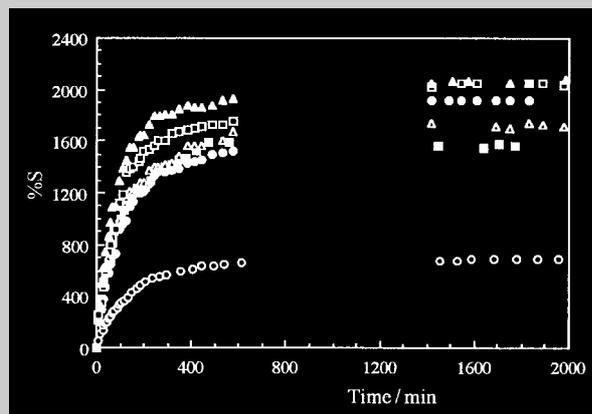**Full Paper:** Acrylamide/itaconic acid hydrogels in the form of rods are prepared by γ-irradiation of ternary mixtures of acrylamide/itaconic acid/water with 2.00–5.71 kGy γ-rays. Spectroscopic and thermal characterization of the copolymers were examined. Dynamic and equilibrium swelling behavior of superabsorbent acrylamide/itaconic acid hydrogels was investigated in water. The equilibrium swelling degree, the swelling rate coefficient, the diffusion constant, the diffusion exponent, the diffusion coefficient, and the intrinsic diffusion coefficient of acrylamide/ itaconic acid hydrogels were calculated. The superabsorbent hydrogels have shown mass swelling capabilities in the range 650–700% (for polyacrylamide hydrogels) and 900–2100% (for acrylamide-itaconic acid hydrogels). Diffusion type of the hydrogels is non-Fickian diffusion. The equilibrium swelling studies were used to determine important parameters of the crosslinked structure of the hydrogels, including the average molar mass between crosslinks and crosslink density.

Swelling vs. time curves of AAm/IA hydrogels; total irradiation dose 2.6 kGy; (○) 0 mg IA, (■) 20 mg IA, (Δ) 30 mg IA, (●) 40 mg IA, (□) 50 mg IA, (▲) 60 mg IA.

Radiation Induced Superabsorbent Hydrogels. Acrylamide/Itaconic Acid Copolymers

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Introduction

Hydrogels are interesting objects which 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. On the other hand, a gel can retain its shape since it has a shear modulus which becomes apparent if the gel is deformed. The modulus is due to the crosslinking of the polymers in the form of a network. These aspects represent the solid nature of gels. In addition to these liquid- and solid-like aspects, a gel can change its state drastically, similar to the way a gas changes its volume more than thousand-fold.[4] A hydrogel can be viewed as a container of water made of a three-dimensional mesh. In dry 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" of 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 find widespread applications in the biomedicine, bioengineering, pharmaceutical, veterinary medicine, food industry, agriculture and related fields. Hydrogels are used as controlled release systems of drugs and some physiological body fluids, production of artificial organs and contact lenses in biomedicine, as an absorbent in environmental applications for the removal of some undesired agents such as waste water of sanitary, agricultural, and industrial sources.[11–15] Polyacrylamide (PAAm) hydrogels and their derivatives were the subject of many studies. PAAm hydrogels have proven capability of water absorption and biocompatibility with physiologic body fluids.[16–20] In our previous study, acrylamide-maleic acid hydrogels containing a number of hydrophilic groups have been used for the adsorption of some heavy metal ions,[21] basic dyes,[22, 23] bovine serum albumin,[24]

and the preparation and characterization of acrylamide-maleic acid have been investigated.[25]

In this study, it is purposed to improve the capability of water absorption of PAAm hydrogels by addition of itaconic acid containing many hydrophilic groups. The novel AAm/IA superabsorbent hydrogels were used for adsorption of basic dyes,[26, 27] uranyl ions,[28] and bovine serum albumin,[29] and in biocompatibility studies.[30]

Experimental Part

Synthesis

Acrylamide and itaconic acid were purchased from B.D.H. (Poole-LJK). For the preparation of copolymer systems, acrylamide (AAm, 1 g) is dissolved in 1 mL of aqueous solutions containing 0, 20, 30, 40, 50 or 60 mg of itaconic acid (IA). Then these solutions are placed into PVC straws and irradiated with γ-rays in a ^{60}Co Gammacell 220 type γ-irradiation source at a fixed dose rate of 0.72 kGy h^{-1}, the dose rate being determined by the conventional Fricke dosimeter. Crosslinked copolymers obtained in long cylindrical shapes are cut into pieces of 3–4 mm length. They are washed and thoroughly rinsed with distilled water, blot dried with filter paper, and then dried in air and vacuum before storage.

