Water absorbency studies of $\gamma$-radiation crosslinked poly(acrylamide-co-2,3-dihydroxybutanedioic acid) hydrogels

Erdener Karadağ $^a$,*, Dursun Saraydin $^b$, Olgun Güven $^c$

$^a$ Fen-Edebiyat Faculty, Department of Chemistry, Adnan Menderes University, TR-09010 Aydın, Turkey
$^b$ Department of Chemistry, Cumhuriyet University, TR-58140 Sivas, Turkey
$^c$ Department of Chemistry, Hacettepe University, Beytepe, 06532 Ankara, Turkey

Received 18 March 2004; received in revised form 6 May 2004

Abstract

Water absorbency behavior of acrylamide (AAm)/2,3-dihydroxybutanedioic acid (DBA) hydrogels synthesized by $\gamma$-radiation crosslinking of AAm and DBA in an aqueous solution was investigated. Different amounts of DBA containing AAm/DBA hydrogels were obtained in the form of rods via a radiation technique. Swelling experiments were performed in water at 25 $^\circ$C, gravimetrically. The influence of absorbed dose and DBA content of the hydrogels on swelling properties were examined. The hydrogels showed enormous swelling in an aqueous medium and displayed swelling characteristics which were highly dependent on the chemical composition of the hydrogels and irradiation dose. Diffusion behavior and some swelling kinetic parameters were investigated. The values of the weight swelling ratio of AAm/DBA hydrogels were between 8.34 and 15.16, while the values of the weight swelling ratio of pure AAm hydrogels were between 7.58 and 8.28. Water diffusion into hydrogels was found to be non-Fickian in character. Equilibrium water contents of the hydrogel systems were changed between 0.8681 and 0.9340.

$^*$Corresponding author. Tel.: +90-256-212-8498; fax: +90-256-213-5379.
E-mail address: ekaradag@adu.edu.tr (E. Karadağ).

Keywords: Acrylamide; 2,3-dihydroxybutanedioic acid; Hydrogel; Gamma radiation; Swelling

1. Introduction

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. Especially polymers can absorb water up to few hundred times of their own weight. These polymers are often called water super absorbents or polymer hydrogels. Water super absorbents generally are low crosslinked hydrophilic electrolytes [1–9].

Hydrogels are often based on water-soluble polymers, in particular, on statistic copolymers of acrylamide with some hydrophilic co-monomers, crosslinked by chemical or radiation techniques. In recent years, it was determined that crosslinked polymeric materials having functional groups such

0168-583X/S - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2004.06.010
as carboxylic acid, amine, hydroxyl and sulfonic acid groups could be used as complexing agent for the removal of metal ions from an aqueous solutions. Polyacrylamide or modified polyacrylamide hydrogels were appropriate materials for, ion exchange, removal of metal ions, treating aquaculture wastewater effluents, chemical precipitation, membrane filtration, coagulation, complexing, solvent extraction, and reducing the nutrient anion concentrations to appropriate levels, and they have found various commercial applications such as recovery of secondary oil, stabilization of mineral sedimentation of wastewater and metal extraction [10–14].

Radiation initiation of chemical reactions has been increasingly used for creation of novel biomaterials such as hydrogels. A radiation technique is more preferable than a chemical one, because of the advantage to control gently the level of crosslinking by variation of the absorbed dose. This method offers unique advantages for the synthesis of new and modification of existing materials: it is a simple, additive-free process at all temperatures, reactions such as polymerization, crosslinking and grafting can easily be controlled, and the treatment can be limited to a specific area. Some specific applications include synthesis of hydrogels; chemical modification of biomaterial surfaces; immobilization of biomaterial surfaces; synthesis of functional microspheres; crosslinking of hydrophobic and hydrophilic and hydrogel biomaterials; and radiation processing of naturally derived biomaterials [15,16].

