Preparation and Swelling Behavior of Biodegradable Superabsorbent Gels Based on Polyaspartic Acid

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Abstract: High molecular weight polysuccinimide (PSI), as the precursor polymer for water-soluble polyaspartic acid, was prepared by the thermal polycondensation of L-aspartic acid. Superabsorbent gels were then prepared based on the crosslinking reaction of polysuccinimide with several oligomeric diamines containing an ethylenimine structural unit in N,N-dimethylformamide and the subsequent hydrolysis of the resulting polymers in an aqueous suspension. The swelling behavior of the crosslinked gels and the effect of the dissolved ions were also investigated.

Keywords: polysuccinimide, polyaspartic acid, superabsorbent, swelling behavior, crosslinking

Introduction

The importance of biodegradable polymers and hydrogel materials is being increasingly recognized and extensive studies have been conducted on their uses in various biomedical applications [1-3]. In particular, biodegradable and water-soluble polymers are very desirable in terms of environmental safety, because water-soluble polymers used, for example, as scale inhibitors and dispersing agents are rarely recovered or collected after use. Poly(amino acids), which have protein-like linkages, are known to be biodegradable and are thus used in medical, cosmetic, fabric, and metal absorbent materials. Among them, polyaspartic acid (PASP) is a promising water-soluble and biodegradable polymer, which can be produced from the hydrolysis of poly(succinimide) (PSI) [4-6]. PSI, the precursor polymer, is prepared by the thermal bulk polycondensation of aspartic acid or the ammonium salts of maleic acid and malic acid [7-10]. PASP consists of racemic aspartic acid residues that have about 70 to 75% and 20 to 25% α- and β-linkages, respectively. When neutralized and crosslinked, PASP has a high absorbency which is pH and electrolyte sensitive in water and body fluids. The superabsorbency of these polymers is based on the formation of partially ionized and lightly crosslinked hydrogel. For the crosslinking of polyaspartic acid, various methods have been introduced, including chemical and radiation processes. Previous research has used a variety of multifunctional amines, amino acids, or their polymeric analogs as the chemical crosslinker, plus physical γ-irradiation to prepare the biodegradable superabsorbent hydrogel [11-14].

Recently, the current authors reported on the preparation of superabsorbent gels based on polyaspartic acid and PEG-diepoxide [15]. As an extension, the current study examine the preparation and swelling behavior of crosslinked hydrogels, produced by the reaction of polysuccinimide with several oligomeric diamine compounds followed by hydrolysis. The diamines used possess ethylenimine units in their structure, analogous to oxethylene in the previous study, and are both hydrophilic and weakly basic in nature.

Experimental

Chemicals and Measurements

The L-aspartic acid and o-phosphoric acid were purchased from Aldrich Chemical Co. The diethylenetriamine (DETA), triethylenetetramine (TETA), and linear poly(ethylene imine) (L-PEI, MW 423) were purchased from Aldrich Co. and used as received. All the other chemicals
purchased were of high quality and used without purification.

The IR spectra were obtained on a Unicam 1000 FT-IR spectrometer. The thermal analysis was carried out on a Perkin Elmer DSC/TGA7 Series thermal analysis system. The solution viscosity was measured in an Ubbelohde capillary viscometer using N,N-dimethylformamide (DMF) as the solvent.

**Preparation of Crosslinked Gels**

The preparation and characterization of polysuccinimide as the precursor for polyaspartic acid has already been described in previous literature [7,15]. The polymer gels were prepared by two-step process including the cross-linking reaction of PSI and subsequent hydrolysis in aqueous medium, as the typical procedure has been described in our previous communication [12,16]. The overall yield was about 70% based on the PSI used.

