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Super Water-Retainer Hydrogels: Crosslinked Acrylamide/Succinic Acid Copolymers

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ABSTRACT: Super water-retainer hydrogels in the rod form were prepared by copolymerization of acrylamide and succinic acid monomers with γ radiation. Swelling took place in water at 25°C and was followed by weighing. The influence of dose and relative content of succinic acid on the swelling properties, diffusional behavior of water, diffusion coefficients and network properties of hydrogel systems were examined. Acrylamide/succinic acid hydrogels were swollen in the range of 750—960%, while polyacrylamide hydrogels at 650—700%. Water diffusion into hydrogels was *non-Fickian* type diffusion. Diffusion coefficients of acrylamide/succinic acid hydrogels were calculated by the short time approximation as 4.6×10^{-7}—7.9×10^{-7} cm^2 s^{-1}.

KEY WORDS Acrylamide-Succinic Acid / Hydrogel / Swelling /

Hydrogels are interesting and have both liquid-like and solid-like properties.[1-10] The liquid-like properties result from the fact that the major constituent of gels is usually a liquid, *e.g.*, water. A hydrogel can be viewed as a container of water made of a three-dimensional mesh. In a dried state, a gel is a solid material. However, a hydrogel swells until it reaches the swelling equilibrium when water is added. Water molecules are kept in the three-dimensional mesh and the combination of mesh and water molecules creates a "world" having characteristic properties. This world can be either isolated from (isochore) or linked to (isobar) its surrounding world by changing the population, *i.e.*, water molecules.[4] Hydrogels have widespread applications in the bioengineering, biomedicine, pharmaceutical, food industry, veterinary, agricultural, environmental and related fields.[11-15]

Polyacrylamide (PAAm) hydrogels and derivatives are used much. PAAm hydrogels have capability of water absorption and biocompatibility with physiologic body fluids.[16-20]

In our previous study, acrylamide based hydrogels such as acrylamide/crotonic acid,[21] acrylamide/maleic acid,[22] acrylamide/itaconic acid,[23] and acrylamide/tartaric acid[24] were prepared and used in adsorptions of some heavy metal ions,[25] uranyl ions,[26] basic dyes,[27-30] bovine serum albumin,[19,31] and biocompatibility studies.[20,32] Increasing water absorption capability of AAm hydrogels with the addition of succinic acid containing hydrophilic groups is purposed. Here aqueous solutions of acrylamide and succinic acid were irradiated under γ-rays at various doses. Swelling properties, diffusional parameters and network properties of hydrogels were studied.

EXPERIMENTAL

For preparation of super water-retainer hydrogel systems, acrylamide (AAm) (B.D.H., Poole-UK) weighing 1 g was dissolved in 1 mL aqueous solutions of 0, 20, 40, and 60 mg succinic acid (SA) (B.D.H., Poole-UK). The solutions were placed in PVC straws of 4 mm diameter and irradiated at 2.60, 3.73, 4.65, 5.20, and 5.71 kGy in air at ambient temperature in a ^{60}Co Gammacell 220 type γ irradiator at a fixed dose rate of 0.72 kGy h^{-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.

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

RESULTS AND DISCUSSION

A radiation technique seems promising for preparation of hydrogels because a polymer in aqueous solution or water-swollen state readily undergoes crosslinking on irradiation to yield a gel-like material. Since this hydrogel is not contaminated with foreign additives and crosslink must be composed of stable C–C bonds, it is of interest to study the preparation of hydrogels by irradiation.[16,17]

Preparation

Ionizing radiation was used for preparation of AAm and AAm/SA copolymers. When monomers of AAm and SA 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 SA were broken by ionization irradiation and free radicals are generated. These free radicals react with each other, and a copolymer of AAm/SA is produced. A possible free radical polymerization reaction of poly(AAm/SA) by γ rays irradiation is shown in Scheme 1. When irradiation dose is increased during ionizing radiation of AAm, SA, and water ternary mixtures, the polymer chains crosslink and gel is obtained. Oxygen does not affect the polymerization of AAm.[33] It is reported that complete gelation of AAm is 2.00 kGy

