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Swelling of Superabsorbent Acrylamide/Sodium Acrylate Hydrogels Prepared Using Multifunctional Crosslinkers

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Superwaterabsorbent acrylamide-sodium acrylate hydrogels were prepared by free radical polymerization in aqueous solutions of acrylamide and of acrylamide with sodium acrylate as comonomer. For each copolymerization, nine different compositions were used and in all systems a concentration of a multifunctional crosslinker such as trimethylolpropane triacrylate, ethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate and N,N′-methylenebisacrylamide was employed. As a result of dynamic swelling tests, the influence of crosslinkers and the relative content of sodium acrylate on the swelling properties, the initial swelling rate and the swelling rate constant, swelling exponent, swelling coefficients and diffusional behaviour of water in the hydrogel systems were examined. Acrylamide-sodium acrylate hydrogels were swollen in the range 860-12870% in water, while acrylamide hydrogels swelled in the range 770-1420%. The equilibrium water content of acrylamide-sodium acrylate hydrogel systems was calculated in the range 0.8851-0.9922. The water intake of hydrogels followed a non-Fickian type diffusion.

Key Words: Swelling, Superwaterabsorbent, Hydrogel, Diffusion, Crosslinking

Introduction

Hydrogels are three-dimensional crosslinked polymeric structures which are able to swell in the aqueous environment. These materials are of great interest due to their promising applications as sensors, separation membranes, adsorbents, and materials in medicine, in pharmacy as drug delivery systems, and in solving some ecological and biological problems as well as in modern technologies. Superwaterabsorbent polymers can swell up to thousands of times their own weight in aqueous media. The swelling behaviour of superabsorbent polymers may be characterized by water adsorption[1−9].

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. The latter involves two steps. In the first step, the linear polymer is synthesizeded in the absence of a

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crosslinking agent, and in the second step, the synthesized polymer is crosslinked using either chemical reagents or irradiation[7].

In recent years, considerable research has been done on the characterization and swelling behaviour of hydrogels prepared by simultaneous free radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent[10−13].

The aim of this study was to investigate the swelling properties of acrylamide hydrogels with the addition of an anionic monomer, such as sodium acrylate, and some multifunctional crosslinkers, such as trimethylolpropane triacrylate, ethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate and N,N′-methylenebisacrylamide. The gelation of acrylamide based hydrogels by free radical polymerization has been reported in many studies[10−13]. However, in the present study, the effect of some multifunctional crosslinkers, such as trimethylolpropane triacrylate, ethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate and N,N′-methylenebisacrylamide, were examined together on the swelling behaviour of prepared hydrogel systems. Equilibrium swelling, some swelling kinetics parameters such as the initial swelling rate and swelling rate constant, and diffusional parameters such as swelling exponent, swelling constant and diffusion coefficients of hydrogels can be determined by swelling studies.

The swelling properties of hydrogels will affect its usability as a biomaterial in medicine, pharmacy and veterinary practice. There is a wide variety of biomaterials used in contact with biological fluids. Many different biomaterials are used clinically, as components of implants or devices for diagnosis or therapy. Since the biologic environment is mainly composed of water, the water wettability and sorption are two important properties of biomaterials. In particular, low or high water sorption properties of hydrogels may be important for the use of sorbents in many immobilization techniques for biomolecules and cells and in many applications of biomaterials in biotechnology[14].

Experimental

Materials

Acrylamide (AAm) was supplied by Merck (Darmstad, Germany) and the anionic comonomer, sodium acrylate (SA) was supplied by Aldrich Chemical Co. (Milwaukee, US). The initiator, ammonium persulphate (APS) and the activator N,N,N′,N′ -tetramethylethylenediamine (TEMED) were also supplied by Merck and were used as the redox initiator pair. The multifunctional crosslinkers, trimethylolpropane triacrylate (TMPTA) and 1,4-butanediol dimethacrylate (BDMA) were purchased from Aldrich Chemical Co. and ethylene glycol dimethacrylate (EGDMA) and N,N′-methylenebisacrylamide (NBisA) were purchased from Merck. All chemicals were used as received. Doubly distilled water was used in the copolymerizations and swelling studies. The chemical structure of the monomers, initiator, activator and crosslinkers used are tabulated in Table 1.

