Polymer Bulletin 57, 703–712 (2006)
DOI 10.1007/s00289-006-0608-1

Polymer Bulletin

Polymeric absorbent for water sorption based on chemically crosslinked poly (acrylamide/2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt) hydrogels

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Received: 13 March 2006 / Revised version: 19 May 2006 / Accepted: 30 May 2006
Published online: 14 June 2006 –

Summary

Swelling equilibrium of polyelectrolyte copolymer gels containing of acrylamide (AAm) and 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) have been studied as a function of copolymer composition. AAm/AMPS hydrogels were prepared by free radical solution polymerization in aqueous solution of AAm with AMPS as anionic comonomer and two multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA) and trimethylolpropane triacrylate (TMPTA). Swelling experiments were performed in water at 25 ^{o}C, gravimetrically. The influence of AMPS content in hydrogels was examined. Swelling of AAm/AMPS hydrogels was increased up to1018% (for containing 2% AMPS and crosslinked by EGDMA) 15246% (for containing 8%AMPS and crosslinked by TMPTA), while AAm hydrogels swelled up to 804% (crosslinked by TMPTA)–770% (crosslinked by EGDMA). The values of equilibrium water content of the hydrogels are 0.8851-0.9935. Diffusion behavior was investigated. Water diffusion into hydrogels was found to be *non-Fickian* in character.

Introduction

Hydrogels are chemically or physically crosslinked structures composed of hydrophilic homopolymers or copolymers. Hydrogels are macromolecular polymer networks immersed in a solvent, synthesized to exhibit large volumetric swelling in response to a variety of environmental stimuli. They are three-dimensional crosslinked polymeric structures that are able to swell in the aqueous environment. Materials with the ability to absorb water in high amounts are again under investigation, because of their potential applications in bioengineering, biomedicine, food industry, communication technology, building industry, chromatography, water purification, separation processes and agriculture. The ability of polymer gels to undergo substantial swelling and collapsing, up to 1000 times in volume, as a function of their environment is one of the most notable properties of these materials. These polymers are often called polymer hydrogels and generally they are low crosslinked hydrophilic

electrolytes [1-5]. The phenomenon of gel volume transition, which can be induced by temperature, pH or ionic strength, among other stimuli, has prompted researches to investigate gels as sensors, controllable membranes for separations and modulators for delivery of drugs. Although many naturally occurring polymers may be used to produce this type of materials, the structural versatility available in synthetic hydrogels has given them distinctive properties, which in turn have enhanced their practical utility [6-10].

In order to increase their swelling capacity, an ionic comonomer is also included in the monomer mixture. Several studies have been reported on the properties of hydrogels as a function of their ionic group content [11-16]. Increasing number of ionic groups in the hydrogels is known to increase their swelling capacity. Polyacrylamide based hydrogels have received considerable attention because of their use in many applications (as specific sorbent, etc.) [11-12]. The aim of the present study is to investigate the swelling properties of a series of hydrogels that are crosslinked some "new" multifunctional crosslinkers such as EGDMA and TMPTA. For this investigation, AMPS was selected as the ionic/anionic comonomer of AAm. AMPS received attention in recent years due to its strongly ionizable sulfonate group [17-20]. AMPS dissociate completely in the overall pH range, and therefore, the hydrogels derived from AMPS exhibit pH indepented swelling behavior.

Experimental

Acrylamide (AAm)/2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) (AAm/AMPS) hydrogels were prepared by free radical crosslinking copolymerization of AAm monomer (Merck, Darmstad, Germany) with addition of an anionic comonomer such as AMPS (Merck, Darmstad, Germany) and two multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA) (Merck) and trimethylolpropane triacrylate (TMPTA) (Aldrich Chemical Co., Milwaukee, US). The initiator, ammonium persulphate (APS) and NaOH were also supplied by Merck. All chemicals were used as received.

AMPS stock solution was prepared by dissolving 20 g of 2-acrylamido-2-methyl-1-propanesulfonic acid, (AMPS-H^+) in about 40 mL of distilled water and adding to this solution 10 mL of a 30% NaOH solution under cooling. Then, the solution was titrated with 1 M NaOH to pH=7.00 and finally, the volume of the solution were completed to 100 mL with distilled water. AMPS stock solution (1 mL) of thus prepared contained 0.966 mmol AMPS.