In our previous studies, copolymeric hydrogels of acrylamide with vinyl groups containing acids and also non-vinyl group containing acids were prepared and used in separation and adsorption of some ions and molecules and biocompatibility studies [17–20]. It was of interest to increase the water absorption capacity of AAm hydrogels with non-vinyl functional groups containing chemical reagents such as DBA via the radiation method. The present paper reports a different study on the water absorption dynamics of a novel type of hydrogel containing acrylamide and 2,3-dihydroxybutanedioic acid by the γ-radiation technique. The swelling properties of AAm/DBA hydrogels were also characterized.

2. Materials and methods

2.1. Experimental materials

The sources of water, the monomers acrylamide and 2,3-dihydroxybutanedioic acid (tartaric acid), γ-irradiation doses were given before [18].

2.2. Preparation of AAm/DBA hydrogels

The method of preparation of the gamma radiation induced AAm/DBA hydrogel systems was the same as described in our earlier communications [18]. To prepare hydrogel systems, AAm weighing 1 g was dissolved in 1 ml aqueous solutions containing 0, 20, 40 and 60 mg DBA the solutions were placed in PVC straws of 3 mm diameter and irradiated to 2.60, 3.73, 4.6, 5.20 and 5.71 kGy in air at ambient temperature in a 60Co Gammaxcel 220 type γ-irradiator at a fixed dose rate of 0.72 kGy h⁻¹. The dose rate was determined by the conventional Fricke dosimeter. 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, blotted dry with filter paper, dried in air and vacuum, and stored for swelling studies.

2.3. Swelling measurements in water

Equilibrium swelling experiments were used to investigate the swelling properties of the materials which were prepared using the various preparation methods. Dry gels were weighed and then immersed in distilled water at 25 ± 0.1 °C. Swollen gels were removed from water at predetermined times, blotted dry, and weighed in air. From these measurements, the weight swelling ratios were determined. The weight swelling ratio, q is defined as

\[ q = \frac{W}{W_0}. \]

Here \( W \) is the weight of a swollen sample and \( W_0 \) is the initial dry weight [21].
3. Results and discussion

A network is obtained by permanently linking polymeric chains together in the form of a three-dimensional structure by high energy radiation (e, γ), peroxide cures and sulphur cures. The processes are known as crosslinking, curing and vulcanization, respectively. Crosslinking can be brought about by either chemical reactions that form covalent bonds between chains or by physical aggregation of units from two or more chains. To crosslink a polymeric system, high-energy radiation (or ionizing radiation), such as electrons (e), and gamma rays (γ) can also be used [15,16].

The radiation technique seems promising for the preparation of hydrogels because a polymer in an aqueous solution or a monomer dissolved in water undergo crosslinking on irradiation to yield a gel-like material. Since these hydrogels are not contaminated with foreign additives and crosslinks are composed of stable C–C bonds, it is of interest to study the preparation of hydrogels by irradiation. There are many works in the literature concerning radiation synthesis of hydrogels with vinyl monomers [22–24]. Although it is possible to find much work on the grafting of vinyl monomers onto polymeric materials, there are very few works done on the incorporation of non-vinyl chemical reagents to polymeric networks via radiation [25].

3.1. Preparation

Ionizing radiation was used for the preparation of AAm and AAm/DBA hydrogels. When monomers of AAm and DBA are irradiated with ionization rays such as γ rays, one double bond of –C=C– on AAm and one or two of C–H bonds of DBA were broken by ionization irradiation and free radicals are generated. These free radicals react with each other, and a copolymer of AAm/DBA is produced. A possible simple polymerization of AAm/DBA hydrogels by γ ray irradiation is suggested in Scheme 1. When AAm, DBA, and water ternary mixtures were irradiated, polymerization and crosslinking occur simultaneously. It is reported that the dose for complete gelation of AAm is 2.00 kGy of γ ray irradiation at ambient temperature [23–26]. So, a minimum dose of 2.60 kGy of γ rays is used for the preparation of AAm/DBA hydrogels.

3.2. Swelling

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. The water intake of initially dry hydrogels was followed for a period of time, gravimetrically. Swelling isotherms of the hydrogels were constructed and representative swelling curves are shown in Figs. 1 and 2.