Copolymer Preparation

For the preparation of superabsorbent acrylamide-sodium acrylate (AAm/SA) hydrogel systems, first 1 g of AAm was dissolved in 1 mL of distilled water, and then 10, 20, 30, 40, 50, 60, 70 and 80 mg of SA were added to the aqueous solutions of AAm. For the investigation of the effect of crosslinkers on the preparation of AAm/SA hydrogel systems, 0.25 mL of 1% concentration of EGDMA, 0.25 mL of 1% concentration of

BDMA, 0.25 mL of 1% concentration of TMPTA, or 0.25 mL of 1% concentration of NBisA was added to the aqueous solutions of AAm or AAm/SA. Then 0.2 mL of APS(5 g/100 mL water) was added this solution as initiator, and finally 0.25 mL of TEMED (1 mL/100 mL water) was added to the solution.

Table 1. Monomers and crosslinkers used in the preparation of hydrogel systems.

	Formula	Abbreviations
Acrylamide (Propene amide)	$H_2C{=}CHCONH_2$	AAm
Sodium acrylate	$H_2C{=}CHCO_2Na$	SA
Ammonium persulphate	$(NH_4)_2S_2O_8$	APS
N,N,N′,N′-Tetramethylethylenediamine	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	TEMED
Trimethylolpropane triacrylate	$[H_2C{=}CHCO_2CH_2]_3CC_2H_5$	TMPTA
Ethylene glycol dimethacrylate	$[H_2C{=}CCH_3COOCH_2]_2$	EGDMA
1,4-Butanediol dimethacrylate	$[H_2C{=}C(CH_3)CO_2CH_2CH_2]_2$	BDMA
N,N′-methylenebisacrylamide	$(H_2C{=}CHCONH)_2CH_2$	NBisA

These solutions were placed in poly(vinyl chloride) straws (as the polymerization reactors) 3 mm in diameter. The polymerization was conducted at room temperature (25°C) for 24 h. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces 3-4 mm in length. These were dried in air and then under vacuum, and stored for swelling studies.

Experiments of Swelling and Diffusion

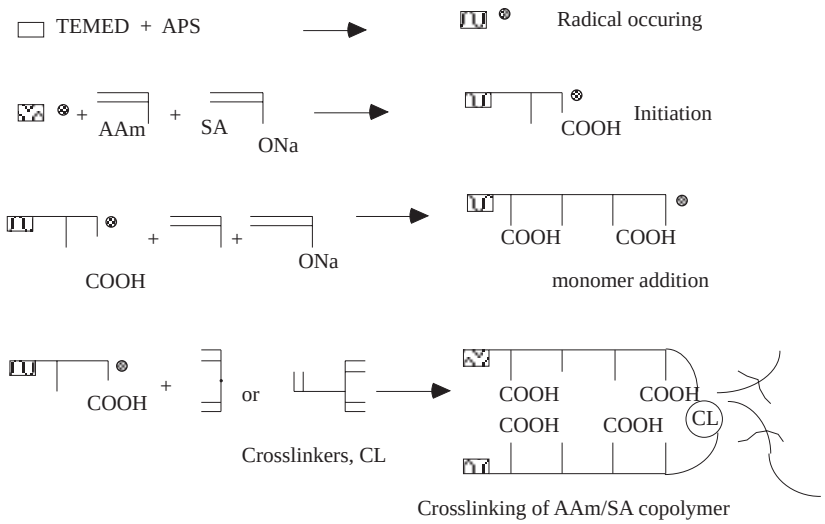
The swelling behaviours of dried hydrogels were determined by immersion in doubly distilled water at 25 ± 0.1°C in a water bath. The water absorbed was calculated by weighing the samples, after wiping, at various time intervals. Swollen gels were weighed by an electronic balance (Sartorius, BP 210S, d = 0.1 mg).

Results and Discussion

Preparation of Crosslinked Copolymers

AAm/SA hydrogels were prepared by free radical polymerization in aqueous solutions of AAm, SA and crosslinkers such as TMPTA, BDMA, EGDMA and NBisA. In the polymerization, the first step is a reaction between APS and TEMED in which the TEMED molecule is left with an unpaired valance electron. The activated TEMED molecule can combine with an AAm and anionic comonomer such as SA or crosslinker molecules; in the process the unpaired electron is transferred to the monomeric units, so that they in turn become reactive. Another monomer or comonomers can therefore be attached and activated in the same way. The polymer (AAm) or copolymer (AAm/SA) can continue growing indefinitely, with the active centre being continually shifted to the free end of the chain. Crosslinker molecules can be incorporated into chains simultaneously and form a permanent link between them[10] (Scheme 1).

