Equilibrium Swelling Studies of Highly Swollen Acrylamide/Mesaconic Acid Hydrogels

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ABSTRACT: Acrylamide/mesaconic acid (AAm/MA) hydrogels were prepared by free radical solution polymerization in aqueous solution of acrylamide (AAm) with mesaconic acid (MA) as comonomer and two multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA) and 1,4-butanediol dimethacrylate (BDMA). Swelling experiments were performed in water at 25°C, gravimetrically. The influence of mesaconic acid content in hydrogels was examined. Swelling of AAm/MA hydrogels was increased up to 2301% (for containing 20 mg MA and crosslinked by EGDMA) to 3296% (for containing 80 mg MA and crosslinked by BDMA), while AAm hydrogels swelled up to 1330% (crosslinked by BDMA) to 1400% (crosslinked by EGDMA). The values of equilibrium water content of the hydrogels are 0.9301–0.9706. Diffusion behavior was investigated. Water diffusion into hydrogels was found to be non-Fickian in character. Diffusion coefficients of AAm/MA hydrogels were calculated by the short time approximation and found to be from 38.01×10^{-6} cm^2 s^{-1} to 182.73×10^{-6} cm^2 s^{-1}. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2253–2259, 2005

Key words: crosslinking; diffusion; hydrogels; hydrophilic polymers; swelling

INTRODUCTION

Hydrogels are a unique class of polymeric materials that imbibe an enormous amount of water when left in a water reservoir for long times. The underlying property for this unusual behavior of hydrogels is their transition from a glassy to a rubbery state when contacted with thermodynamically compatible solvents. This water sorption property of hydrogels accounts for a great number of biomedical and technological applications, such as artificial implants, contact lenses, enzyme immobilization, catheters, wound dressings, and biosensors. One of the most powerful applications of hydrogels is in controlled release systems 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. After intimate contact is established, the rate and duration of drug release depends on the swelling behavior of the hydrogel.[1–7]

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.[8–10] 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. Because of the presence of carboxylic acid side groups, the swelling behavior of copolymeric acrylamide hydrogels is highly dependent on the surrounding medium.[10–14]

In our previous study, copolymeric hydrogels of acrylamide with maleic acid,[15] crotonic acid,[16] and sodium acrylate[17] were prepared by free radical solution polymerization and used in separation and adsorption of some dye molecules.[15,18] For synthesis of acrylamide-based hydrogel systems, γ-radiation technique was used in our previous studies.[19–21] It was of interest to increase the water absorption capacity of AAm hydrogels with vinyl functional groups containing chemical reagents such as mesaconic acid (MA) via a free radical solution polymerization method. Here, in this work we investigated the incorporation of a vinyl chemical such as MA into AAm hydrogel during free radical solution polymerization synthesis. The aim of this study was to investigate the sorption properties of AAm hydrogels with addition of an anionic monomer such as MA. Swelling properties and diffusional and network properties of these hydrogels were then studied.

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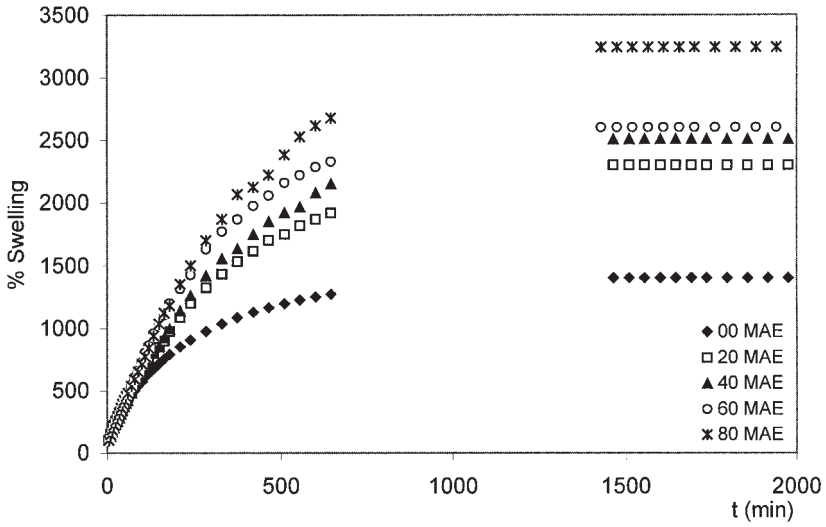

Figure 1 Swelling isotherms of AAm/MA hydrogels crosslinked by EGDMA.