Analysis

For spectroscopic characterization of the dried samples, a photoacoustic unit of a Nicolet 520 model Fourier-Transform Infrared Spectrophotometer was used, because the dried copolymers are too hard for the preparation of KBr discs.

Thermal characterization of the dried samples was performed to study the variation of the glass transition temperature of the copolymers. For this purpose, differential scanning calorimetry (DSC) thermograms were taken on a DuPont 9900 model thermal analyser. About 10 mg of samples were heated under dynamic nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

The dried crosslinked copolymers were accurately weighed and transferred into water in a 100 mL beaker. The water uptake with respect to time was obtained by periodically taking 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

Preparation

For the preparation of acrylamide and acrylamide/itaconic acid superabsorbent hydrogels, ionizing radiation processing is used.[31–[34]

Ionizing radiation such as ^{60}Co γ-radiation is very useful in producing polymers from monomeric units and in modifying the properties of pre-existing polymers. Ionizing radiation provides a very clean method for the production and modification of polymers. No chemicals or catalysts have to be added to the reaction matrix. The polymerization is achieved by free radicals (occasionally ions) created in the material at the end of process. Therefore, no chemicals or catalysts remain in the material after radiation.[32]

When acrylamide and itaconic acid are irradiated with ionizing radiation such as γ-rays in aqueous solutions, free radicals are generated. Random reactions of these radicals with the monomers lead to the formation of copolymers of acrylamide/itaconic acid. When the irradiation dose is increased beyond a certain value the polymer chains crosslink and then a gel is obtained. Possible copolymerization and crosslinking reaction mechanisms between acrylamide and itaconic acid monomers are shown in Scheme 1.

It has been reported that complete gelation of acrylamide occurs at irradiation doses of 2.00 kGy of γ-rays at ambient temperature[34]. Hence, an γ-irradiation dose of 2.00 kGy is based for the preparation of the hydrogels.

The radiation technique is used as a sterilization method in many applications; during polymerization and crosslinking reactions, all monomers are reacted at the applied γ-irradiation. This process is used for simultaneous sterilization of hydrogel systems. It can be stated that there is no monomer (such as toxic acrylamide) at the end of the copolymerization and crosslinking reaction between acrylamide and itaconic acid, because 2.00 kGy is a sufficient dose for gelation[34].

The dried copolymers described here are glassy and very hard, but the swollen gels are very soft. The crosslinked copolymers were obtained in the form of cylinders. Upon swelling the hydrogels retained their shapes. If 80–100 mg of IA was used in the preparation of superabsorbent hydrogels, during swelling tests the hydrogels show some deformation, dispersion and dissolution.

For the understanding of binding and crosslinking of the samples during the polymerization, FTIR spectra of the dried crosslinked copolymers of AAm/IA are evaluated. FTIR spectra of the copolymers containing 0–60 mg of IA are presented in Figure 1.

In the spectra, the bands at about 1700 cm^{-1} and 3200–3600 cm^{-1} are important. The bands at about 1700 cm^{-1} could be attributed to the shift in the stretching vibration associated with hydrogen that is bonded directly to a carbonyl carbon atom. The peak at 1650 cm^{-1} indicates the carbonyl group of the amide functions. Absorption peaks in the region of 3200 and 3600 cm^{-1} are attributed to O—H and N—H bands.

The peak at 3600 cm^{-1} is characteristic of a primary amine, the 1550 cm^{-1} signal is attributed to an O—H band related to a carbonyl group, and peaks at 1725–1700 cm^{-1} characterize C=O groups in carboxylic acids. It is stated that the peak at 1200 cm^{-1} is related to a C—N band and the peak at 1400 cm^{-1} is related to —CH$_2$— groups on the chains.[35]