Polymerization and crosslinking took an hour in AAm/SA gelation. However, for all hydrogel systems, a waiting period of 24 h gave good gelation. Crosslinked copolymers are colourless, and some are semi-transparent. On the addition of SA (e.g. above of 50 mg SA) the dull character or mat appearance of gel samples is increased from 60 mg SA to 80 mg SA. They are soft and elastic, with a slippery or slimy surface. There is no difference in the external appearance of crosslinked copolymeric samples when changing their crosslinker molecular structure.



Scheme 1. Copolymerization and crosslinking mechanism of AAm/SA hydrogels.

Swelling Studies

A fundamental relationship exists between the swelling of a polymer in a solvent and the natures of the polymer and the solvent. Percentage swelling (or mass swelling) is the most important parameter in swelling studies. Percentage swelling (% S) was calculated from the following equation:

$$\%S = \frac{M_t - M_0}{M_0} \times 100 \tag{1}$$

where M_t is the mass (g) of the swollen gel at time t, and M_o is the mass (g) of the dry gel at time 0.

The water intake of initially dry hydrogels was followed over a long period. Swelling isotherms of AAm/SA hydrogel systems using four different crosslinkers are plotted and are shown in Figures 1-4.

If Figures 1-4 are examined together, it is seen that percentage swelling increases with time until a certain point, after which it becomes constant. This value of percentage swelling may be named "equilibrium" swelling. The values of equilibrium swelling of AAm and AAm/SA hydrogel systems are used for the calculation of some characterization parameters. The values of equilibrium swelling of AAm and AAm/SA hydrogel systems are given in Table 2.

Table 2. Equilibrium swelling of AAm/SA hydrogel systems.

SA/mg	00	10	20	30	40	50	60	70	80
	Equilibrium swelling, % S								
BDMA	1360	1520	3750	5180	6470	7840	9750	11890	12840
EGDMA	770	1690	2790	4810	6150	7330	8010	10660	12870
NBisA	1420	2440	5610	7190	8430	11490	12170	12740	12830
TMPTA	780	860	940	1360	1740	3120	4110	4160	4510

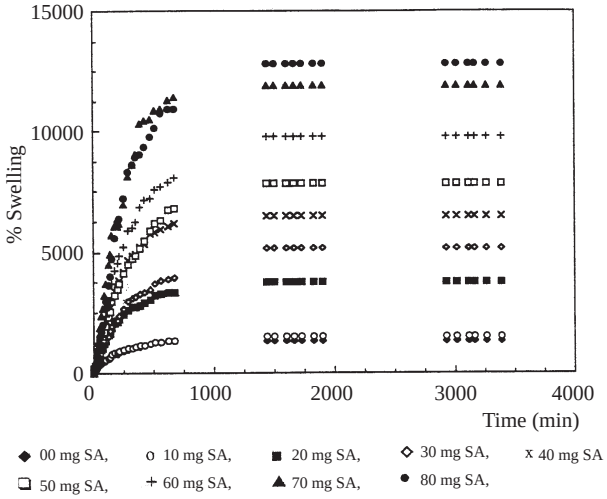


Figure 1. Swelling isotherms of AAm/SA hydrogels crosslinked by BDMA.

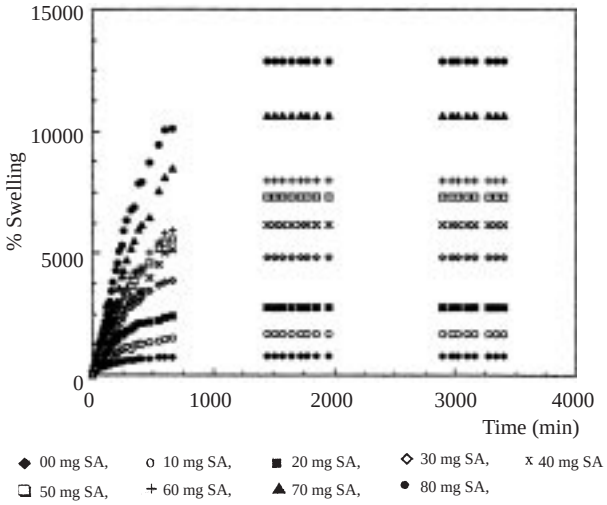


Figure 2. Swelling isotherms of AAm/SA hydrogels crosslinked by EGDMA.