EXPERIMENTAL

Materials

Acrylamide–mesaconic acid (AAm/MA) hydrogels were prepared by free radical crosslinking copolymerization of AAm monomer (Merck, Darmstadt, Germany) with addition of an anionic comonomer such as MA (Aldrich Chemical Co., Milwaukee, WI) and two multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA) (Merck) and 1,4-butanediol dimethacrylate (BDMA) (Aldrich Chemical Co., Milwaukee, WI). The initiator, ammonium persulphate (APS), and the activator *N,N,N′,N′*-tetramethylethylenediamine (TEMED) were also supplied by Merck and used as the redox initiator pair. All chemicals were used as received. There were two abbreviations used in text, MAB and MAE. MAE is the abbreviation of acrylamide/mesaconic acid hydrogels crosslinked by ethylene glycol dimethacrylate (EGDMA) and MAB is the abbreviation of acrylamide/mesaconic acid hydrogels crosslinked by 1,4-butanediol dimethacrylate (BDMA).

Copolymer preparation

To prepare superabsorbent AAm/MA hydrogel systems, acrylamide (AAm) weighing 1 g was dissolved in 1 mL aqueous solutions containing 0, 20, 40, 60, and 80 mg mesaconic acid (MA). For the synthesis, 0.25 mL of 1% concentration crosslinker solution was added this aqueous solution. 0.20 mL of APS (5 g/100 mL water) and 0.25 mL of TEMED (1 mL/100 mL water) were then added to the solution.

The solutions were placed in PVC straws of 3 mm diameter. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm in length. They

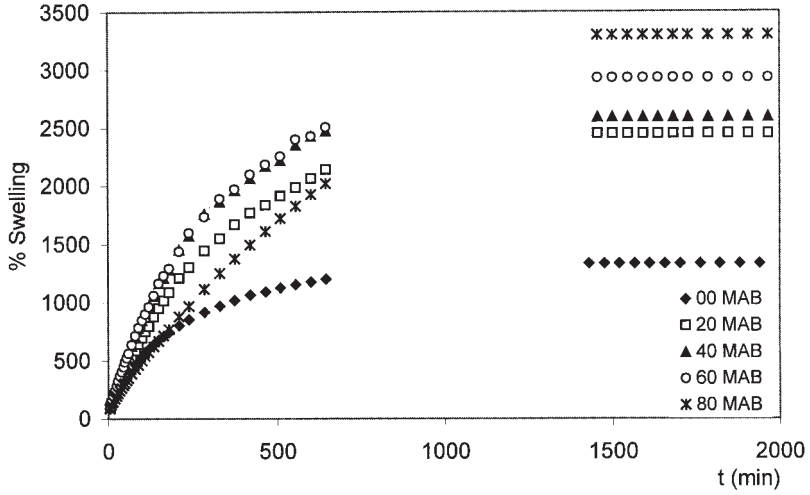

Figure 2 Swelling isotherms of AAm/MA hydrogels crosslinked by BDMA.

TABLE I
Equilibrium Swelling of AAm/MA Hydrogel Systems

MA/mg	00	20	40	60	80
	Equilibrium swelling (% *S*)				
EGDMA	1400	2301	2510	2603	3243
BDMA	1330	2445	2589	2929	3296

TABLE II
Equilibrium Water Content (EWC) of AAm/MA Hydrogel Systems

MA/mg	00	20	40	60	80
	Equilibrium water content (EWC)				
EGDMA	0.9333	0.9584	0.9617	0.9630	0.9701
BDMA	0.9301	0.9607	0.9628	0.9670	0.9706

were washed and thoroughly rinsed with distilled water, blotted dry with filter paper, dried in air and vacuum, and stored for swelling studies.

Swelling and diffusion

Chemically 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 ± 0.1°C in a water bath.