**Measurement of Water Absorbency**

The water absorbency and swelling rate were tested using a simple Tea-bag method in different media. A certain amount of dry gel powder (w2) was weighed into an empty bag, and then placed in a deionized water until near equilibrium swelling was obtained. The weight of the swollen gel including the bag (w1) was measured, then the weight of the wet tea-bag without the sample (w3) was subtracted to obtain the pure weight of the swollen gel resulting from the dry polymer. The water absorbency (or swelling ratio) was simply calculated using the equation below;

\[
\text{Water Absorbency (Swelling Ratio)} = \frac{(w_1 - w_3)}{w_p}
\]

**Results and Discussion**

**Preparation of Superabsorbent Gels**

High molecular weight PSI was prepared by the thermal condensation of L-aspartic acid in the presence of o-phosphoric acid under reduced pressure. The polymer possessed a reduced viscosity of 0.55 dL/g in DMF. The molecular weight was estimated to be about 180000 Da, as calculated from an empirical equation relating the solution viscosity to the molecular weight [9]. Superabsorbent polymers were prepared by reacting PSI with three homologous diamines as the reaction scheme is shown below. The crosslinked PSI powder, finely ground, was dispersed in water and then hydrolyzed with a molar equivalent of a 1N aqueous NaOH solution. A clear gel was formed as hydrolysis was proceeded. In this study, it was interesting to introduce a diamine crosslinker containing ethylenecime structural unit, as is not only hydrophilic but also basic in nature.

Figure 1 shows the IR spectra of the crosslinked PSI (a) and its hydrolyzed product (b). The spectrum (a) shows characteristic bands of succinimide at 1727, 1393, 1217, and 1163 cm⁻¹, plus additional absorption bands due to amide (1666, 1539 cm⁻¹) and imine groups (1029, 757 cm⁻¹). The hydrolyzed form (b) shows broad characteristic carboxylate groups (1500~1700 cm⁻¹) in the polyaspartate backbone. From the TGA thermogram of the prepared gels, the materials were found to be stable to about 250°C in nitrogen.

**Swelling Behavior of Prepared Gels**

The prepared gels were tested as regards their swelling in an aqueous solution by Tea-bag method. Figure 2 shows a typical water absorbing rate curve for the gel samples from the homologous diamines. The initial fast swelling seemed to level off after 1~2 h, then a gradual increase in swelling was observed thereafter. The swollen gels exhibited a relatively good gel strength. The gels swollen within the capacity in vial stayed without

![Figure 1. IR spectra of crosslinked PSI (a) and its hydrolyzed product (b), (L-PEI 5 mol%).](image-url)
falling when the vial containing the gel was turned upside down.

Table 1 shows a comparison of the typical water absorbency of the gel samples in both distilled water and 0.9 wt% NaCl solution. The absorbency in the 0.9 wt% NaCl solution were 15 ± 3% compared to those in the pure water.

Figure 3 shows the dependence of the water absorbency on the amount of crosslinking agent (PEI in this example). With a content of 3 mol%, the absorbency were slightly higher than with 2 or 5 mol% when the values were measured as a function of time.

Figure 4 shows water absorbency measured at several different temperatures as a function of the soaking time. The initial water absorption increased slightly at a higher temperature probably due to the thermal expansion effect. In contrast, a substantial increases in the apparent swelling degree was observed as a function of the soaking time, and the rate increase was higher at an elevated temperature. At a temperature of 50°C the swelling rapidly decreased after about 10 h, thereby suggesting the occurrence of gel decomposition at this relatively high temperature. This behavior was seemingly related to the hydrolytic degradation of the gels in an aqueous environment, which was accelerated at a higher temperature. Aspects related to the gel degradation are discussed further below. Figure 5 shows the swelling at different pHs, which was measured in a buffer solution at room temperature (20°C). The absorbency were within a range of ca. 35 ~ 45 g/g-dry gel. The absorbency seemed to increase at a higher pH, yet the difference was small.