There were used two abbreviations in text/in Figures as AMPS/E and AMPS/T. AMPS/E is abbreviation of AAm/AMPS hydrogels crosslinked by ethylene glycol dimethacrylate (EGDMA) and AMPS/T is abbreviation of AAm/AMPS hydrogels crosslinked by trimethylolpropane triacrylate (TMPTA).

To prepare super absorbent AAm/AMPS hydrogel systems, acrylamide (AAm) weighing 1 g was dissolved in 2 mL water. Then related amount of AMPS stock solution was added to this solution. For example, for 2% AMPS solutions, 0.3 mL AMPS stock solution was added to this mixture. After this addition, for the synthesis, 0.0262 g crosslinker (0.024 mL / 8.91×10^{-5} mol of TMPTA or 0.025 mL / 1.30×10^{-4} mol of EGDMA) and 0.64 mL aqueous solution of APS (0.040 g APS / 1.72×10^{-4} mol /10 mL water) were added this aqueous solution. For the other sample solutions

(4,6 and 8% AMPS) the method was repeated with aqueous solutions of containing 4, 6, and 8% AMPS.

The solutions were placed in PVC straws of 3 mm diameter, then, they were waited for 1 day in an oven at 40^{o}C. 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.

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

AMPS received attention in recent years due to its strongly ionizable sulfonate group. The synthesis of AAm/AMPS via radical chain polymerization is a well-established procedure. AMPS dissociate completely in the overall pH range, and therefore, the hydrogels derived from AMPS exhibit pH indepented swelling behavior.

AAm/AMPS hydrogels were prepared by free radical solution polymerization. At polymerization, the possible step is a reaction between an AAm and anionic comonomer such as AMPS 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/AMPS) can continue growing indefinetly, 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. Dried AAm/AMPS 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. There have been presented the photographs of AAm/AMPS hydrogels containing 8% AMPS crosslinked by EGDMA or TMPTA at Figure 1 and Figure 2 as dry state and as swollen state. The capacity of swelling of the hydrogel systems can be seen from their photographs.

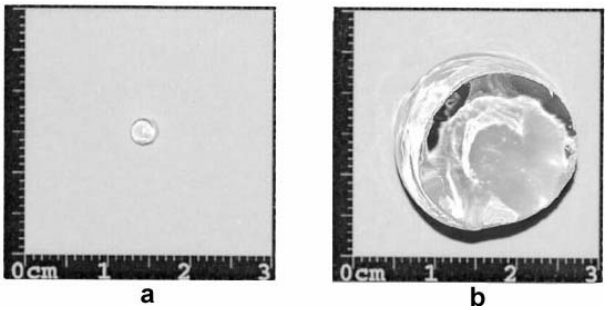

Figure 1. The photographs of AAm/AMPS hydrogel containing 8% AMPS Crosslinked by EGDMA (a; dry state b; swollen state)

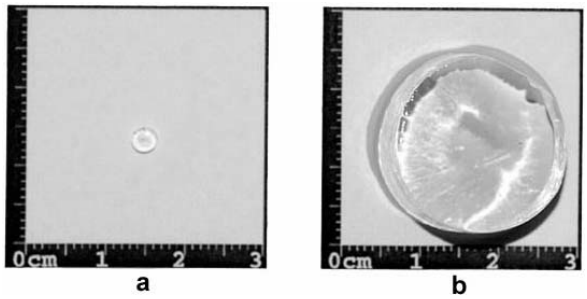

Figure 2. The photographs of AAm/AMPS hydrogel containing 8% AMPS Crosslinked by TMPTA (a; dry state b; swollen state)

Equilibrium swelling studies

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. The percentage swelling (S%) of the hydrogels in distilled water was calculated from the following relation.

$$S\% = \frac{m_t - m_o}{m_o} x\,100 \qquad (\mathbf{1})$$

Where m_t is the mass of the swollen gel at time t and m_o 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 Figure 3. Figure 3 shows that swelling increases with time up to certain level, then levels off. This value of swelling may be called the equilibrium swelling percentage (S_{eq}%). The values of S_{eq}% of AAm/AMPS copolymers are used for the calculation of network characterization parameters. The values of S_{eq}% of AAm/AMPS copolymers are given Table 1. Table 1 shows that the values of S_{eq}% of AAm are 770-804%, but S_{eq}% of AAm/AMPS hydrogels are 1018-15426% with the incorporation of AMPS groups into AAm chains. Hydrophilicity of AAm/AMPS copolymers becomes greater than that of AAm, so, the swelling of AAm/AMPS copolymers is greater than the swelling of AAm hydrogels. In Table 1,