$$H_2O \xrightarrow{\gamma-rays} R\cdot \ (H\cdot, HO\cdot, etc.,) \qquad \text{radical formation}$$
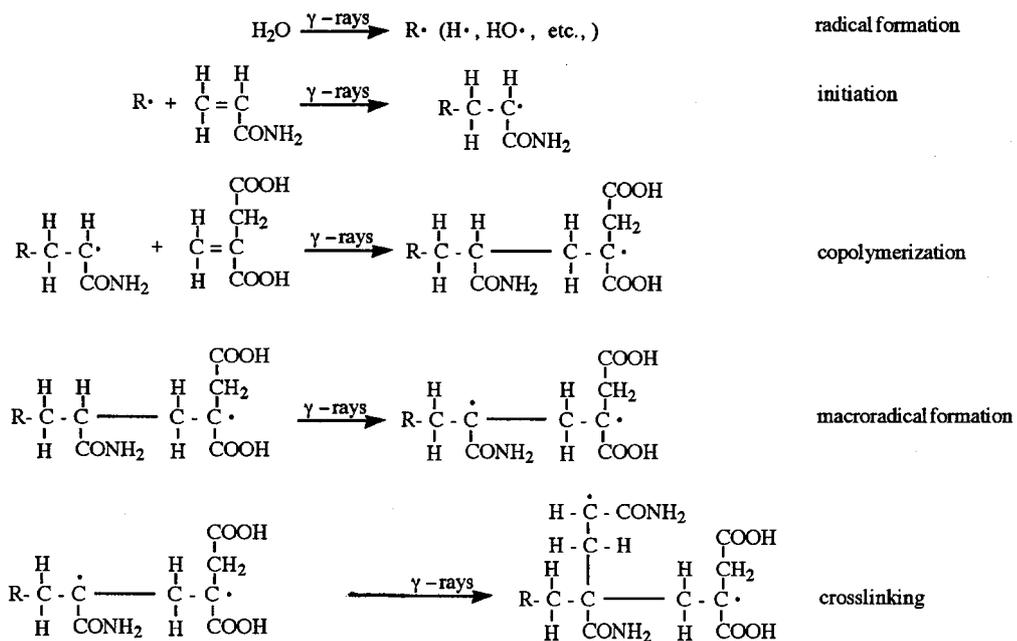
Scheme 1. Possible copolymerization and crosslinking reaction mechanisms between acrylamide and itaconic acid monomers.
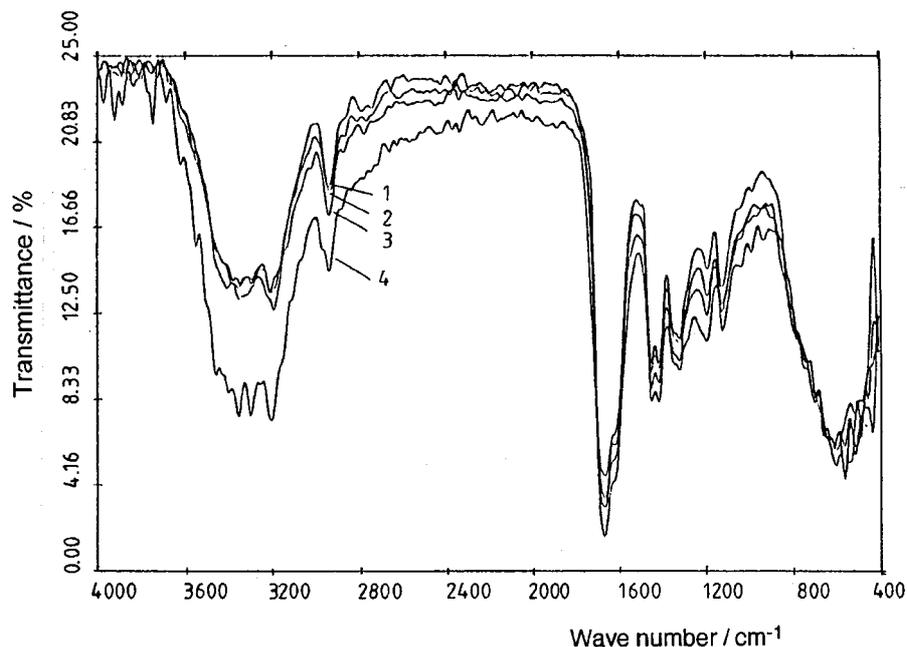

Figure 1. FTIR spectra of the hydrogels; total irradiation dose 5.20 kGy; (1) 0 mg IA, (2) 20 mg IA, (3) 40 mg IA, (4) 60 mg IA.

It can be seen from Figure 1 that polymerization of the hydrogels took place involving the double bonds of acrylamide and itaconic acid, because N—H bonds are found in large amounts in the crosslinked structure. Specially, the peak at about $3200-3600$ cm^{-1} (N—H) is important for the examination of binding and crosslinking. Furthermore, the bands at about 1700 and $3200-3600$ cm^{-1} increased gradually with the increase of the content of IA in the hydrogels.