RESULTS AND DISCUSSION

Preparation

Acrylamide/mesaconic acid (AAm/MA) hydrogels were prepared by free radical solution polymerization. At 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 MA 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/MA) can continue growing indefinitely, with the active center being continually shifted to the free end of the chain. Crosslinker molecules can be incorporated into chains simultaneously and from a permanent link between them. Dried AAm/MA 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.

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:

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

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 Figures 1 and 2.

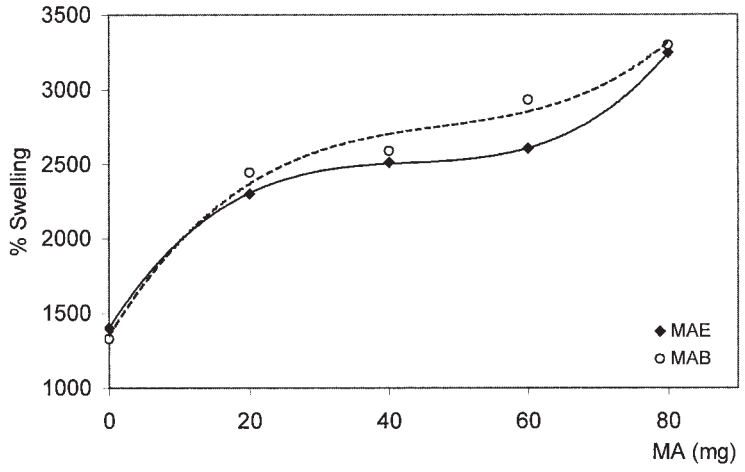

Figure 3 Effect of crosslinkers on swelling of AAm/MA hydrogels.

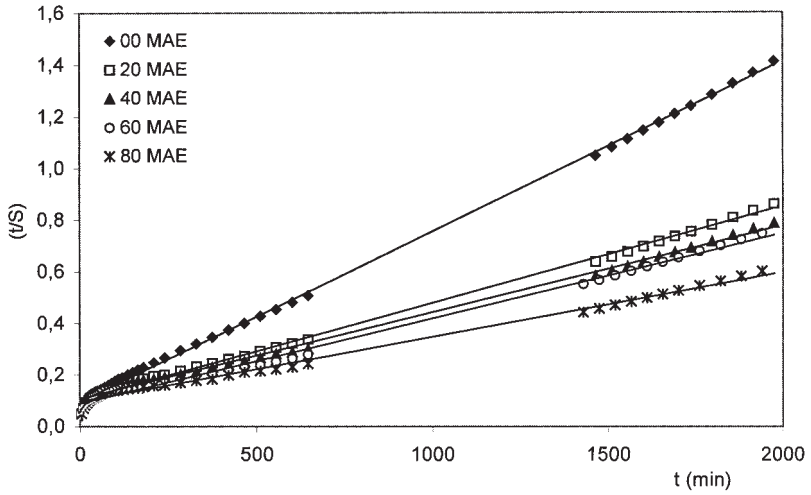

Figure 4 Swelling rate curves of AAm/MA hydrogels crosslinked by EGDMA.

Figures 1 and 2 show that swelling increases with time up to certain level and then levels off. This value of swelling may be called the equilibrium swelling percentage (*S*%). *S*% of AAm/MA copolymers is used for the calculation of network characterization parameters. *S*% of AAm/MA copolymers is given Table I.

Table I shows that *S*% of AAm is 1330–1400%, but *S*% of AAm/MA hydrogels is 2301–3296% with the incorporation of MA groups into AAm chains. Hydrophilicity of AAm/MA copolymers becomes greater than that of AAm, so, the swelling of AAm/MA copolymers is greater than the swelling of AAm hydrogels.

For understanding the effect of MA content on the swelling behavior, *S*% of the hydrogels versus the content of MA is plotted in Figure 3.

In Figure 3, *S*% of the hydrogels increased with the MA content in the copolymers. *S*% of AAm/MA hydrogels is higher than *S*% of pure AAm hydrogels. The reason for this is the hydrophilic groups on the MA. The greater the number of hydrophilic groups in the AAm/MA, the greater the swelling of the AAm/MA hydrogels.