Figs. 1 and 2 show that weight swelling ratio increases with time up to a certain level, then levels off. This value of swelling ratio may be called the equilibrium weight swelling ratio ($q_{eq}$). $q_{eq}$ values of AAm/DBA copolymers are used for the calculation of some swelling kinetic characterization parameters. $q_{eq}$ values of AAm/DBA copolymers are given in Table 1.

Table 1 shows that $q_{eq}$ values of AAm are 8.28–7.58, but $q_{eq}$ of AAm/DBA hydrogels are 8.34–15.16 with the incorporation of 2,3-dihydroxybutanedioic acid (DBA) groups into crosslinked copolymeric structure. Hydrophilicity of AAm/DBA copolymers becomes greater than that of AAm, so, the swelling
of AAm/DBA copolymers is greater than the swelling of AAm hydrogels. In Table 1, $q_{eq}$ values of the hydrogels decreased with the increase in the irradiation dose, and increased with the DBA content in the copolymers. $q_{eq}$ values of AAm/DBA hydrogels is higher than $q_{eq}$ of pure AAm hydrogels. The reason for this is the hydrophilic groups on the DBA. The more hydrophilic groups on the DBA, the more swelling degree is on AAm/DBA hydrogels.

The increase in the amount of absorbed dose lessens the number of small chains. Thus, hydrogels exposed higher doses has higher crosslink density than hydrogel exposed lower doses. This means that a high amount of adsorbed dose decreases the number average molar mass between crosslinks while a low amount of adsorbed dose increases the number average molar mass between crosslinks.

### 3.3. Swelling kinetic studies

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/DBA 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

$$\frac{dq}{dt} = k_{2.5}(q_{eq} - q)^2,$$

(2)

where $k_{2.5}$ is the rate constant of swelling and $q_{eq}$ denotes the weight swelling ratio at equilibrium. After definite integration by applying the initial conditions $q = 0$ at $t = 0$ and $q = q$ at $t = t$, Eq. (2) becomes

$$\frac{t}{q} = A + Bt,$$

(3)

where $A$ is reciprocal of initial swelling rate $r_0$ or $1/k_{2.5}q_{eq}^2$ and $B$ is inverse of the maximum (the theoretical) weight swelling ratio at equilibrium. $k$ is the swelling rate constant. Inverse of $B$ may be named as the same as $q_{max}$ [27].

To test the kinetic model, $t/q$ versus $t$ graphs are plotted and representative graphs are illustrated in Fig. 3. The calculated kinetic parameters are tabulated in Table 2.

<table>
<thead>
<tr>
<th>DBA Content</th>
<th>Dose, kGy</th>
<th>2.60</th>
<th>3.73</th>
<th>4.65</th>
<th>5.20</th>
<th>5.71</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 mg DBA</td>
<td>8.28</td>
<td>8.11</td>
<td>7.81</td>
<td>7.71</td>
<td>7.58</td>
<td></td>
</tr>
<tr>
<td>20 mg DBA</td>
<td>11.33</td>
<td>11.26</td>
<td>10.70</td>
<td>10.15</td>
<td>9.52</td>
<td></td>
</tr>
<tr>
<td>40 mg DBA</td>
<td>12.65</td>
<td>12.89</td>
<td>12.04</td>
<td>10.88</td>
<td>10.33</td>
<td></td>
</tr>
<tr>
<td>60 mg DBA</td>
<td>15.16</td>
<td>13.94</td>
<td>11.50</td>
<td>12.45</td>
<td>8.34</td>
<td></td>
</tr>
</tbody>
</table>

$T_{1}$ is the swelling rate constant. Inverse of $B$ may be named as the same as $q_{max}$ [27]. To test the kinetic model, $t/q$ versus $t$ graphs are plotted and representative graphs are illustrated in Fig. 3. The calculated kinetic parameters are tabulated in Table 2.
As can be seen from Table 2, the kinetic model is in agreement with the swelling experiments, since, as depicted in Table 1, $q_{eq}$ values are increased with DBA contents and decreased with irradiation doses. But, the initial swelling rate is increased with irradiation doses and decreased with DBA content. This is reasonable since the hydrophilicity of the network is enhanced with the extent of DBA groups in structure. However, the increase in the absorbed dose makes the structure tighter for water to diffuse. These two phenomena determine the rate of swelling.