Table 1. Water Absorbency of Crosslinked Gel (2 h soaking)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Crosslinking agent (5 mol%)</th>
<th>In distilled water (g/g-dry gel)</th>
<th>In 0.9 wt% NaCl (g/g-dry gel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASP</td>
<td>TETA</td>
<td>~90</td>
<td>~16</td>
</tr>
<tr>
<td></td>
<td>TETA</td>
<td>~280</td>
<td>~42</td>
</tr>
<tr>
<td></td>
<td>L-PEI</td>
<td>~140</td>
<td>~25</td>
</tr>
</tbody>
</table>

**Figure 2.** Water absorbing rate curve for gel samples from different diamine crosslinking agents (5 mol%).

**Figure 3.** Dependence of swelling on amount of crosslinking agents (L-PEI 2, 3, and 5 mol%).

**Figure 4.** Water absorbency at different temperatures as a function of soaking time (TETA 5 mol%).

**Figure 5.** Absorbency in different pH buffer solutions (TETA 5 mol%, soaking time: 2 h).

**Swelling and Stability of Gels in Ion-Containing Aqueous Solution**

A relatively low level of swelling in a salt solution or physiological medium has generally been observed with most other known superabsorbent polymers, which results from the high ionic strength of medium acting...
adversely on the equilibrium swelling capacity. Also, the sensitivity of the swelling capacity to electrolytes and the stability of gels in different aqueous environments have often been observed and reported for many types of hydrogels. The swelling degrees of the gels in an aqueous solution containing different concentrations of salt (NaCl and CaCl₂) is shown in Figure 6. As expected, the absorbency showed a monotonous decreasing tendency as the salt concentration increased. The absorbency in the divalent CaCl₂ solution was much lower than that in NaCl solution, and rapidly decreased with a lower concentration. Also, the stability of the gels was checked by measuring the absorbency as a function of the soaking time, as the results of which are plotted in Figures 7 and 8. In the case of NaCl solution, the absorbency remained stable as a function of time for a relatively long period (up to 10 h). In contrast, the absorbency in different CaCl₂ solutions rapidly decreased as soaking time elapsed, and was completely lost within a relatively short period, except in an ultimately dilute solution. This behavior may have been caused by the formation of additional crosslinks due to the ion exchange between Ca²⁺ and Na⁺ ions in the carboxylic groups or the counter-ion condensation predicted theoretically [17,18]. As such, the change in the swelling due to ion-exchange was tested by the elution of an aqueous solution containing divalent Ca²⁺ ions (about half mol concentration of calculated Na⁺) through the original pre-swollen gel, placed in a column with fritted glass. After a certain elution period through the packed column, the gel was found to shrink to a level of about 30 vol% of the original gel, accompanied by the drainage of excess water.

**Gel Decomposition Behavior**

Finally, the degradation behavior of the swollen gel in an aqueous environment was investigated by monitoring the water absorbency and weight loss of the material as a function of the immersion time. A typical result is plotted in Figure 9. A series of swollen gels within tea-bags was placed in a constant-temperature bath controlled at 40°C and then sampled out after a certain period of time to measure the instant water absorbency and weight loss, measurable after freeze-drying the remaining gel. As shown by the curves, no appreciable weight loss was
observed during the initial 2 days, however, a relatively fast decrease was observed thereafter. In contrast, the degree of swelling in the samples continued to increase to about 2 times of the initial swelling, showed a maximum after around 2 days, and then decreased gradually along with a weight loss. It would seem that the reduction in gel swelling after a certain period of time was caused by the hydrolytic decomposition of the amide linking groups, occurring in excess water catalyzed by the acidic carboxylic group in the backbone. Also, the above gel decomposition appeared to occur relatively fast at an elevated temperature. Due to its complexity, further studies on gel decomposition by hydrolysis and its dependence on temperature and different media are currently in progress.

To summarize, polymeric hydrogels based on polyaspartic acid were prepared and the swelling behavior was investigated. These materials exhibited a medium to high water absorbency (90–280 g/g-polymer) depending on their molecular size and the content of the crosslinking agent. In addition, the swelling and stability in the ion-containing (NaCl and CaCl₂) aqueous solution was also compared. The prepared gels were found to decompose within a relatively short time in an aqueous environment.

Acknowledgement

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References