The values of equilibrium swelling of AAm are 770-1420% , but the values of equilibrium swelling of AAm/SA hydrogels vary between 860 and 12870%. It is well known that the swelling of a hydrogel is induced by the electrostatic repulsion of the ionic charges of its network. The ionic charge content is important. SA contains many ionic units (–COONa). As seen in Table 2, the swelling increase is due to an increase in the anionic units. On the other hand, salts of weak acids are decomposed by water with the formation of free acid and free base, and the process of hydrolysis is reversible. The salt group is almost completely ionized, and a large number of hydrophilic groups occur[15]. The hydrophilic group numbers of AAm/SA copolymers are higher than those of AAm, and so the swelling of AAm/SA copolymers is greater than that of AAm copolymers. If the content of SA in AAm/SA copolymers increases, the equilibrium swelling of AAm/SA copolymers increases. Furthermore, as mentioned before, the equilibrium swelling of AAm is lower than that of AAm/SA copolymers. The reason for this is the existence of hydrophilic groups SA causing a greater degree of swelling AAm/SA copolymeric hydrogels.

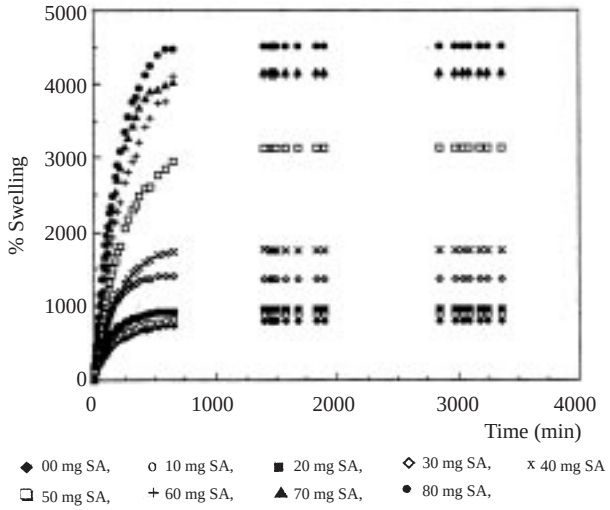


Figure 3. Swelling isotherms of AAm/SA hydrogels crosslinked by TMPTA

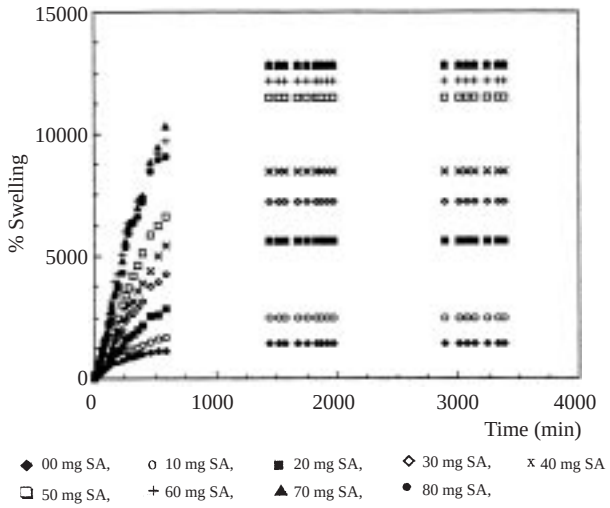


Figure 4. Swelling isotherms of AAm/SA hydrogels crosslinked by NBisA

The effect of crosslinkers is important for the preparation of AAm based hydrogels[10,16–18]. For this, swelling isotherms of AAm/SA hydrogel systems using four different crosslinkers are plotted to the SA mass (Figure 5).

As seen in Table 2 and Figure 5, the equilibrium mass swelling of AAm and AAm/SA hydrogels increased in the following order:

$$S_{NBisA} > S_{BDMA} > S_{EGDMA} > S_{TMPTA}$$

The reason for this arrangement may be the molecular structure of crosslinkers. Firstly, NBisA, BDMA and EGDMA are tetrafunctional crosslinkers and TMPTA is a hexafunctional crosslinker (Schemes 2-5). Because TMPTA is a hexafunctional crosslinker, lower swelling values were seen among the other three crosslinkers. This chemical arrangement of TMPTA caused the decreasing of swelling with the degree of crosslinking[15].