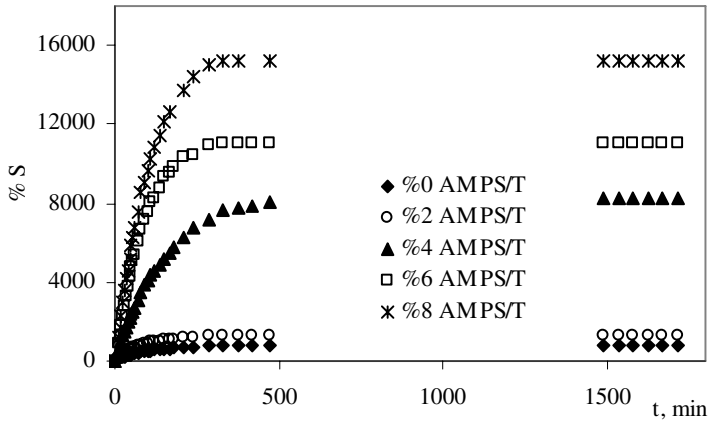

Figure 3. Swelling isotherms of poly (AAm/AMPS) hydrogels crosslinked by TMPTA

S_{eq}% of the hydrogels increased with the AMPS content in the copolymers. S_{eq}% of AAm/AMPS hydrogels is higher than S_{eq}% of pure AAm hydrogels. The reason of this is the hydrophilic groups on the AMPS. AMPS has got strongly ionizable sulfonate group. The more hydrophilic groups in the AAm/AMPS get the more the swelling of the AAm/AMPS hydrogels. This is an expected result about swelling of AAm/AMPS hydrogel systems.
The effect of crosslinkers is important for the preparation of AAm/AMPS hydrogel systems. As seen in Table 1, equilibrium percentage swelling of AAm and AAm/AMPS hydrogel systems increased in the following order:

$$S_{eq}\ (TMPTA) > S_{eq}\ (EGDMA)$$

Table 1. Equilibrium swelling of AAm/AMPS hydrogel systems.

AMPS	0%	2%	4%	6%	8%
	Equilibrium percentage swelling, S_{eq}%				
EGDMA	770	1018	7575	8859	9424
TMPTA	804	1275	8288	10991	15246

The reason for this arrangement may be the molecular structure and mass of used crosslinkers. Firstly EGDMA has got two functionalities for crosslinking, but TMPTA has got three functionalities. On the other hand used crosslinker contents were different for preparing of hydrogel systems. For the synthesis, the mol numbers of the crosslinkers were different (0.024 mL / 8.91×10^{-5} mol of TMPTA or 0.025 mL / 1.30×10^{-4} mol of EGDMA). TMPTA (MW=296.32 g mol^{-1}) has got bigger molecular structure than EGDMA (MW=198.22 g mol^{-1}). Then, there were a lot of porous for water sorption and swelling.

Equilibrium water content

Absorbed water by AAm/AMPS hydrogels is quantitatively represented by the equilibrium water content (EWC) [21-22], where

$$EWC = \frac{ms - mo}{ms} \qquad (\mathbf{2})$$

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 values of EWC of all AAm and AAm/AMPS hydrogel systems were calculated, and were tabulated in Table 2. All EWC values of the hydrogels (0.8851-0.9935) were greater than the percent water content values of the body about 0.60(or 60%). Thus, the AAm and AAm/AMPS hydrogels exhibited fluid contents similar to those of living tissues.

Table 2. Equilibrium water content (EWC) of AAm/AMPS hydrogel systems.

AMPS	0%	2%	4%	6%	8%
	Equilibrium water content, EWC				
EGDMA	0.8851	0.9105	0.9870	0.9888	0.9875
TMPTA	0.8894	0.9273	0.9881	0.9910	0.9935

Diffusion

When a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the network expands resulting in swelling of the hydrogel. Diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. Swelling of the hydrogel involves larger segmental motion resulting, ultimately, in increased separation between hydrogel chains. Analysis of the mechanisms of water diffusion into swellable polymeric systems has received considerable attention in recent years, because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering. The following equation is used to determine the nature of diffusion of water into hydrogels.

$$F = kt^n \qquad (3)$$

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. Eq. 3 is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by n values of 0.5 and 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. That is reflected by n between 0.5 and 1 [23-24]. For chemically crosslinked hydrogels, ln F *vs*. ln t graphs are plotted and representative results are shown in Figure 4. Diffusion exponents and diffusion constants are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table 3.