Equilibrium water content

The water absorbed by AAm/MA hydrogels is quantitatively represented by the Equilibrium Water Content (EWC),[22,23] where

$$\mathrm{EWC} = \frac{m_s - m_0}{m_s} \tag{2}$$

Here, m_s is the mass of the swollen gel at time t (equilibrium) and m_0 is the mass of the dry gel at time 0. The EWCs of all AAm and AAm/MA hydrogel systems were calculated. The values of EWC of the hydrogels are tabulated in Table II. All EWC values of the hydrogels (0.9301–0.9706) were greater than the percent water content values of the body, which were about 0.60 (or 60%). Thus, the AAm and AAm/MA hydrogels exhibited fluid contents similar to those of living tissues.

Swelling kinetics

To examine the controlling mechanism of the swelling processes, several kinetic models are used to test ex-

TABLE III
Swelling Rate Parameters of AAm/MA Hydrogel Systems

MA/mg	00	20	40	60	80
		Initial swelling rate $(dS/dt)_0$; g_{water}/g_{gel} min			
EGDMA	10.52	9.67	9.32	11.28	10.25
BDMA	9.69	10.39	13.50	12.28	5.19
		Swelling rate constant $(k_s \times 10^6)$; g_{gel}/g_{water} min			
EGDMA	4.57	1.36	1.05	1.23	0.64
BDMA	4.63	1.29	1.57	1.06	0.90
		Theoretical equilibrium swelling (S_{max}); g_{water}/g_{gel}			
EGDMA	1517	2670	2984	3035	4006
BDMA	1446	2843	2937	3411	5225

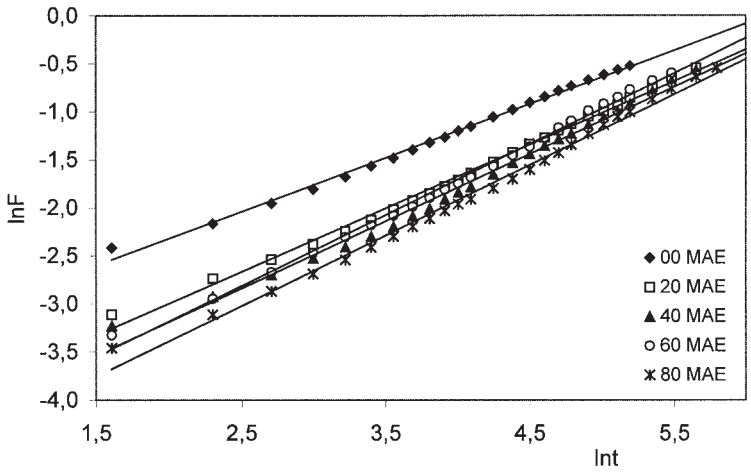

Figure 5 Swelling kinetics curves of AAm/MA hydrogels crosslinked by EGDMA.

perimental data. The large number and array of different chemical groups on the AAm/MA 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[24]

$$\frac{dS}{\mathrm{dt}} = k_{2,S}(S - St)^2 \tag{3}$$

where $k_{2,S}$ is the rate constant of swelling and S denotes the degree of swelling at equilibrium. After definite integration by applying the initial conditions $S = 0$ at $t = 0$ and $S = St$ at $t = t$, eq. (3) becomes

$$\frac{t}{\mathrm{S}} = A + Bt \tag{4}$$

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

To test the kinetics model, t/S versus t graphs are plotted and representative graphs are illustrated in Figure 4. The calculated kinetic parameters are tabulated in Table III.

As can be seen from Table III, the kinetics model is in agreement with the swelling experiments, since, as depicted in Table I, S (S%) is changed with MA content. Again, the initial swelling rate is changed with MA content. This may be plausible since the hydrophilicity of the network is enhanced with the extent of MA groups in structure. It may be important to note that the extent of MA determines the swelling rate by increasing hydrophilicity.

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 preexisting 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.