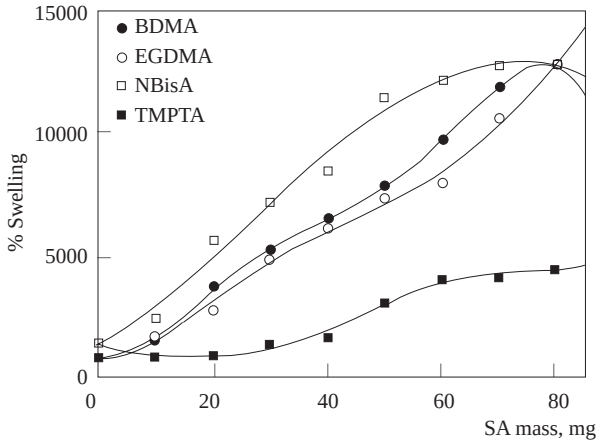
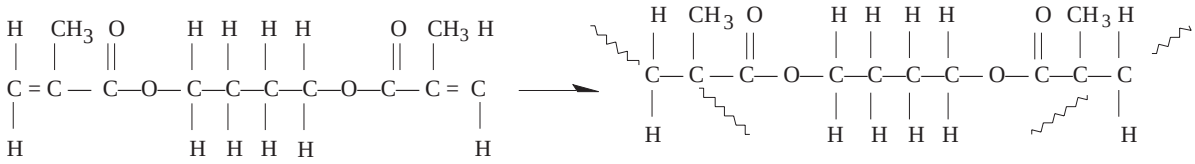
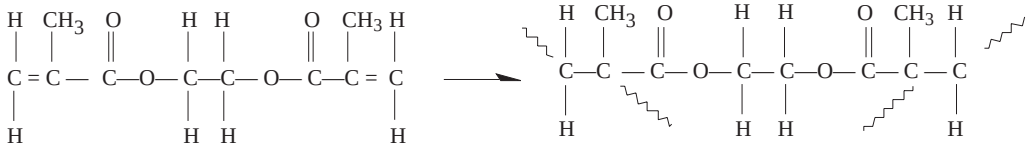


Figure 5. Effect of crosslinkers on swelling of AAm/SA hydrogels.



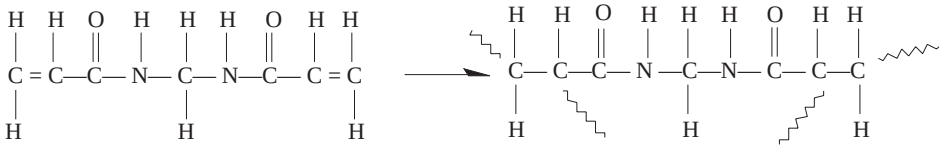
1,4-Butanediol dimethacrylate

Scheme 2. Linking sites of 1,4-butanediol dimetacrylate.



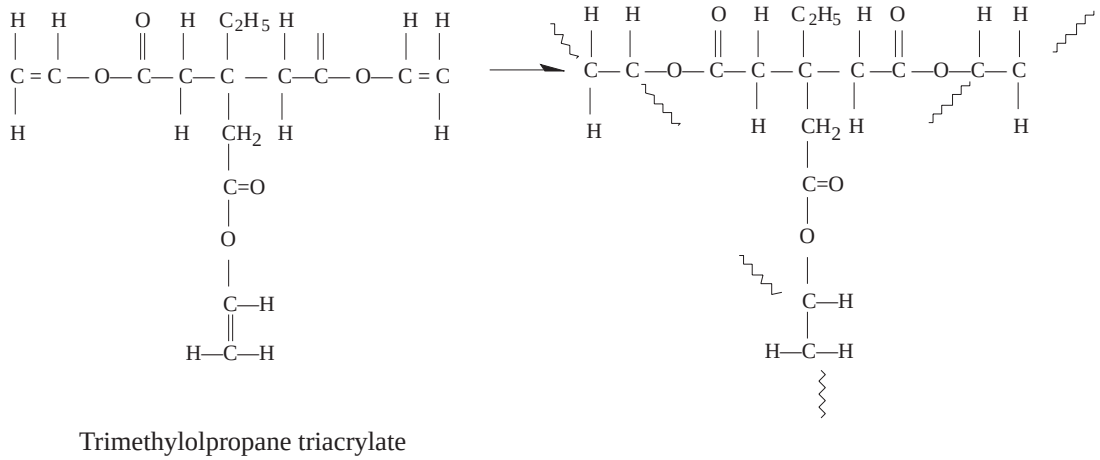
Ethylene glycol dimethacrylate

Scheme 3. Linking sites of ethylene glycol dimethacrylate.



N,N'-methylenebisacrylamide

Scheme 4. Linking sites of N, N'-methylenebisacrylamide.



Trimethylolpropane triacrylate

Scheme 5. Linking sites of trimethylolpropane triacrylate.