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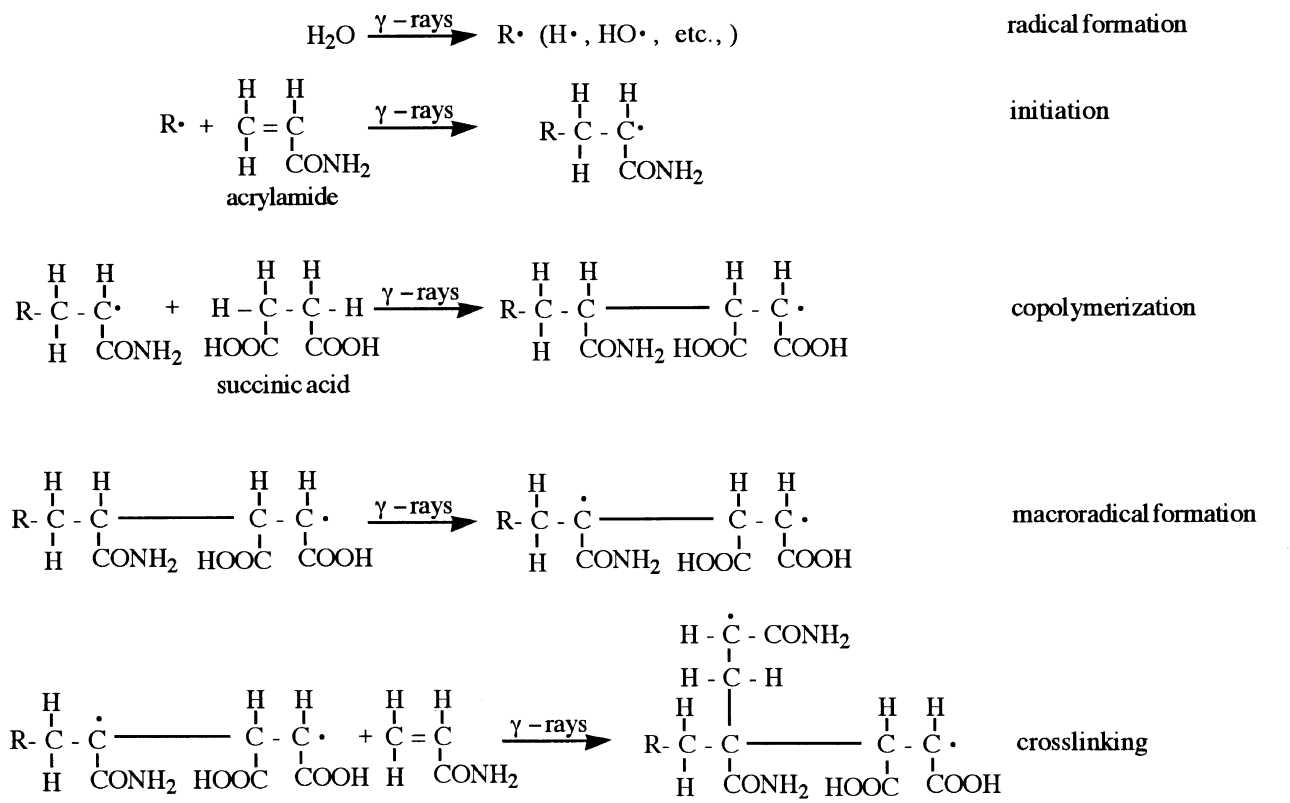

Scheme 1. Possible copolymerization and crosslinking mechanisms of acrylamide and succinic acid.

of γ rays irradiation doses at ambient temperature.[34] So, a dose of 2.60 kGy of γ rays is used for preparation of AAm/SA hydrogels.

