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Swelling studies of super water retainer acrylamide/crotonic acid hydrogels crosslinked by trimethylolpropane triacrylate and 1,4-butanediol dimethacrylate

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Summary

Superswelling acrylamide/crotonic acid (AAm/CA) hydrogels were prepared by free radical polymerization in aqueous solution of acrylamide (AAm) with crotonic acid (CA) as comonomer. For each copolymerization, four different composition of CA and a concentration of multifunctional crosslinkers such as trimethylolpropane triacrylate (TMPTA) and 1,4-butanediol dimethacrylate (BDMA) were used. As a result of dynamic swelling tests, the influence of the crosslinkers and the relative content of CA on the swelling properties were examined. AAm/CA hydrogels were swelled in the range of 1520-2980% in water, while AAm hydrogels swelled as 780 and 1360%. Equilibrium water content of AAm/CA hydrogels was calculated in the range of 88.73 and 96.75%. Water uptake of hydrogels was followed non-*Fickian* type diffusion.

Introduction

Hydrogels may be conveniently described as hydrophilic polymers that are swollen by, but do not dissolve in water. They are three-dimensional crosslinked polymeric structures that are able to swell in the aqueous environment. 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. Due to characteristic properties such as swellability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical, environmental applications (1-8).
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 which, in the first step, the linear polymer is synthesized in the absence of a crosslinking agent and in the second step the synthesized polymer is crosslinked using either chemical reagents or irradiation (1). 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 (9-11). It has reported many studies about gelation of AAm based hydrogels by free radical polymerization (9-11).
The aim of this study is to investigate the swelling properties of AAm hydrogels with addition of an anionic monomer such as CA and some multifunctional crosslinkers such as TMPTA and BDMA. Swelling behavior of superadsorbent polymers may be characterized by water adsorption. In this study, equilibrium swelling, some swelling kinetics parameters such as the initial swelling rate, the swelling rate constant, and diffusional parameters such as swelling exponent, swelling constant and diffusion coefficients of hydrogels were determined by dynamic swelling studies. These swelling properties will be effected that usability of its as biomaterial in biological, medical, pharmaceutical applications and as an adsorbent in environmental applications.

Experimental

Acrylamide (AAm) supplied by from Merck (Darmstadt, Germany) and the anionic comonomer, crotonic acid (CA) supplied by from Aldrich Chemical Co. (Milwaukee, US). The initiator, ammonium persulfate (APS) and the activator *N,N,N',N'*-tetramethylethylenediamine (TEMED) supplied from Merck(Darmstadt, Germany) 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.(Milwaukee, US)(Table 1). All chemicals were used as received. Doubly distilled water was used in the copolymerization and swelling studies.
To prepare AAm/CA hydrogels, first, 1 g of AAm was dissolved in 1 mL distilled water, and then 0, 20, 40, and 60 mg CA were added to the aqueous solutions of AAm. For investigation of the effect of crosslinkers on preparation of AAm/CA hydrogels, 0.25 mL of 1% concentration of TMPTA, or 0.25 mL of 1% concentration of BDMA were added to the aqueous solutions of AAm or AAm/CA. 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 into the solution.
These solutions mentioned above were placed in PVC straws (as the polymerization reactors) of 3 mm diameter. The polymerization was conducted for 24 hours. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3-4 mm length. These were dried in air and then under vacuum, and stored for swelling studies. The swelling behaviors of dried hydrogels were carried out by immersion in doubly distilled water at 25±0.1 ^{0}C in a water bath. The water absorbed was determined by weighing the samples, after wiping, at various time intervals. Swollen gels weighed by an electronic balance (SARTORIUS, BP 210S, d= 0.1 mg).

Table 1. Used monomers and crosslinkers in the preparation of hydrogel systems

Name	Formula	Abbreviations
Acrylamide (Propen amid)	$H_2C=CHCONH_2$	AAm
Crotonic acid	$CH_3CH=CHCOOH$	CA
Ammonium persulfate	$(NH_4)_2S_2O_8$	APS
N,N,N',N'-Tetramethylethylenediamine	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	TEMED
Trimethylolpropane triacrylate	$[H_2C=CHCOOCH_2]_3CC_2H_5$	TMPTA
1,4-Butanediol dimethacrylate	$[H_2C=C(CH_3)COOCH_2CH_2]_2$	BDMA

Results and Discussion

Preparation of Crosslinked Copolymers

The copolymerizations of AAm with anionic comonomers such as itaconic acid (2), maleic acid (12), crotonic acid (13) and succinic acid (14) have been studied by γ radiation in our previous study. In this study, AAm/CA hydrogels were prepared by free radical polymerization in aqueous solutions of AAm, CA and crosslinkers such as TMPTA and BDMA.