From Figure 1 it can be said that there is random copolymerization. For the investigation of this property, commercial PAAm and IA were irradiated together, but no
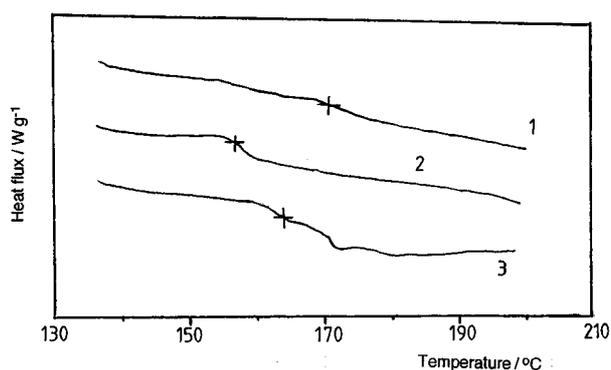
Figure 2. DSC thermograms of AAm/IA hydrogels containing 40 mg of IA and irradiated at different irradiation doses: (1) 5.71 kGy, (2) 4.65 kGy, (3) 2.00 kGy.

Figure 3. DSC thermograms of the hydrogels; total irradiation dose 4.65 kGy; (1) 0 mg IA, (2) 20 mg IA, (3) 40 mg IA, (4) 60 mg IA.

gelation was found at the end of irradiation. It is said that random copolymerization of AAm occurred with IA in the presence of ionizing radiation and not any graft copolymerization of IA in the crosslinked copolymeric system was observed.

For the examination of the thermal properties of the dried crosslinked copolymers it was investigated whether the glass transition temperature (T_g) of the copolymers is changed after crosslinking has occurred. DSC thermograms of the dried crosslinked copolymers of AAm/IA containing 40 mg of IA and irradiated at various irradiation doses are shown in Figure 2.

The glass transition temperature of crosslinked PAAm is ~190 °C (Figure 2), while T_g commercial PAAm is 164 °C.[36] It is seen that the glass transition temperature of the crosslinked PAAm is higher than that of commercial PAAm. The reason of this increase is crosslinking of the monomers[37].

In Figure 2 it is seen that T_g of AAm/IA copolymer samples irradiated at 4.65 kGy is 160 °C, and T_g of samples irradiated at 5.71 kGy is about 170 °C. It is said that if the γ-ray dose is increased, crosslinking of the monomers is more than and T_g is bigger than in the previous state.

From Figure 3 it can be seen that T_g is very high for the crosslinked AAm, but this temperature for AAm/IA samples has been decreased with the adding of IA. The reason for this decrease of the glass transition temperature may be due to the plasticizer effect of itaconic acid.[37] Then, the glass transition temperature has increased with the IA content in the crosslinked copolymers. The interactions of carboxy groups in itaconic acid have caused this increase of the glass transition temperature.

If the IA content in the copolymers is increased, the number-average molar mass between the crosslinks of the hydrogels has increased and the crosslinking density of the hydrogels has decreased. Translating into the elastic state, if crosslinking density has increased, the glass tran-
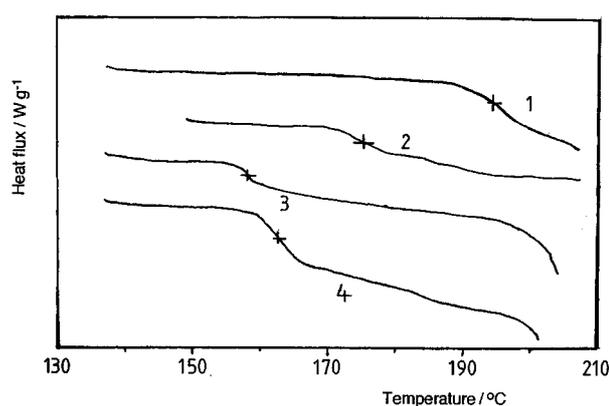
sition temperature is higher than in the previous state.[25, 37]

Swelling Studies

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent, respectively.

Mass Swelling

Swelling studies were made gravimetrically. The mass swelling is the most important parameter about swelling studies.[38–42] The mass swelling, %S(m), is calculated from Equation (1):

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

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

The water uptake of initially dry hydrogels was followed for a long time. Swelling curves of the superabsorbent hydrogels are shown in Figure 4.
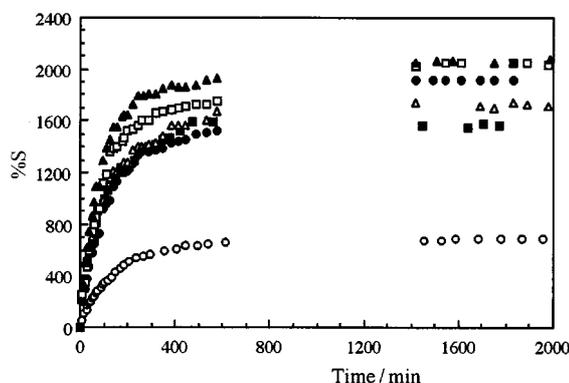

Figure 4. Swelling vs. time curves of AAm/IA hydrogels; total irradiation dose 2.6 kGy; (○) 0 mg IA, (■) 20 mg IA, (Δ) 30 mg IA, (●) 40 mg IA, (□) 50 mg IA, (▲) 60 mg IA.