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

Swelling

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent.[35,36] The mass swelling [$\%S(m)$] of the super water-retainer hydrogels in distilled water was calculated from the following relation[35]

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

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 long time. Swelling curves of the hydrogels are plotted and representative swelling curves are shown in Figures 1 and 2.

Figures 1 and 2 show that swelling is increased by time, but after some time, it shows constant swelling. This value of swelling may be named mass equilibrium swelling (MES). MES of AAm/SA copolymers are used for the calculation of some network characterization parameters. MES of AAm/SA copolymers are given Table I.

To determine the volumetric equilibrium swelling (VES), it is necessary to place a sample of known density in the chosen solvent until mass measurements indicate

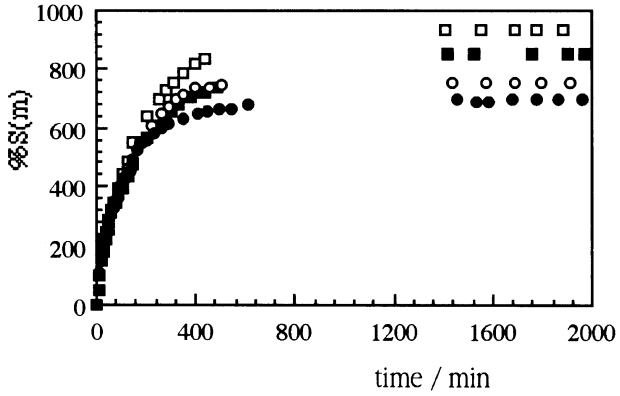

Figure 1. Combined effects of water and succinic acid on the swelling of AAm/SA copolymers. Total dose given 5.2 kGy. —●—, 0 mg SA; —○—, 20 mg SA; —■—, 40 mg SA; —□—, 60 mg SA.

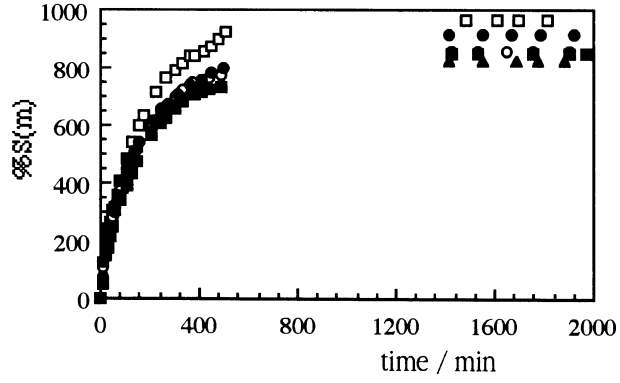

Figure 2. Combined effects of water and irradiation dose on the swelling of AAm/SA copolymers containing 40 mg succinic acid. —□—, 2.60 kGy; —●—, 3.73 kGy; —○—, 4.65 kGy; —■—, 5.20 kGy; —▲—, 5.71 kGy.

Table I. Variation of MES and VES of AAm/SA hydrogels with SA content and irradiation dose

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy		5.71 kGy	
SA	MES	VES	MES	VES	MES	VES	MES	VES	MES	VES
0 mg	685	895	665	865	675	880	695	910	695	910
20 mg	875	1140	855	1120	825	1080	755	985	755	990
40 mg	965	1260	915	1200	860	1125	855	1115	825	1080
60 mg	965	1260	940	1230	950	1240	935	1220	850	1110

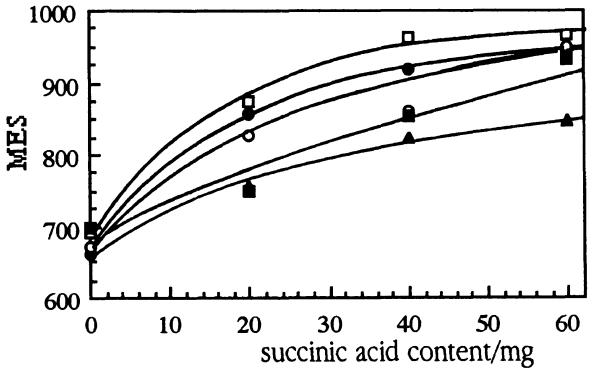

Figure 3. Variation of MES of AAm/SA copolymers with SA content in hydrogels. —□—, 2.60 kGy; —●—, 3.73 kGy; —○—, 4.65 kGy; —■—, 5.20 kGy; —▲—, 5.71 kGy.