The swelling properties of hydrogels crosslinked with different the crosslinkers are changed by the structure of crosslinker, and generally, when crosslinkers are added to hydrogel systems, it is known that there will be some differences in the swelling ratio of hydrogels, because the molecules of crosslinkers which are hydrophobic are placed between the chains of the monomer and comonomers. If crosslinking density is increased by adding crosslinkers, it is seen that the hydrodynamic volume of the hydrogels decreases. If the hydrophobic group number is increased and the hydrophilic group number is decreased, the swelling ratio is decreased[15,17].

As shown in Table 2, the equilibrium swelling of AAm and AAm/SA containing NBisA is higher than the equilibrium swelling of AAm and AAm/SA hydrogels containing BDMA, TMPTA and EGDMA. The reason for this effect may be the (CO-OR) groups of the crosslinkers. The (CO-NH-R) groups of NBisA may increase the swelling of AAm and AAm/SA hydrogels. New hydrophilic interactions from the (CO-NH-R) groups of NBisA may cause higher swelling ratio than the other crosslinkers.

TMPTA is a hexafunctional crosslinker. Therefore, there are many many crosslinking sites, and crosslinking density will be higher than for the other crosslinkers. For this reason, the swelling degree of AAm/SA hydrogels crosslinked by TMPTA may be decreased.

Equilibrium Water Content

The water absorbed by AAm/SA is quantitatively represented by the Equilibrium water content (EWC) [19−21], where:

$$\text{Equilibrium Water Content } = \frac{M_s - M_0}{M_s} \tag{2}$$

Here M_s is the mass of the swollen gel at time t (equilibrium), and M_o is the mass of the dry gel at time 0. The EWCs of all AAm and AAm/SA hydrogel systems were calculated. The values of EWC of the hydrogels are tabulated in Table 3. All EWC values of the hydrogels (0.8851-0.9923) were greater than the percent water content values of the by body about 0.60 (or 60%). Thus, the AAm and AAm/SA hydrogels exhibited fluid contents similar to those of living tissues.

Table 3. Equilibrium water content (EWC) of AAm/SA hydrogel systems.

SA/mg	00	10	20	30	40	50	60	70	80
	Equilibrium water contents, EWC								
BDMA	0.9316	0.9385	0.9740	0.9810	0.9847	0.9874	0.9898	0.9916	0.9922
EGDMA	0.8851	0.9443	0.9654	0.9796	0.9840	0.9865	0.9876	0.9907	0,9923
NBisA	0.9342	0.9606	0.9825	0.9862	0.9882	0.9913	0.9918	0.9807	0.9922
TMPTA	0.8871	0.8964	0.9047	0.9316	0.9459	0.9690	0.9762	0.9765	0.9782

Swelling Kinetics Studies

For extensive swelling of polymers, the following second order kinetics relation can be used[22,23]:

$$\frac{t}{S} = A + Bt \tag{3}$$

where t is time, S is swelling at t, $B = 1/Seq$ is the inverse of the maximum or equilibrium swelling, $A = 1/k_S Seq^2$ is the reciprocal of the initial swelling rate $[(dS/dt)_0]$ of the hydrogel, and k_S is swelling rate constant.

Figure 6 shows the linear regression of the swelling curves obtained by means of Equation 3 for the AAm and AAm/SA hydrogels crosslinked by TMPTA in water. The initial swelling rate, the swelling rate constant and the values of theoretical equilibrium swelling of all hydrogels were calculated from the slope and the intersection of the lines, respectively. The results are presented in Table 4.

Table 4. Swelling rate parameters of AAm/SA hydrogel systems.

SA/mg	00	10	20	30	40	50	60	70	80
	The initial swelling rate, r $(dS/dt)_o$; g_{water} / g_{gel} min								
BDMA	12.317	10.863	24.126	19.453	38.121	28.408	35.901	63.463	46.479
EGDMA	7.8437	10.579	15.546	17.571	14.591	16.480	19.513	59.580	52.274
NBisA	7.9226	7.352	6.925	10.092	29.401	21.766	43.344	38.144	39.413
TMPTA	8.7351	9.223	13.709	25.839	17.345	21.355	26.982	37.328	41.625
	The swelling rate constant, k_s x 10^6 ; g_{gel} / g_{water} min								
BDMA	6.060	4.162	1.509	0.581	0.787	0.365	0.300	0.382	0.223
EGDMA	12.244	3.248	1.731	0.607	0.270	0.210	0.216	0.457	0.260
NBisA	3.404	0.937	0.121	0.115	0.327	0.114	0.232	0.177	0.183
TMPTA	13.157	11.411	14.369	13.298	5.215	1.934	1.404	1.958	1.872
	The theoretical equilibrium swelling, S_{max}; g_{water} / g_{gel}								
BDMA	1430	1610	3990	5780	6960	8820	10930	12880	14430
EGDMA	800	1800	2990	5370	7340	8840	9480	11410	14160
NBisA	1530	2800	7560	9360	9470	13800	13660	14650	14670
TMPTA	810	890	970	1390	1820	3320	4380	4360	4710