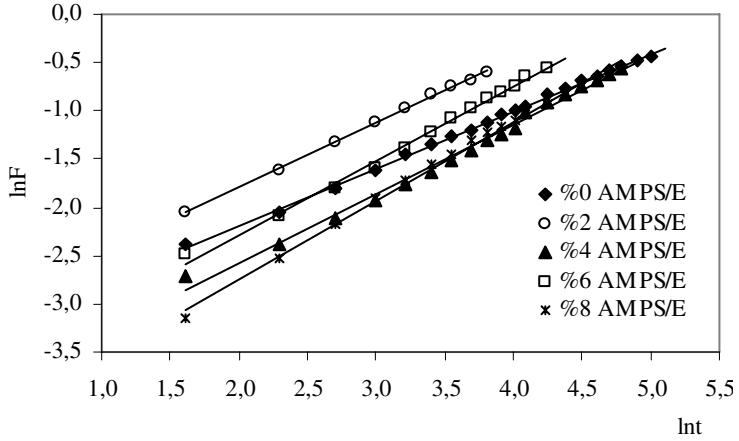

Figure 4. Plots of lnF *vs* lnt for poly (AAm/AMPS) hydrogels crosslinked by EGDMA

Table 3 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 [23]. 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.

Table 3. Diffusion exponents and diffusion constants of AAm/AMPS hydrogel systems.

AMPS	0%	2%	4%	6%	8%
	Diffusion exponent, n				
EGDMA	0.59	0.67	0.72	0.76	0.81
TMPTA	0.67	0.66	0.85	1.03	0.91
	Diffusion constant, K x 10^2				
EGDMA	3.5	4.4	1.8	2.2	1.3
TMPTA	3.1	3.6	1.0	0.8	1.1

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/AMPS hydrogels. The short time approximation is valid for the first 60% of initial swelling [24]. The diffusion coefficients of the cylindrical AAm/AMPS hydrogels are calculated from the following relations:

$$F = 4\left[\frac{D\,t}{\pi\, r^2}\right]^{1/2} - \pi\left[\frac{D\,t}{\pi\, r^2}\right] - \frac{\pi}{3}\left[\frac{D\,t}{\pi\, r^2}\right]^{3/2} + \ldots\ldots \qquad (\mathbf{4})$$

where D is in $cm^2\ s^{-1}$, t in sec and r is the radius of a cylindrical polymer sample. Graphical comparisons of related equations shows the semi-empirical equation (4) with n=0.5 and k = 4 $(D/\pi r^2)^{1/2}$. For the hydrogels, F versus $t^{1/2}$ plots are constructed and representative results are shown in Figure 5. The diffusion coefficients were calculated from the slope of the lines. The values of diffusion coefficient determined for the hydrogels are listed in Table 4.

Table 4 shows that the values of the diffusion coefficient of the AAm/AMPS hydrogels vary from 103.5 x 10^{-6} $cm^2\ s^{-1}$ to 1294.0 x 10^{-6} $cm^2\ s^{-1}$.

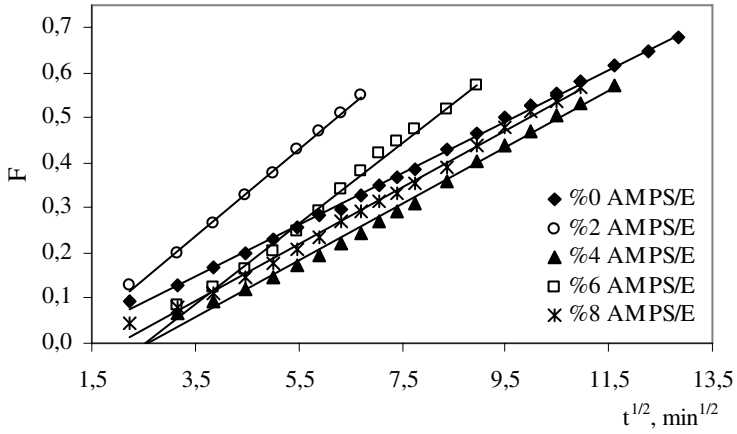

Figure 5. Plots of F *vs* $t^{1/2}$ for poly (AAm/AMPS) hydrogels crosslinked by EGDMA

Table 4. Diffusion coefficients of AAm/AMPS hydrogel systems.