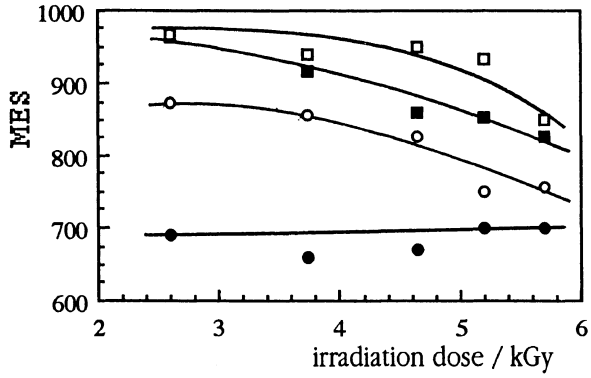

Figure 4. Variation of MES of AAm/SA copolymers with the irradiation dose. —●—, 0 mg SA; —○—, 20 mg SA; —■—, 40 mg SA; —□—, 60 mg SA.

the cessation of uptake of liquid by the polymer. If nothing is extractable and if all imbibed solvent causes swelling, Volumetric swelling; $\%S(v)$, is given by

$$\%S(V)=\frac{(m_t-m_0)d_p}{m_0 d_s}\times 100 \qquad (2)$$

where d_s and d_p are the water density and polymer density, respectively.[37] m_0 and m_t were defined earlier.

VES of AAm/SA hydrogels is given in Table I.

Table I shows that MES of AAm are 650—700%, but MES of AAm/SA super water-retainer hydrogels are 750—960%. VES are varied similarly as the results of MES. VES of AAm/SA super water-retainer hydrogels are varied at 1000—1260%. Hydrophilic groups of AAm/SA copolymers are greater than those of AAm, so, the swelling of AAm/SA copolymers is greater than swelling of AAm hydrogels.

For understanding the effect of the content of SA in the super water-retainer hydrogels and γ rays dose, MES

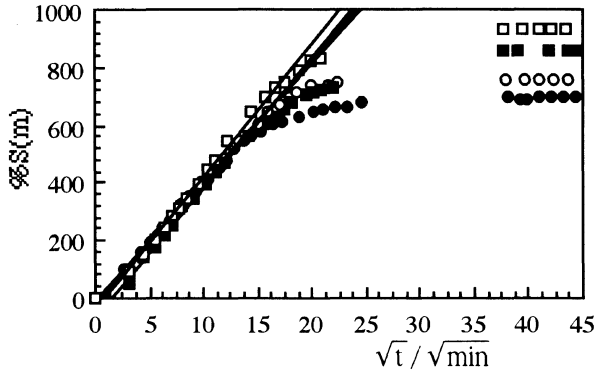

Figure 5. Plots of swelling rate for AAm/SA copolymers. Total dose given 5.20 kGy. —●—, 0 mg SA; —○—, 20 mg SA; —■—, 40 mg SA; —□—, 60 mg SA.

Table II. Variation of the swelling rate constant (k_s) of AAm/SA hydrogels with SA content and irradiation dose

SA	2.60 kGy	3.73 kGy	4.65 kGy	5.20 kGy	5.71 kGy
0 mg	39.43	37.55	40.74	41.31	40.60
20 mg	46.11	60.03	49.60	44.94	41.70
40 mg	50.58	47.17	49.98	46.98	46.24
60 mg	49.62	49.33	49.99	49.15	46.45

of the hydrogels *versus* the content of SA and γ rays dose are plotted in Figures 3 and 4.