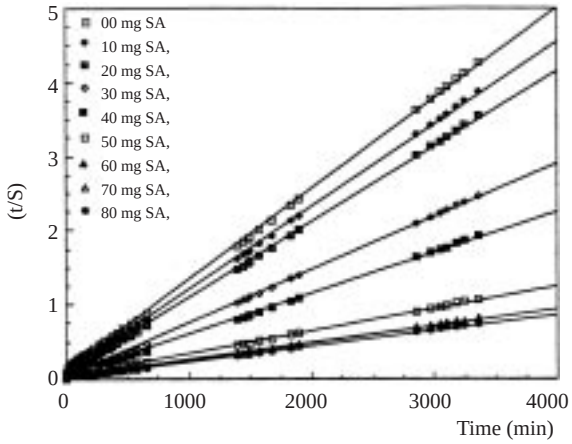


Figure 6. Swelling rate curves of AAm/SA hydrogels crosslinked by TMPTA.

The values of theoretical equilibrium swelling of the hydrogels are parallel to the results of gel swelling (Table 2).

Determination of Swelling Power

When a glassy hydrogel is brought into contact with water, the 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. Analysis of the mechanisms of water diffusion in swellable polymeric systems has received considerable attention in recent years, because of the important applications of swellable polymers in the biomedical, pharmaceutical, environmental, and agricultural engineering fields.

The swelling mechanism of the samples was determined using the following equation[24]:

$$F_{swp} = \frac{M_t - M_0}{M_0} = Kt^n \tag{4}$$

where M_t and M_o are the mass of the swollen and dry sample at time t, respectively, t is the time, K is the swelling constant, and n is the swelling exponent[24,25].

For cylindrical shapes, n = 0.45-0.50 and corresponds to Fickian diffusion, whereas $0.50 < n < 1.0$ indicates that diffusion is non-Fickian. This equation is applied to the initial stages of swelling and plots of $\ln F_{swp}$versus $\ln t$ yield straight lines up to almost 60% increases in the mass of hydrogel[24,25]. For the hydrogels, $\ln F_{swp}$ versus $\ln t$ plots were drawn using the kinetics of swelling and some representative results are shown in Figure 7. The swelling exponents n were calculated from the slopes of the lines and are listed in Table-5. The values of the diffusional exponent range is generally between 0.594 and 1.065. The average of swelling exponents is 0.81661. In the experiments, the number to determine type of diffusion (n) was found to be generally over 0.50. Hence the diffusion of water into AAm and AAm/SA hydrogel systems had a *non-Fickian* character[24,25].

Table 5. Swelling exponents and swelling constants of AAm/SA hydrogel systems.

SA/mg	00	10	20	30	40	50	60	70	80
	Swelling exponent,n								
BDMA	0.633	0.642	0.803	0.829	0.841	0.931	0.933	0.925	1.028
EGDMA	0.581	0.675	0.736	0.827	0.875	0.933	0.881	0.994	1.002
NBisA	0.645	0.698	0.905	0.939	0.959	1.026	1.041	1.025	1.065
TMPTA	0.594	0.604	0.603	0.610	0.655	0.717	0.743	0.750	0.750
	Swelling constant, K								
BDMA	0.2942	0.2904	0.3164	0.2746	0.4240	0.2477	0.3077	0.4894	0.2569
EGDMA	0.2414	0.2609	0.2985	0.2505	0.1838	0.1611	0.2398	0.1610	0.2176
NBisA	0.2351	0.2103	0.092	0.1130	0.1191	0.1045	0.1634	0.1728	0.1308
TMPTA	0.2391	0.2461	0.3051	0.4524	0.3677	0.3990	0.4495	0.5255	0.5775

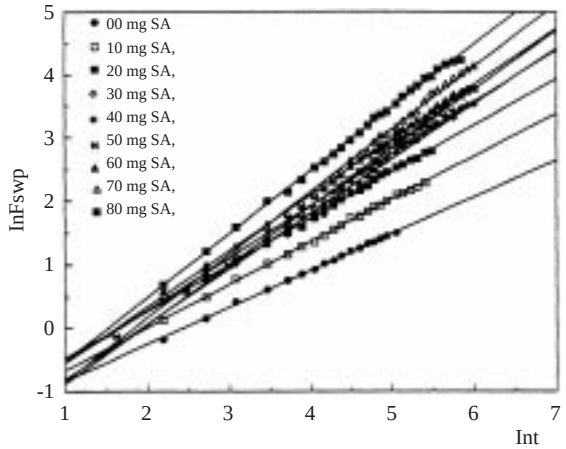


Figure 7. Swelling kinetics curves of AAm/SA hydrogels crosslinked by EGDMA.