AMPS	0%	2%	4%	6%	8%
	Diffusion coefficients, D x10^6 /cm^2 s^{-1}				
EGDMA	103.5	163.2	438.4	767.2	242.8
TMPTA	139.2	203.6	535.8	1294.0	1154.9

Swelling kinetics

In order to examine the controlling mechanism of the swelling processes, several kinetic models are used to test experimental data. The large number and array of different chemical groups on the AAm/AMPS chains (e.g., amide, carbonyl) 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 [25]

$$\frac{d\,S}{\mathrm{d\,t}} = k_{2,S}\,\left(\mathrm{S} - S_t\right)^2 \qquad (\mathbf{5})$$

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, equation (5) becomes

$$\frac{\mathrm{t}}{\mathrm{S}} = \mathrm{A} + \mathrm{B\,t} \qquad (\mathbf{6})$$

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

To test the kinetics model, t/S vs. t graphs are plotted and representative graphs are illustrated in Figure 6. The calculated kinetic parameters are tabulated in Table 5.

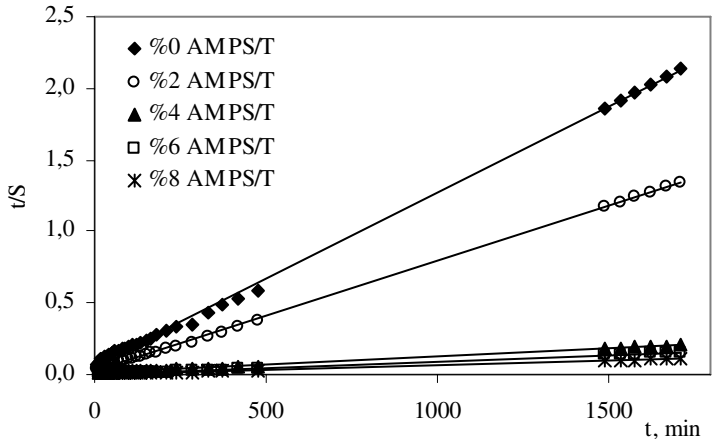

Figure 6. Swelling kinetics curves of poly(AAm/AMPS) hydrogels crosslinked by TMPTA

Table 5. Swelling kinetics parameters of AAm/AMPS hydrogel systems.

AMPS	0%	2%	4%	6%	8%
	The initial swelling rate, r $(dS/dt)_o$; g_{water} / g_{gel} min				
EGDMA	9.13	41.72	74.18	146.26	99.11
TMPTA	14.33	30.78	75.24	193.35	220.36
	The swelling rate constant, k_s x 10^6 ; g_{gel} / g_{water} min				
EGDMA	13.72	38.79	1.12	1.70	0.96
TMPTA	14.31	17.80	0.94	1.47	0.86
	The theoretical equilibrium swelling, S_{max} ; g_{water} / g_{gel}				
EGDMA	816	1037	8130	9285	10168
TMPTA	837	1315	8969	11473	16036

As can be seen from Table 5, kinetics model is agreement with swelling experiments, since, as depicted in Table 1, S_{eq}% is changed with AMPS content. Again, the initial swelling rate is changed with AMPS content. This may be plausible since the hydrophilicity of the network is enhanced with the extent of AMPS groups in structure. It may be important to note that extent of AMPS determines the swelling rate by increasing hydrophilicity.

Conclusion

Incorporation of hydrophilic group containing chemicals such as AMPS in AAm hydrogels can be obtained successively by free radical solution polymerization method. Two multifunctional crosslinker such as EGDMA and TMPTA used at the polymerization process. The hydrogels showed high water absorbency (swelling ratio range770-15426%) and high equilibrium water content (0.8851-0.9935). This result showed that AAm/AMPS hydrogels would be used as a biomaterial on some biomedical applications, because equilibrium water contents was bigger than the percent water content value of the body about 0.60 (60%). It was seen that swelling of AAm/AMPS hydrogels increased with the increasing of content of AMPS. This type of work could encourage the synthesis of new hydrogels, where some functionality is required, for specific purposes. This is under investigation for the separation and selectivity of special spices. The new hydrogels reported can be used to carry substances in an aquatic field for pharmaceutical, agricultural, environmental and biomedical applications.

Acknowledgements. Work was supported by Adnan Menderes University Research Fund, under project number; FEF 03 008.

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