Table 1. Mass and volumetric equilibrium swelling of the superabsorbent hydrogels.

| IA (mg) | Dose (kGy) | | | | | | | | | | | |
| | 2.00 | | 2.60 | | 3.73 | | 4.65 | | 5.20 | | 5.71 | |
	%S(m)	%S(v)	%S(m)	%S(v)	%S(m)	%S(v)	%S(m)	%S(v)	%S(m)	%S(v)	%S(m)	%S(v)
0	654	854	686	895	664	867	673	879	696	909	695	908
20	1573	2054	1560	2037	1543	2016	1360	1776	1190	1554	868	1133
30	1616	2110	1723	2250	1609	2101	1377	1798	1205	1574	913	1192
40	1816	2371	1917	2504	1663	2172	1495	1953	1395	1774	964	1258
50	1862	2432	2042	2667	1761	2269	1578	2061	1406	1836	1004	1311
60	2142	2797	2061	2691	2005	2618	1846	2410	1521	1986	1141	1490

In Figure 4 it is shown that swelling is increased by time, but after a certain time it remains constant. This value of swelling may be named "equilibrium swelling". The values of equilibrium swelling of the superabsorbent hydrogels are used for the calculation of some characterization parameters.

Volumetric Swelling

To determine the volumetric equilibrium swelling, it is necessary to place a sample of known density in the chosen solvent until mass measurements indicate the cessation of uptake of liquid by the polymer. If no extractable is present, and all the imbibed solvent causes swelling, the volumetric swelling, %S(v) is given by Equation (2):[43]

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

where m_0 is the mass of the dry gel at time 0 and m_t is the mass of the swollen gel at time t, as defined earlier, d_s and d_p are the water and polymer density, respectively. The value of volumetric equilibrium swelling is changed similar to the results of the mass equilibrium swelling. The values of volumetric equilibrium swelling of the superabsorbent hydrogels are in the range of 850–2800%.

The volumetric swelling parameters are used to calculate the diffusion coefficient and the intrinsic diffusion coefficient. The values of mass and volumetric equilibrium swelling of the hydrogels are given in Table 1.

It is shown that the value of mass equilibrium swelling of AAm hydrogel irradiated at 2.60 kGy is 690%, whereas the value of mass equilibrium swelling of acrylamide/itaconic acid hydrogel containing 40 mg IA is 1920% at the same irradiation dose. The hydrophilic group number of AAm/IA hydrogels is higher than the hydrophilic group number of the acrylamide hydrogels. Thus, AAm/IA hydrogels have swelled more than AAm hydrogels. Similar swelling behavior was reported in our previous studies about acrylamide-based hydrogels.[44, 45] For a better understanding of the effect of the IA content in the hydrogels and γ-irradiation doses, the equilibrium percentage swelling of the hydrogels is plotted versus the
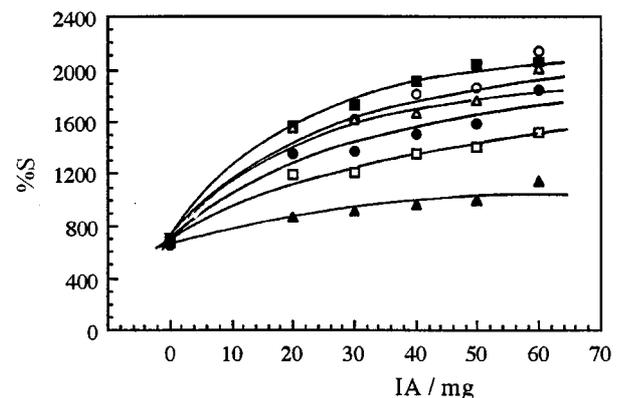