The following equation is used to determine the nature of diffusion of water into hydrogels:[25]

$$F = kt^n \tag{5}$$

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 (5) is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II

TABLE IV
Swelling Exponents and Swelling Constants of AAm/MA Hydrogel Systems

MA/mg	00	20	40	60	80
	Swelling exponent (n)				
EGDMA	0.560	0.660	0.698	0.737	0.732
BDMA	0.580	0.729	0.758	0.758	0.737
	Swelling constant ($k \times 10^3$)				
EGDMA	31.93	13.28	10.17	9.468	7.778
BDMA	17.82	9.432	9.956	8.580	5.171

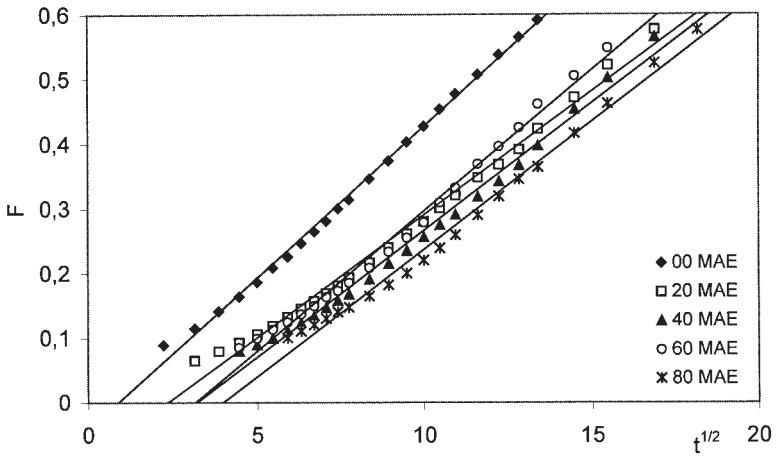

Figure 6 Diffusion curves of AAm/MA hydrogels crosslinked by EGDMA.

transport are defined by n values of 0.5 and 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. That is reflected by n values between 0.5 and 1.[25]

For chemically crosslinked hydrogels, ln$F$ versus ln$t$ graphs are plotted and representative results are shown in Figure 5. n exponents and k parameters are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table IV.

Table IV 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.[25] 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.[25]

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/MA hydrogels. The short time approximation is valid for the first 60% of initial swelling.[26]

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

$$F = 4\left[\frac{Dt}{\pi r^2}\right]^{1/2} - \pi\left[\frac{Dt}{\pi r^2}\right] - \frac{\pi}{3}\left[\frac{Dt}{\pi r^2}\right]^{3/2} + \ldots\ldots \quad (6)$$

where D is in cm^2 s^{-1}, t is in seconds, and r is the radius of a cylindrical polymer sample. A comparison of eqs. (5) and (6) shows the semiempirical eq. (5) 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 Figure 6. The diffusion coefficients were calculated from the slope of the lines. The values of diffusion coefficient determined for the hydrogels are listed in Table V.

Table V shows that the values of the diffusion coefficient of the AAm/MA hydrogels vary from 38.01 $\times$ 10^{-6} cm^2 s^{-1} to 182.73 $\times$ 10^{-6} cm^2 s^{-1}.

CONCLUSIONS

Incorporation of a hydrophilic group containing chemicals such as MA in AAm hydrogels can be obtained successively by free radical solution polymerization method. Two multifunctional crosslinkers such as EGDMA and BDMA are used in the polymerization process. The hydrogels showed high water absorbency (swelling ratio range 1330–3296%) and high equilibrium water content (0.9301–0.9706). This result showed that AAm/MA hydrogels could be used as a biomaterial on some biomedical applications, because equilibrium water contents were bigger than the percent water content value of the body of about 0.60 (60%). It was seen that swelling of AAm/MA hydrogels increased with the increasing of content of MA.

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 species. The new hydrogels reported can be used to carry substances in an aquatic field for pharmaceutical, agricultural, environmental, and biomedical applications.

TABLE V
Diffusion Coefficients of AAm/MA Hydrogel Systems

MA/mg	00	20	40	60	80
	Diffusion coefficients ($D \times 10^6$/cm^2 s^{-1})				
EGDMA	165.92	102.45	91.75	120.58	125.29
BDMA	38.01	78.05	182.73	153.98	68.10

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