Diffusion of water

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behaviour. The complete swelling-time curves for hydrogels in water are used to calculated diffusion coefficient. Diffusion coefficients of hydrogels can be calculated by various methods[2,17,21,23,26]. One of these methods is 'the short time approximation method'. The short time approximation is valid only for the first 60% of the swelling process[17,23,26].

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

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

where D is in $cm^2\ s^{-1}$, t is in s and r is the radius of cylindrical polymer sample. Graphical comparisons of related equations shows the semi-empirical equation (5) with n = 0.5 and $k = 4(D/\pi r^2)^{1/2}$.

For the hydrogels, F versus $t^{1/2}$ plots were plotted and some representative results are shown in Figure 8. The diffusion coefficients were calculated from the slope of the lines. The values of diffusion coefficient determined for the hydrogels are listed in Table 6.

Table 6. Diffusion coefficients of AAm/SA hydrogel systems.

SA/mg	00	10	20	30	40	50	60	70	80
	Diffusion coefficients, D x 10^6/cm^2s^{-1}								
BDMA	77.86	85.87	189.30	130.36	364.88	537.11	328.90	439.11	320.24
EGDMA	91.51	111.53	163.85	178.42	163.77	278.36	232.87	246.13	175.43
NBisA	84.34	75.29	100.12	121.01	193.38	202.59	483.79	366.53	435.60
TMPTA	94.44	85.82	143.78	201.69	161.21	192.39	199.60	573.81	301.91

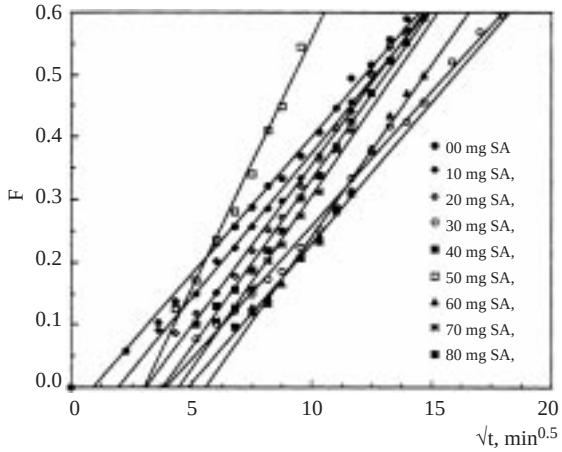


Figure 8. Diffusion curves of AAm / SA hydrogels crosslinked by BDMA.

The values of the diffusion coefficient of the hydrogels varied from 75.29 x 10^{-6} cm^2 s^{-1} to 573.81 x 10^{-6} cm^2 s^{-1}. The diffusion of the water to the AAm/SA hydrogel content 70 mg SA is faster than the others.

Conclusion

AAm/SA hydrogels were prepared by free radical polymerization. Some multifunctional crosslinkers such as trimethylolpropane triacrylate, ethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate and N, N'-methylenebisacrylamide were used in the polymerization experiments. Hydrogels were prepared in water, and swollen to equilibrium in water. Hydrogel systems swelled in the range 770-12870% . Equilibrium swelling data were used for the determination of equilibrium water contents, some swelling parameters such as the initial swelling rate and swelling rate constant, swelling exponent, swelling coefficients and the diffusional behaviour in water of the hydrogel systems. The values of equilibrium water contents were in the range 0.8851-0.9822. These results showed that acrylamide-sodium acrylate hydrogels could be used as a biomaterial in some biomedical applications, because equilibrium water contents was higher than the percent water content value of the body by about 0.60. The diffusion type of hydrogels was non-Fickian. It was seen that the swelling of acrylamide-sodium acrylate hydrogels increased with the increasing content of sodium acrylate.

In conclusion AAm/SA hydrogels can be used as a super water retainer for carrying some substances in aquatic fields in pharmaceutical, agricultural, environmental and biomedical applications, or in the applications of immobilized biologically active molecules.

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