In the polymerization process, 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 CA and 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/CA) can continue growing indefinitely, with the active center being continually shifted to the free end of the chain. Crosslinker molecules can incorporate into chains simultaneously and forms a permanent link between them (9).

The process of polymerization and crosslinking has been taken an hour for the gelation of AAm/CA. However, for all hydrogels, it has been waited for 24 hours for good gelation. The crosslinked copolymers were colorless and some of them were semi-transparent. They were soft, elastic, and slippery or slimly with surface. There was no difference an external appearance of crosslinked copolymeric samples about change of molecular structure of crosslinker.

Swelling Measurements

At the many studies for hydrogel characterization, swelling parameters were investigated. On crosslinked AAm/CA hydrogels, dynamic swelling experiment were performed in distilled water and the increase in mass were followed as a function of time. Because, a fundamental relationship existence the swelling of a polymer in a solvent and between the nature of the solvent and polymer.

The swelling [S%] of the hydrogels in distilled water was calculated from the following relation (2-6),

$$S\% = \frac{M_t - M_o}{M_o} \times 100 \quad (1)$$

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 uptake of initially dry hydrogels was followed gravimetrically. The swelling isotherms of AAm/CA hydrogels crosslinked by TMPTA are shown in Fig.1. The common properties of these swelling graphs are that the swelling were increased sharply at the beginning and slowly leveling off with time. This constant S% value may be named as equilibrium swelling percentage (S_{eq}%). The S_{eq}% values of the hydrogels were used for the calculation of some characterization parameters (Table 2). The values of S_{eq}% of AAm are 780 and 1360%, but the values of S_{eq}% of AAm/CA hydrogels vary between 1520-2980%. It is well known that the swelling of hydrogel is induced by the electrostatic repulsion of the ionic charges of its network (2-6,15,16). The ionic charge content in the polymeric structure is important. Crotonic acid contains many hydrophilic units (–COOH) and the swelling of the hydrogels increase due to an increase of the hydrophilic units. The hydrophilic group numbers of AAm/CA copolymers are more than AAm, so, the swelling of AAm/CA copolymers is more than that of AAm copolymers (2-6,15,16).

Effect of Crosslinkers

The effect of crosslinkers is important to preparing of AAm based hydrogels (9-11,16). The values of S_{eq}% of AAm/CA hydrogels are increased following order;

$S_{TMPTA} > S_{BDMA}$

The reason of this arrangement may be molecular structure of crosslinkers. Firstly, BDMA is tetrafunctional crosslinker and TMPTA is hexafunctional crosslinker. There will be the less swelling when using of BDMA. Because TMPTA is hexafunctional crosslinker, there will be many crosslinking between chains. On the other hand, with the increasing concentration of CA, swelling of hydrogels may be increased. This difference of the swelling is about chemical arrangement of crosslinkers and concentration of CA.

Equilibrium Water Content

Another parameter for hydrogel swelling is percentage equilibrium water content (EWC%), which can be calculated from following equation (17,18);

$$EWC\% = \frac{M_s - M_o}{M_s} \times 100 \quad (2)$$

where M_s is the mass of the swollen gel at equilibrium, and M_0 is the mass of the dry gel at time 0. The values of EWC% of obtained hydrogels were calculated and, are tabulated in Table 2. All values of EWC% of the hydrogels (88.73% - 96.75%) were greater than the percent water content values of the body about 60%. Thus, the hydrogels were exhibit similarity of the fluid contents with those of living tissues. It can be said that AAm/CA hydrogels crosslinked BDMA and TMPTA used as a new material as a biomaterial in medicine, pharmacy or veterinary.

Swelling Kinetics Studies

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 chains (e.g., amine, amide, carbonyl, carboxyl or hydroxyl) imply that there are many types of polymer-solvent interactions. It is probable that any kinetic 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 the second order equation in the form of (19-21);

$$\frac{dS}{dt} = k_S \left(S_{eq} - S\right)^2 \qquad (3)$$

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

$$\frac{t}{S} = A + Bt \qquad (4)$$

Where $B=1/S_{eq}$ is the inverse of the maximum or equilibrium swelling, $A=1/k_S S_{eq}^2$ is the reciprocal of the initial swelling rate $[(dS/dt)_0]$ of the hydrogel, and k_S is swelling rate constant.