### 3.4. Determination of swelling power

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 an 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 swelling mechanism of the samples was determined using the following equation [28]:

$$F_{sp} = \frac{W_t - W_0}{W_0} = Kt^n,$$

where $W_t$ and $W_0$ are the weight 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. $F_{sp}$ is the swelling power at time $t$, $K$ is a constant incorporating characteristic of the macromolecular network system and the penetrant, and $n$ is the swelling (diffusional) exponent, which

<table>
<thead>
<tr>
<th>Dose, kGy</th>
<th>2.60</th>
<th>3.73</th>
<th>4.65</th>
<th>5.20</th>
<th>5.71</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAB content (mg)</td>
<td>Initial swelling rate, $r_0$, $(dq/dt)_0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>00 mg</td>
<td>0.1265</td>
<td>0.1342</td>
<td>0.1664</td>
<td>0.1730</td>
<td>0.1329</td>
</tr>
<tr>
<td>20 mg</td>
<td>0.1143</td>
<td>0.1174</td>
<td>0.1383</td>
<td>0.1261</td>
<td>0.1340</td>
</tr>
<tr>
<td>40 mg</td>
<td>0.1176</td>
<td>0.1185</td>
<td>0.1399</td>
<td>0.1221</td>
<td>0.1104</td>
</tr>
<tr>
<td>60 mg</td>
<td>0.0984</td>
<td>0.1072</td>
<td>0.1156</td>
<td>0.1222</td>
<td>0.1143</td>
</tr>
<tr>
<td>Swelling rate constant, $k \times 10^3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>00 mg</td>
<td>1.708</td>
<td>1.8980</td>
<td>2.5719</td>
<td>2.7479</td>
<td>2.0679</td>
</tr>
<tr>
<td>20 mg</td>
<td>0.791</td>
<td>0.8290</td>
<td>1.1036</td>
<td>1.1126</td>
<td>1.7856</td>
</tr>
<tr>
<td>40 mg</td>
<td>0.649</td>
<td>0.6281</td>
<td>0.9569</td>
<td>0.9226</td>
<td>1.1019</td>
</tr>
<tr>
<td>60 mg</td>
<td>0.356</td>
<td>0.4766</td>
<td>0.7074</td>
<td>0.6981</td>
<td>0.9591</td>
</tr>
<tr>
<td>The maximum (theoretical) weight swelling ratio, $q_{max}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>00 mg</td>
<td>8.605</td>
<td>8.410</td>
<td>8.045</td>
<td>7.936</td>
<td>8.091</td>
</tr>
<tr>
<td>20 mg</td>
<td>12.019</td>
<td>11.904</td>
<td>11.198</td>
<td>10.649</td>
<td>8.665</td>
</tr>
<tr>
<td>40 mg</td>
<td>13.458</td>
<td>13.736</td>
<td>12.092</td>
<td>11.507</td>
<td>10.010</td>
</tr>
<tr>
<td>60 mg</td>
<td>16.611</td>
<td>14.492</td>
<td>12.780</td>
<td>13.227</td>
<td>10.917</td>
</tr>
</tbody>
</table>
is indicative of the transport mechanism. Eq. (4) 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 an intermediate between Fickian and Case II. That is reflected by \( n \) between 0.5 and 1 [29].

For \( \gamma \)-rays induced AAm/DBA hydrogels, \( \ln F_{sp} \) versus \( \ln t \) graphs are plotted and representative results are shown in Fig. 4. Swelling exponents, \( n \) and swelling constants, \( K \) are calculated from the slopes and intercepts of the lines, respectively, and were listed in Table 3.

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 [29]. 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.