In Figures 3 and 4, MES of the super water-retainer hydrogels is decreased with increase of irradiation dose and, increased with the SA content in the copolymers. MES of AAm/SA hydrogels is higher than MES of AAm hydrogels. The reason of this is the hydrophilic groups on the SA. The more the hydrophilic groups on the SA, the more swelling on the AAm/SA hydrogels.

If γ ray dose increases during ionizing radiation of AAm, SA, and water ternary mixtures, the number of the small chains increases at unit copolymerization time, and the crosslink density of the hydrogels is higher than the lower γ ray doses, and at the same time, the number-average molar mass of the polymer between crosslinks, is smaller than the lower γ ray dose.

For examination of swelling characteristic of AAm/SA super water-retainer hydrogels, other important parameter is swelling rate coefficient. This parameter is about swelling ability of hydrogel system. To determine the swelling rate coefficient, swelling *vs.* the square root of immersion time was plotted, and representative curves are shown in Figure 5. Swelling rate coefficients were calculated from the slopes of the straight portion of the curves[38] in Figure 5, and are tabulated in Table II.

Table II shows that the similar results and identical

behavior of swelling of AAm/SA hydrogels with the changing content of SA and irradiation dose.

Diffusion

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 spaces between hydrogel chains. Swelling of the hydrogel involves larger segmental motion resulting, ultimately, in increased separation between hydrogel chains.[39-44]

Analysis of the mechanisms of water diffusion in swellable polymeric systems has received considerable attention in recent years, because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering.[45-49]

The following equations are used to determine the nature of diffusion of water into hydrogels.

$$F=kt^n \tag{3}$$

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 3 is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by n equal to 1/2 and n equal to 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. This is reflected by anomalous behavior defined by values of n between 1/2 and 1.[50]

For super water-retainer hydrogels, ln F *vs.* ln t graphs is plotted and representative results are shown in Figure 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 shows the number determining type of diffusion (n) is over 0.50. Hence the diffusion of water into the super water-retainer hydrogels is generally taken as a *non-Fickian* character.[50] When diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. As the solvent diffuses into the hydrogel, rearrangement of chains does not occur immediately.

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behavior.[51] For hydrogel characterization, diffusion coefficient can be calculated by various methods.[51-55] The short time approximation method is used for calculation of diffusion coefficients of AAm/SA hydrogels.[52] The short time approximation is valid for the first 60% of swelling.

The diffusion coefficients of the cylindirical AAm/SA hydrogels are calculated from the following relations:

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

Where D in $cm^2 s^{-1}$, t in second and r is the radius of cylindrical polymer sample. A graphical comparation of eq 3 and 4 shows the semi-empirical eq 3 with $n=0.5$ $k=4(D/\pi r^2)^{1/2}$.

For hydrogels, F *versus* $t^{1/2}$ plots is plotted and representative results are shown in Figure 6. The diffusion coefficients were calculated from the slope of the lines. The values of diffusion coefficient determined for the super water-retainer hydrogels are listed in Table IV.

Table IV shows that the values of the diffusion coefficient of the AAm/SA hydrogels vary from 4.6×10^{-7} $cm^2 s^{-1}$ to 7.9×10^{-7} $cm^2 s^{-1}$.

Network Studies

One important structural parameter characterizing

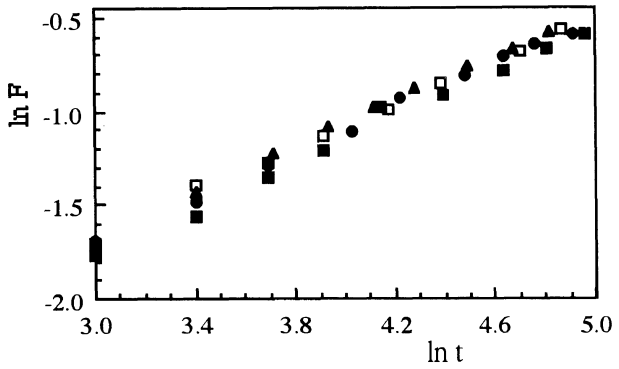

Figure 6. Plots of ln F *vs.* ln t for AAm/SA copolymers containing 40 mg SA. —□—, 2.60 kGy; —●—, 3.73 kGy; —■—, 5.20 kGy; —▲—, 5.71 kGy.