To test the kinetics models, t/S vs. t graphs were plotted and representative graphs are illustrated in Fig. 2 for the AAm and AAm/CA hydrogels crosslinked by BDMA. The values of initial swelling rate, swelling rate constant and maximum equilibrium swelling of the hydrogels were calculated from the slope and the intersection of the lines, respectively (Table 2). As depicted from Table 2, the results of kinetic model are in agreement with swelling experiment.

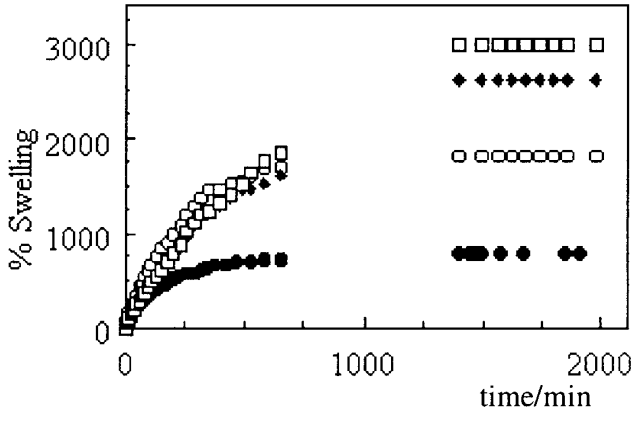

Fig. 1. Swelling isotherms of AAm/CA hydrogels prepared by TMPTA ●; 0 mg CA, ○; 20 mg CA □; 40 mg CA ♦; 60 mg CA.

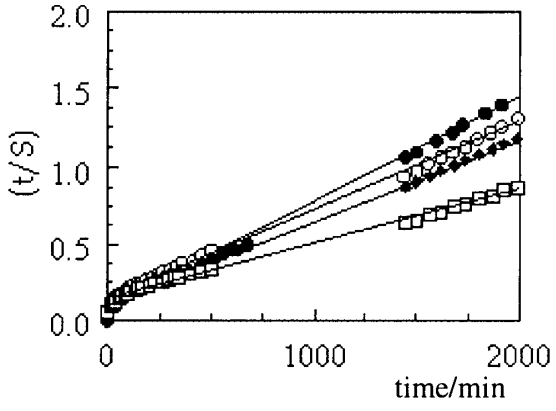

Fig. 2. Swelling rate curves of AAm/CA hydrogels prepared by BDMA, ●; 0 mg CA, ○; 20 mg CA □; 40 mg CA ♦; 60 mg CA.

Determination of Swelling Power

Due to important applications of swellable polymers in biomedicine, pharmaceutical, environmental and agricultural engineering, analysis of the mechanisms of water diffusion in swellable polymeric systems has gained considerable attention lately.
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.
Exploiting swelling experiment, the diffusion of water into hydrogel can be determined. Applying the following equation to the 60% of swelling curves, the nature of diffusion of water into hydrogels can be evaluated (22).

$$F_{swp} = \frac{M_t - M_o}{M_o} = Kt^n \qquad (5)$$

Here, 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 (22).
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* type. This equation is applied to the initial stages of swelling and plots of ln F_{swp} versus ln t yields straight lines up to almost %60 increase in the mass of hydrogel (22,23).
The swelling exponents (n) were calculated from the slopes of the lines of lnF_{sw} - ln t plots and are tabulated in Table 2. The values of n range generally between 0.60 and 0.72. The number to determine hydrogels had a *non-Fickian* character. In this diffusion, diffusion and relaxation are said to be isochronal effective (22,23).

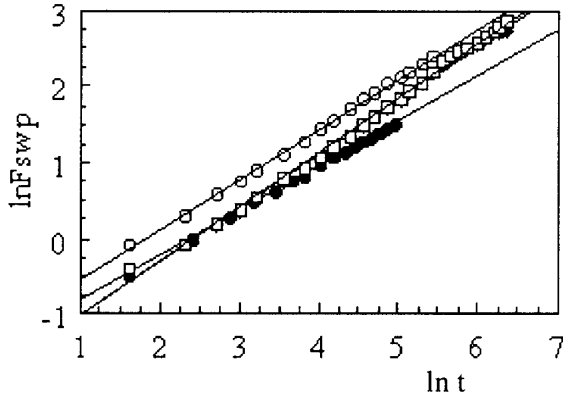

Fig. 3. Swelling kinetic curves of AAm/CA hydrogels crosslinked by TMPTA, ●; 0 mg CA ○, 20 mg CA □; 40 mg CA ♦; 60 mg CA.

