance in the freely jointed state is determined as

$$\bar{r}_f = l\sqrt{N} \tag{9}$$

where $l = 1.54$ Å and the number of links, $N = \lambda M_c / M_o$ and $\lambda = 2$ [26]. The end-to-end distance in the unperturbed state is calculated through the characteristic ratio $C_n = 6.32$

$$\bar{r}_0^2 = C_n \bar{r}_f^2 \tag{10}$$

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

$$\xi = v_s^{-1/3} r_0 \tag{11}$$

The porosity (P%) of the hydrogels is

$$P\% = \frac{V_d}{1 - V_d} \times 100 \tag{12}$$

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

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

TABLE VI The values of number of repeating units between crosslinks (N) and mesh size (ξ/Å) of AAm/MAc hydrogels

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy	
MAc	N	ξ/Å	N	ξ/Å	N	ξ/Å	N	ξ/Å
0 mg	252	148	230	121	240	124	263	131
20 mg	426	177	330	151	316	147	293	140
40 mg	450	183	428	178	374	163	365	161
60 mg	485	192	444	182	427	178	421	176

TABLE VII The values of the porosity (P%) of AAm/MAc hydrogels

MAc	2.60 kGy	3.73 kGy	4.65 kGy	5.20 kGy
0 mg	89.52	89.95	89.65	89.79
20 mg	91.58	90.80	90.69	90.46
40 mg	91.75	91.61	91.22	91.15
60 mg	91.98	91.73	91.62	91.58

Tables VI and VII show similar results and identical behavior of M_c of AAm/MAc hydrogels with changing MAc content and irradiation dose.

4. Conclusion

Incorporation of non-vinyl group containing chemicals such as MAc in AAm hydrogels can be obtained successively by a radiation method. Even using relatively low amounts of MAc during polymerization and crosslinking remarkably affect the swelling behavior of AAm/MAc hydrogels from ∼700 to ∼900% with a low irradiation dose. A mechanism for the polymerization and crosslinking has been proposed and the effect of radiation dose and MAc content on swelling %, M_c, porosity etc. were found to be in accordance with those of vinyl group containing hydrogels obtained with radiation.

This type of work could encourage the synthesis of new hydrogels, where some functionalities are required, for specific purposes. This is under investigation for the separation and selectivity of special spices. The new hydrogels reported can be used to carry substances in an aquatic field for pharmaceutical, agricultural, environmental and biomedical applications.

References
1. E. JABBARI and S. NOZARI, *Eur. Polym. J.* **36** (2000) 2685.
2. I. KAETSU, K. UCHIDA, H. SHINDO, S. GOMI and K. SUTANI, *Radiat. Phys. Chem.* **55** (1999) 193.
3. I. KATIME, R. NOVOA, E. DIAZ DE APODACA, E. MENDIZÀBAL and J. PUIG, *Polym. Testing* **18** (1999) 559.
4. D. SARAYDIN, E. KARADAĞ and O. GÜVEN, *Tr. J. Chemistry* **19** (1995) 179.
5. *Idem.*, *Polym. Adv. Technol.* **6** (1995) 719.
6. E. KARADAĞ, D. SARAYDIN and O. GÜVEN, *Macromol. Mater. Eng.* **286** (2001) 34.
7. *Idem.*, *Ir. J. Polym. Sci. Technol.* **4** (1995) 218.
8. D. SARAYDIN, E. KARADAĞ and O. GÜVEN, *Polym. J.* **29** (1997) 631.
9. E. KARADAĞ, D. SARAYDIN, N. SAHINER and O. GÜVEN, *J. M. S. Pure Appl. Chem.* A **38** (2001) 1105.
10. A. M. MARTHUR, S. K. MOORJANI and A. B. SCRANTON, *J. M. S.-Rev. Macromol. Chem. Phys.* C **36** (1996) 405.
11. Ö. KANTOĞLU, M. ŞEN and O. GÜVEN, *Nucl. Instr. and Meth. in Phys. Res.* B **151** (1999) 218.
12. N. SAHINER, N. PEKEL, P. AKKAS and O. GÜVEN, *J. M. S.-Pure Appl. Chem.* A **37** (2000) 1159.
13. O. GÜVEN, M. ŞEN, E. KARADAĞ and D. SARAYDIN, *Radiat. Phys. Chem.* **56** (1999) 561.

14. D. SARAYDIN, E. KARADAĞ and O. GÜVEN, *Sep. Sci. Technol.* **30** (1995) 3291.
15. *Idem., J. Appl. Polym. Sci.* **79** (2001) 1809.
16. D. SARAYDIN, E. KARADAĞ, Y. ÇALDIRAN and O. GÜVEN, *Radiat. Phys. Chem.* **60** (2001) 203.
17. D. SARAYDIN, E. KARADAĞ, S. ÇETINKAYA and O. GÜVEN, *ibid.* **46** (1995) 1049.
18. E. KARADAĞ, D. SARAYDIN, S. ÇETINKAYA and O. GÜVEN, *Biomaterials* **17** (1996) 664.
19. D. SARAYDIN, E. KOPTAGEL, S. Ü. SARAYDIN, E. KARADAĞ and O. GÜVEN, *J. Mater. Sci.* **36** (2001) 2473.
20. J. ROSIAK, K. BURCZAK, T. CZOLOZYNSKA and W. PEKALA, *Radiat. Phys. Chem.* **22** (1983) 907.
21. J. ROSIAK, K. BURCZAK, W. PEKALA, N. PISLEVSKI, S. IDZIAK and A. CHARLESBY, *ibid.* **32** (1988) 793.
22. N. PEKEL, N. SAHINER and O. GÜVEN, *ibid.* **59** (2000) 485.
23. N. SAHINER, D. SARAYDIN, E. KARADAĞ and O. GÜVEN, *Polym. Bull.* **41** (1998) 371.
24. H. BODUGÖZ, N. PEKEL and O. GÜVEN, *Radiat. Phys. Chem.* **55** (1999) 667.
25. J. ROSIAK, K. BURCZAK, T. CZOLOZYNSKA and W. PEKALA, *ibid.* **22** (1983) 917.
26. D. HARIHARAN and N. A. PEPPAS, *Polymer* **37** (1996) 149.
27. J. M. ROSIAK and P. ULANSKI, *Radiat. Phys. Chem.* **55** (1999) 139.
28. Z. Y. DING, J. J. AKLONIS and R. SALOVEY, *J. Polym. Sci.: Part B: Polym. Phys.* **29** (1991) 1035.