Table III. Variation of n and k of AAm/SA hydrogels with SA content and irradiation dose

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy		5.71 kGy	
SA	$k\times10^2$	n	$k\times10^2$	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	4.95	0.53
20 mg	3.30	0.58	2.54	0.64	4.35	0.56	3.45	0.60	3.37	0.60
40 mg	3.35	0.58	3.54	0.56	3.10	0.60	2.72	0.61	2.71	0.64
60 mg	4.80	0.51	3.30	0.58	3.64	0.57	2.35	0.65	2.52	0.65

Table IV. Variation of the diffusion coefficient ($D\,cm^{-2}s^{-1}$) of AAm/SA hydrogels with SA content and irradiation dose

SA	2.60 kGy	3.73 kGy	4.65 kGy	5.20 kGy	5.71 kGy
0 mg	8.0×10^{-7}	8.9×10^{-7}	10.0×10^{-7}	9.0×10^{-7}	9.6×10^{-7}
20 mg	5.8×10^{-7}	5.0×10^{-7}	6.6×10^{-7}	6.9×10^{-7}	6.2×10^{-7}
40 mg	5.3×10^{-7}	5.8×10^{-7}	6.1×10^{-7}	4.6×10^{-7}	6.6×10^{-7}
60 mg	7.9×10^{-7}	7.2×10^{-7}	7.0×10^{-7}	5.3×10^{-7}	7.0×10^{-7}

crosslinked polymers is M_c, the average molar mass between crosslinks 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

$$M_c = -V_1 d_p \frac{v_s^{1/3} - v_s/2}{\ln(1-v_s) + v_s + \chi v_s^2} \quad (5)$$

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.[56]

The swelling ratio (Q) is equal to $1/v_s$. Here, the crosslink density, q, is defined as the mol fraction of crosslinked units.[56]

$$q = M_0/M_c \quad (6)$$

where, M_0 is the molar mass of the repeating unit.

Other authors define a crosslink density, v_e, as the number of elastically effective chains, totally included in a network, per unit volume. v_e is simply related to q since

$$v_e = d_p N_A/M_c \quad (7)$$

where N_A is Avogadro number.

Since hydrogel is copolymeric structure, the molar mass of the polymer repeat unit, M_0, can be calculated following equation,

$$M_0 = \frac{n_{AAm} \times M_{AAm} + n_{SA} \times M_{SA}}{n_{AAm} + n_{SA}} \quad (8)$$

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

V_1, d_p, and χ were taken from related literature.[16,57,58] M_c, q, and v_e of AAm and AAm/SA hydrogels are calculated and listed in Tables V and VI.

Table V. Variation of number-average molar mass between crosslinks (M_c) in AAm/SA hydrogels with SA content and irradiation dose

SA	2.60 kGy	3.73 kGy	4.65 kGy	5.20 kGy	5.71 kGy
0 mg	17900	16300	17000	18600	18600
20 mg	34500	32800	29800	23300	23400
40 mg	45000	39500	33600	32400	29700
60 mg	45100	42300	43300	41200	32100

Table V shows that the number-average molar mass between crosslinks of hydrogels increases with SA content of AAm/SA hydrogels while it decreases with increasing of irradiation dose. Because the SA in hydrogels includes many hydrophilic groups, AAm/SA hydrogels can swell much. Crosslink density and the number of elastically effective chains are inverse due to the value of the number-average molar mass between crosslinks (Table VI).