Figure 5. Variation of the equilibrium percentage mass swelling of the hydrogels with irradiation doses; (○) 0 mg IA, (■) 20 mg IA, (Δ) 30 mg IA, (●) 40 mg IA, (□) 50 mg IA, (▲) 60 mg IA.
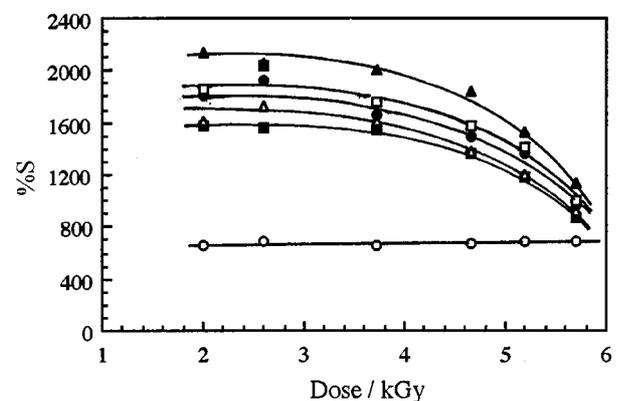
Figure 6. Variation of the equilibrium percentage mass swelling of the hydrogels with IA contents; (○) 2.00 kGy, (■) 2.60 kGy, (Δ) 3.73 kGy, (●) 4.65 kGy, (□) 5.20 kGy, (▲) 5.71 kGy.

content of IA and γ-irradiation doses, as presented in Figure 5 and Figure 6, respectively.

It is shown in these figures that the mass equilibrium swelling of the superabsorbent hydrogels is decreased with the increase of irradiation dose and is increased with the increase of the IA content in the copolymers. On the other hand, as mentioned before, the equilibrium swelling of AAm/IA hydrogels is higher than the equilibrium swelling of acrylamide hydrogels. The reason for this are

Table 2. Swelling rate coefficients of the superabsorbent hydrogels.

IA (mg)	2.00 kGy	2.60 kGy	3.73 kGy	4.65 kGy	5.20 kGy	5.71 kGy
0	0.365	0.363	0.355	0.398	0.410	0.398
20	0.743	1.022	0.917	0.845	0.560	0.553
30	0.691	1.084	0.853	0.851	0.548	0.532
40	1.065	0.970	1.065	0.836	0.998	0.483
50	0.756	1.172	0.691	0.643	0.641	0.585
60	1.136	1.363	0.884	0.858	0.865	0.647

Figure 7. % Swelling vs. square root of time curves of AAm/IA hydrogels; total irradiation dose 2.6 kGy; (○) 0 mg IA, (■) 20 mg IA, (Δ) 30 mg IA, (●) 40 mg IA, (□) 50 mg IA, (▲) 60 mg IA.

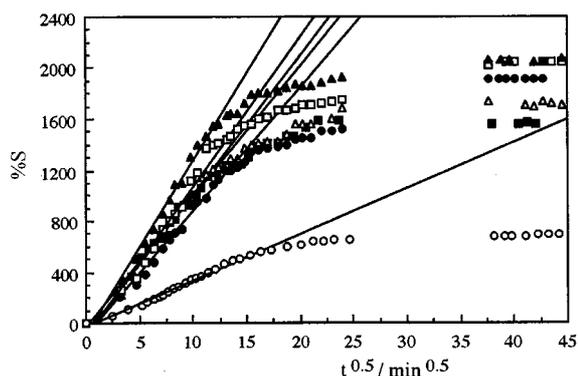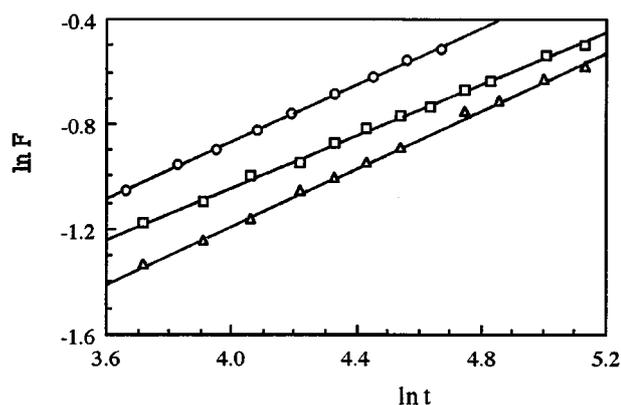Figure 8. Plots of ln F vs. ln t for various hydrogels; total irradiation dose 5.20 kGy; (○) 0 mg IA, (Δ) 30 mg IA, (□) 50 mg IA.

the hydrophilic groups on the itaconic acid which favor the swelling of the AAm/IA hydrogels.