### 3.5. Water sorption rate

An another important diffusional parameter can be ‘water sorption rate constant’, \( K_{sr} \). According to the water sorption equation [30]

\[
- \ln[1 - (m_t/m_s)] = K_{sr} + E,
\]

where \( t \) is sorption of time, \( K_{sr} \) is water sorption rate constant, \( m_t \) is the sorption water amount at time \( (t) \), \( m_s \) an equilibrium sorption water amount at equilibrium and \( E \) is a constant. The plots of \(- \ln(1 - F) \) versus \( t \) where \( F = m_t/m_s \) are shown in Fig. 5. The water sorption rate constants of the AAm and the AAm/DBA hydrogels having different DBA contents calculated from the slope of the plots, and they are tabulated in Table 4. The water sorption rate constants of the hydrogels are between \( 3.0 \times 10^{-3} \) and \( 7.9 \times 10^{-3} \). The results presented in Table 4 showed that water sorption rate constant of AAm hydrogels is higher than that of AAm/DBA hydrogels. It is seen that water diffusion is more stable into AAm hydrogel systems. If DBA contents are increased in AAm/DBA hydrogels, the sorption of water is decreased. The reason for this may be the hydrophilic characteristics of DBA. DBA molecules may interact with water molecules, and sorption may be slower.

### Table 3
Swelling exponents and swelling constants of AAm/DBA hydrogel systems

<table>
<thead>
<tr>
<th>Dose, kGy</th>
<th>2.60</th>
<th>3.73</th>
<th>4.65</th>
<th>5.20</th>
<th>5.71</th>
</tr>
</thead>
<tbody>
<tr>
<td>00 mg DBA</td>
<td>0.578</td>
<td>0.578</td>
<td>0.555</td>
<td>0.567</td>
<td>0.595</td>
</tr>
<tr>
<td>20 mg DBA</td>
<td>0.604</td>
<td>0.591</td>
<td>0.592</td>
<td>0.628</td>
<td>0.588</td>
</tr>
<tr>
<td>40 mg DBA</td>
<td>0.645</td>
<td>0.577</td>
<td>0.625</td>
<td>0.627</td>
<td>0.644</td>
</tr>
<tr>
<td>60 mg DBA</td>
<td>0.567</td>
<td>0.573</td>
<td>0.623</td>
<td>0.608</td>
<td>0.625</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Swelling constant, ( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>00 mg DBA</td>
</tr>
<tr>
<td>20 mg DBA</td>
</tr>
<tr>
<td>40 mg DBA</td>
</tr>
<tr>
<td>60 mg DBA</td>
</tr>
</tbody>
</table>

**Fig. 4.** Plots of \( \ln F_{sp} \) versus \( \ln t \) for AAm/DBA hydrogels. Total dose given 4.65 kGy.
3.6. Equilibrium water content

The water absorbed by AAm/DBA hydrogels is quantitatively represented by the equilibrium water content (EWC) [31,32], where

\[
EWC = \frac{W_{eq} - W_0}{W_{eq}}.
\]  

Here, \(W_{eq}\) is the weight of the swollen gel at time \(t\) (equilibrium), and \(W_0\) is the weight of the dry gel at time 0. The values of EWC of all AAm and AAm/DBA hydrogel systems were calculated. The values of EWC of the hydrogels are tabulated in Table 5. All EWC values of the hydrogels (0.8681–0.9340) were greater than the percent water content values of the body about 0.60 (or 60%). Thus, the AAm and AAm/DBA hydrogels exhibited fluid contents similar to those of living tissues.

4. Conclusion

The hydrogels showed high water absorbency. The weight swelling ratio were changed between 7.58 and 15.16. It was seen that swelling of AAm/DBA hydrogels increased with an increase of content of DBA. 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 spices. The values of equilibrium water contents of the hydrogel systems were changed between 0.8681 and 0.9340. These data may be important for AAm/DBA hydrogel systems as a biomaterial. It can be concluded from the data presented in this paper, that is hydrogel is an appropriate matrix for pharmaceutical formulations and for biotechnological applications due its, favourable physicochemical properties. The AAm/DBA hydrogels reported can be used to carry substances in an aquatic field for pharmaceutical, agricultural, environmental and biomedical applications.

Acknowledgements

The authors gratefully acknowledge the support of the Polymer Group in the Department of Chemistry, Hacettepe University.

References