An other important parameter of networks is gel pore size or mesh size (ξ).[59] For determining this parameter, the end-to-end distance in the freely jointed state is determined as

$$\bar{r}_f = l\sqrt{N} \quad (9)$$

where $l = 1.54$ Å and the number of links, $N = \lambda M_c/M_0$ and $\lambda = 2$. The end-to-end distance in the unperturbed state is calculated through the characteristic ratio $C_n = 10$

$$\bar{r}_0^2 = C_n \bar{r}_f^2 \quad (10)$$

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

$$\xi = v_s^{-1/3} r_0 \quad (11)$$

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

Table VII is shown similar results and identical behavior of M_c of AAm/SA hydrogels with changing content of SA and irradiation dose.

CONCLUSION

For AAm/SA super water-retainer hydrogels, favorable SA contents are in the range of 20—60 mg SA and favorable irradiation, 2.60—5.71 kGy. AAm/SA copoly-

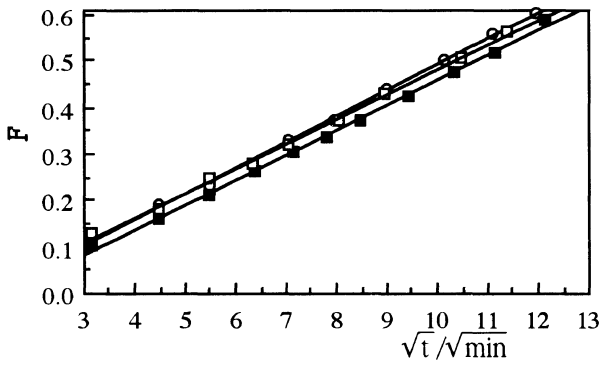

Figure 7. Plots of F *vs.* $\sqrt{t}$ for AAm/SA copolymers containing 60 mg SA. —□—, 2.60 kGy; —○—, 4.65 kGy; —■—, 5.20 kGy.

Table VI. Variation of the crosslink density (q) and the number of elastically effective chains (v_e) of AAm/SA hydrogels with SA content and irradiation dose

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy		5.71 kGy	
SA	$q \times 10^3$	$v_e \times 10^{-18}$	$q \times 10^3$	$v_e \times 10^{-18}$	$q \times 10^3$	$v_e \times 10^{-18}$	$q \times 10^3$	$v_e \times 10^{-18}$	$q \times 10^3$	$v_e \times 10^{-18}$
0 mg	3.97	43.76	4.34	47.87	4.17	46.01	3.80	41.93	3.82	42.12
20 mg	2.08	22.69	2.19	23.91	2.40	26.29	3.07	33.62	3.06	33.45
40 mg	1.62	17.43	1.85	19.85	2.17	23.55	2.25	24.19	2.46	26.39
60 mg	1.67	17.36	1.78	18.54	1.74	18.10	1.83	19.02	2.35	24.43

Table VII. Variation of number of repeating units between crosslinks (N) and mesh size (ξ/Å) of AAm/SA hydrogels with SA content and irradiation dose

Dose	2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy		5.71 kGy	
SA	N	ξ	N	ξ	N	ξ	N	ξ	N	ξ
0 mg	252	148	230	160	240	152	263	165	262	164
20 mg	964	340	915	330	832	310	651	267	654	267
40 mg	1231	397	1081	336	921	331	887	332	813	307
60 mg	1198	392	1122	376	1150	382	1094	371	851	317

mers swelled 750—960%, while polyacrylamide swelled 650—700%. Water diffusion to AAm/SA hydrogels was of *non-Fickian* type diffusion.

The number-average molar mass between crosslinks increased with SA in the hydrogels and decreased by increasing irradiation, while crosslink density and numbers of elastically effective chains decreased by increasing SA in the hydrogels and increased with irradiation doses.

Highly swollen AAm/SA hydrogels can thus be used a super water-retainers for carrying substances in aquatic fields involving pharmaceutical, agricultural, environmental, and biomedical applications.

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