If the γ-irradiation dose is increased during ionizing radiation of acrylamide, itaconic acid 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-irradiation doses. At the same time, the number-average molar mass of the polymer between crosslinks, is smaller than the lower γ-irradiation doses.

To determine the swelling rate coefficient, swelling of the crosslinked AAm/IA copolymer vs. the square root of immersion time is plotted. The representative curves are shown in Figure 7.

The swelling rate coefficient[46] was calculated from the linear slope in Figure 8. All values are listed in Table 2.

Table 2 shows that the swelling rate coefficients of AAm/IA copolymers decreased with an increase of the irradiation dose, whereas these parameters generally increased with an increase of the IA content in acrylamide/itaconic acid superabsorbent hydrogels.

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 scale

segmental motion resulting, ultimately, in an increased distance of separation between hydrogel chains.[47–[52]

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.[11–20] Equation (3) is used to determine the nature of water diffusion into hydrogels.

$$F = \frac{M_t}{M_\infty} \ kt^n \qquad (3)$$

Here, F is the fractional uptake, M_t is the amount of diffusant sorbed at time t, M_∞ is the maximum amount absorbed, k is a constant incorporating characteristics 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 normalized solvent uptake. Fickian diffusion and Case II transport are defined by n equal to and n equal to 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II, this is reflected by the fact that anomalous behavior is defined by n values between 1/2 and 1.[38]

In Figure 8 such graphs are plotted and some representative results are shown for the hydrogels. The exponents are calculated from the slope of the lines and are listed in Table 3.

Table 3. The values of n and k of the hydrogels.

Dose	2.00 kGy		2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy		5.71 kGy	
IA/mg	$k \times 10^2$	n	$k \times 10^2$	n	$k \times 10^2$	n	$k \times 10^2$	n	$k \times 10^2$	n	$k \times 10^2$	n
0	3.17	0.61	2.61	0.64	3.39	0.59	5.00	0.53	5.04	0.53	4.95	0.53
20	3.32	0.57	4.47	0.58	3.32	0.62	3.93	0.61	3.84	0.54	2.18	0.73
30	4.14	0.51	2.32	0.72	3.00	0.61	2.60	0.71	2.72	0.60	3.36	0.61
40	4.28	0.56	2.25	0.65	3.38	0.64	4.24	0.56	6.10	0.59	3.50	0.57
50	2.29	0.61	2.28	0.69	4.70	0.48	2.95	0.56	3.76	0.55	1.77	0.75
60	2.65	0.64	3.35	0.64	3.20	0.56	4.00	0.53	7.76	0.44	4.04	0.57

Table 4. Diffusion and intrinsic diffusion coefficient of the hydrogels.

Dose	2.00 kGy		2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy		5.71 kGy	
IA/mg	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$	$D \times 10^6$ $cm^2\,s^{-1}$
0	3.23	3.74	2.88	3.23	3.20	3.74	3.76	4.23	3.39	3.82	3.68	4.22
20	4.05	5.80	4.29	5.99	5.91	7.81	7.57	10.11	3.46	4.56	3.10	3.49
30	3.37	5.23	6.76	9.53	4.23	5.98	7.30	10.06	2.36	3.11	3.05	3.70
40	4.83	6.86	5.44	9.68	7.00	9.80	5.68	7.65	9.35	11.29	2.88	3.62
50	3.17	5.02	6.38	10.46	3.99	6.06	3.04	4.20	4.21	5.29	3.33	4.07
60	4.74	7.28	8.58	13.72	4.92	9.53	4.94	7.67	5.93	8.41	3.60	4.65

It can be seen that the number to determine the type of diffusion (n) is found over 0.50. Hence, the diffusion of water into the superabsorbent hydrogels has generally taken a non-Fickian character.[38] When the diffusion type is of anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. As the solvent diffuses into the hydrogel, rearrangement of the chains does not occur immediately.

The study of diffusion phenomena in hydrogels and water is valuable since it clarifies the polymer behavior. The complete swelling-time curves for hydrogels in water are used to calculated the diffusion coefficient and the intrinsic diffusion coefficient[53].