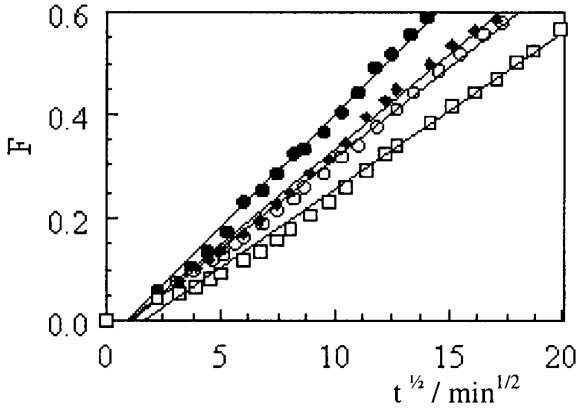

Fig. 4. Diffusion curves of AAm/CA hydrogels crosslinked by BDMA,
●; 0 mg CA, ○; 20 mg CA □; 40 mg CA ♦; 60 mg CA.

Diffusion of water

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behavior. 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 (3,18,21,24). One of these methods is *'the short time approximation method'*. The short time approximation is valid only for the first 60% of the swelling (21,24). The diffusion coefficients of the cylindrical AAm and AAm/CA hydrogels were calculated from the following relations:

$$F = 4\left[\frac{D}{\pi r^2}\right]^{1/2} t^{1/2} \qquad (6)$$

Where D is in $cm^2\ s^{-1}$, t in sec and r is the radius of cylindrical polymer sample (cm). For the hydrogels, F versus $t^{1/2}$ plots were plotted and some representative results are shown in Fig.4. The diffusion coefficients were calculated from the slope of the lines.

Table 2. Some swelling parameters of AAm/CA hydrogels

CA, mg	00	20	40	60
Equilibrium swelling, S_{eq}%				
TMPTA	780	1820	2600	2980
BDMA	1360	1520	1670	2280
Equilibrium water contents, EWC%				
TMPTA	88.73	94.81	96.29	96.75
BDMA	93.16	93.83	94.37	95.80
The initial swelling rate, r or $(dS/dt)_o$ / g_{water} $(g_{gel})^{-1}$ min^{-1}				
TMPTA	7.92	12.18	5.03	4.89
BDMA	11.06	7.34	9.10	7.53
The swelling rate constant, k_S x 10^6 / g_{gel} $(g_{water})^{-1}$ min^{-1}				
TMPTA	11.27	3.01	0.38	0.24
BDMA	5.05	2.47	2.60	0.99
Maximum equilibrium swelling, S_{max} / g_{water} $(g_{gel})^{-1}$				
TMPTA	837	2012	3640	4530
BDMA	1470	1720	1860	2750
Swelling exponent, n				
TMPTA	0.59	0.67	0.72	0.72
BDMA	0.63	0.60	0.60	0.64
Swelling constant, K				
TMPTA	0.239	0.294	0.171	0.172
BDMA	0.294	0.295	0.337	0.286
Diffusion coefficients, D x 10^7 / cm^2 s^{-1}				
TMPTA	9.44	10.64	6.51	6.15
BDMA	7.79	4.96	6.73	5.44

The values of diffusion coefficient determined for the hydrogels are listed in Table 2. It is shown that the values of D of the hydrogels varied from $4.96x10^{-7}$ cm^2 s^{-1} to $10.64x10^{-7}$ cm^2 s^{-1}. The diffusion of the water to the AAm/CA hydrogel content 20 mg CA is faster than the others.

Conclusion

In this study, AAm/CA hydrogels were obtained from a neutral AAm monomer with the incorporation of carboxylic acid group containing comonomer (CA) by free radical polymerization in aqueous media. Some multifunctional crosslinker such as TMPTA and BDMA used at the polymerization process. AAm/CA hydrogels were swollen to equilibrium in distilled water. Hydrogel systems swelled in the range 780-2980%. The values of EWC% were calculated in the range 88.73-96.75. This result showed that AAm/CA 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 60%. The diffusion type of hydrogels was a non-fickian diffusion character. It was seen that swelling of AAm/CA hydrogels increased with the increasing of content of CA.

The utilization of these types of hydrogels, in biomedicine, controlled drug delivery, pharmaceuticals, agriculture, biotechnology, environment, adsorption, separation, purification, immobilization and enrichment of some species makes hydrogel more popular.

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