For hydrogel characterization, diffusion coefficients D [in $cm^2\,s^{-1}$] are calculated from Equation (4):

$$D = 0.049/(t/41^2)_{1/2} \qquad (4)$$

where t is the time at which the swelling is one half the equilibrium value ($V/V_0 = 1/2$) and l is the radius of the cylindrical polymer sample. The intrinsic diffusion coefficient, D_{int}, may be expressed as

$$D_{int} = D(1 - V)^{-3} \qquad (5)$$

where V is the volume fraction of solvent penetrating the polymer in the time t defined above.[53]

The values of the diffusion coefficients and intrinsic diffusion coefficients of the hydrogels are listed in Table 4. From Table 4 it is found that the values of the intrinsic diffusion coefficient of the superabsorbent hydrogels are bigger than the values of the diffusion coefficient. Equation (4) gives a measure not only of diffusion but also of the mass flow of the whole system. Equation (5) gives the intrinsic diffusion coefficient for cases where no mass action effects enter.[50]

Network Studies

One of the important structural parameters 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. According to the theory of Flory and Rehner,[54, 55] for a network M_c is calculated according to Equation (6):

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

where V_1 is the molar volume of the swelling agent (in $cm^3\,mol^{-1}$), d_p is the polymer density (in $g\,mL^{-1}$), v_s is the volume fraction of polymer in the swollen gel, χ is the Flory-Huggins interaction parameter between solvent and polymer.[55]

The swelling ratio (Q) is equal to $1/v_s$. Here, the crosslink density, q, is defined as the mol fraction of crosslinked units.[55]

$$q = M_0/M_c \qquad (7)$$

Table 5. Average molar mass between crosslinks (M_c) and crosslink density (q) of the superadsorbent hydrogels.

Dose	2.00 kGy		2.60 kGy		3.73 kGy		4.65 kGy		5.20 kGy		5.71 kGy	
IA/mg	M_c	$q \times 10^4$	M_c	$q \times 10^4$	M_c	$q \times 10^4$	M_c	$q \times 10^4$	M_c	$q \times 10^4$	M_c	$q \times 10^4$
0	15 700	45.18	17 900	39.69	16 300	43.41	17 000	41.72	18 600	38.02	18 600	38.19
20	161 500	4.47	158 300	4.56	153 900	4.69	111 200	6.49	78 500	9.19	33 900	21.25
30	173 000	4.20	203 700	3.57	170 900	4.25	114 700	6.34	81 200	8.96	38 900	18.68
40	237 000	3.25	266 400	2.75	186 600	3.93	142 075	5.16	110 900	6.61	44 900	16.30
50	243 800	3.00	312 240	2.36	214 900	3.43	163 000	4.53	121 100	6.09	50 100	14.72
60	350 000	2.12	319 000	2.33	298 300	2.49	242 600	3.06	148 000	5.02	70 300	10.57

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

Since the hydrogel has a copolymeric structure, the molar mass of the polymer repeating unit, M_0, can be calculated according to Equation (8):

$$M_0 = \frac{n_{AAm} \times M_{AAm} + n_{IA} \times M_{IA}}{n_{AAm} + n_{IA}} \tag{8}$$

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

The polymer/solvent interaction parameter, χ, was assumed to be 0.494,[16, 56] by analogy to those of other acrylamide polymers. The density of the polymer was assumed[57] as 1.302 g cm^{-3}. Molar volume of water was taken as 18 cm^3 mol^{-1}. Finally, the swelling of the AAm/IA hydrogel was considered ideal. M_c, and q of AAm and AAm/IA hydrogels were calculated and presented in Table 5.

In Table 5 it is shown that the number-average molar mass between crosslinks of hydrogels has increased by increasing the IA content of AAm/IA hydrogels, whereas it decreased with increasing the irradiation dose. Because the IA in hydrogels includes many hydrophilic groups, AAm/IA hydrogels can swell to a great degree. The values of the crosslink density and the number of elastically effective chains are inverse due to the value of the number-average molar mass between the crosslinks.

Conclusion

For the AAm/IA superabsorbent hydrogels it is found that suitable IA contents are in the range of 20–60 mg IA, and suitable irradiation doses are in the range of 2.00–5.71 kGy.

The FT-IR spectra of AAm/IA copolymeric samples obtained by using a photoacoustic cell showed that the polymerization reaction of acrylamide and itaconic acid monomers takes place at the double bonds. DSC thermograms showed that the glass transition temperature of AAm hydrogel is decreased by the plasticizer effect of IA. AAm/IA hydrogels are swelled among 900–2100%, whereas AAm hydrogels are swelled among 650–700%.

Water diffusion to AAm/IA hydrogels is of non-Fickian type. The number-average molar mass between the crosslinks increased by increasing the IA content in the hydrogels and decreased by increasing the irradiation dose. The crosslink density decreased with increasing IA content in the hydrogels and increased with increasing irradiation doses.

It can be concluded that AAm/IA superabsorbent hydrogels can be used as water retainer for carrying some substances in aquatic fields in biomedical, bioengineering, pharmacy, agriculture and environmental applications.

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