

Superabsorbent hydrogels from poly(aspartic acid) with salt-, temperature- and pH-responsiveness properties

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Abstract

Polyaspartic acid (PAsp) resin was synthesized by polysuccinimide (PSI), through chemical cross-linking using the cross-linking agent (diamine). The effects of reaction variables, such as PSI concentration and terminal pH on the water absorbent capacity have been studied. These phenomena were discussed according to structural parameters, which were confirmed by SEM. Water absorbencies were compared for the hydrogels at terminal pH 8 and 10. The water absorbent capacity enhanced with increasing terminal pH and decreasing PSI concentration. The swelling/deswelling kinetics of the super-absorbent hydrogels was investigated as well. It is found that the hydrogels showed ampholytic and reversible pH-responsiveness properties. The variational water absorbencies were attributed to swelling theory based on the hydrogel physical and chemical structure. The swelling was also extremely sensitive to the temperature, ionic strength and cationic kind. The reversible pH-responsiveness, salt- and temperature-sensitivity of the hydrogels make this intelligentized polymer had wider applications. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Polyaspartic acid; Hydrogel; Superabsorbent

1. Introduction

Super-absorbent polymers are lightly cross-linked networks of hydrophilic polymer chains. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. The network can swell in water and hold a large amount of water while maintaining the physical dimension structure [1,2]. They are widely used in sanitary products, such as sanitary napkins and disposable diapers, and also in a variety of other fields. It was known that commercially used water-absorbent polymeric materials employed in such applications including partial neutralization products of cross-linked polyacrylic acids, partial hydrolysis products of starch–acrylonitrile copolymers, starch–acrylic acid graft copolymers and so on. These polymers are poor in degradability and remain semipermanently in water or soil. At present, material's biodegradability is an important focus of the research in this field

because of the renewed attention towards environmental protection issues [3].

On the other hand, biodegradable polymers have attracted interest as 'globe-compatible materials' in recent years. Their use as super-absorbent polymers has also been proposed. Known examples of biodegradable super-absorbent polymers employed in such applications include cross-linked polyethylene oxide, cross-linked polyvinyl alcohol, cross-linked carboxy-methylcellulose, cross-linked alginic acid, cross-linked starches, and cross-linked polyamino acids. Among these, the cross-linked polyethylene oxide and cross-linked polyvinyl alcohol have low water absorption ability and are not particularly suited for use as materials in products requiring high water-absorbency such as sanitary products, disposable diapers, disposable dust cloths and paper towels [4,5].

Further, these compounds can be biodegraded only by certain particular bacteria, so that under general conditions, their biodegradation will be slow or will not take place at all. Moreover, the biodegradability will be reduced extremely when the molecular weight was high [5]. In addition, cross-linked saccharides such as cross-linked carboxy-methylcellulose, cross-linked alginic acid and cross-linked starches contain many firm hydrogen bonds in their molecules,

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thereby exhibiting strong interaction between water molecules and polymers. Accordingly, molecular chains cannot be opened widely indicating that their water-absorbency was low [4,6]. However, a high demand has remained for super-absorbent polymers having high saline-absorbency and excellent water-absorbency, resulting in a large demand for polymers with high performance.

Polyaspartic acid has free carboxylic acid group or amino group. As a modification of polyaspartic acid, PAsp resin was a kind of biodegradable material with high water-absorbency, and it is commonly used as soil amendments, and in manufacturing of diapers, sanitary napkins, medicals, cosmetics, fabrics, metal absorbent materials and etc. It has been studied actively in recent years [7–9].

PAsp resin was prepared by γ -irradiation from PAsp by Mitsubishi Chemical Corporation in Japan, and its maximum swelling ratio in deionized water system was 3400 g/g [10]. From an industrial viewpoint, however, a Co^{60} irradiation system used in this method requires special equipment for shielding radiation, and sufficient care was also required for its control. This technology was therefore not practical [11]. Nowadays the maximum swelling ratio of PAsp resin which was prepared by cross-linking reaction with the attendance of a cross-linking agents from PSI, was 983 g/g in deionized water system, and it was reported that this kind of material was prepared by Mitsui Toatsu Chemical Corporation [4,5].

As a kind of functional material, PAsp resin must possess various predominant properties. Especially, it should have super-absorption, fluid retention capacity and stability. Many structural factors (e.g. charge, concentration and pK_a of the ionizable group, degree of ionization, crosslink density and hydrophilicity) influence the degree of swelling of ionic polymers [12–14]. In addition, properties of the swelling medium (e.g. pH, ionic strength and the counter ion and its valency) affect the swelling characteristics [15–17]. These responsive or smart hydrogels have become an important area of research and development in the field of medicine, pharmacy and biotechnology. Therefore, in order to develop its application, it is necessary to study properties of PAsp resin. In this article, PAsp resin was prepared from PSI with the existence of the cross-linking agents. And its properties mentioned above were studied.

2. Experimental

2.1. Materials

L-Aspartic acid was obtained from the Sigma Chemical Corporation (St Louis, USA). Polysuccinimide (PSI) with high molecular weight was prepared in our laboratory [18]. Its chemical structure of the repeat unit was shown in Scheme 1. Phosphoric acid, methanol, sodium hydroxide, hydrochloric acid, *N,N*-dimethylformamide (DMF), the cross-linking agents, sodium chloride, potassium chloride,

ammonium chloride, magnesium chloride, calcium chloride, potassium sulfate, sodium sulfate, magnesium sulfate and ammonium sulfate were of analytical grade.

2.2. Measurements of the molecular weight of PSI

The molecular weight of PSI was estimated by a correlation method with the molecular weight of corresponding sodium polyaspartate. The PSI was hydrolyzed with NaOH to obtain the corresponding sodium polyaspartate. The molecular weight of sodium polyaspartate was measured in a buffer containing 0.02 M H_3PO_4 using gel filtration chromatography (GFC) by a column Superose 12 (Pharmacia Biotech Corp., $1 \times 30 \text{ cm}^2$) and detector was at UV 206 nm (LKB 2238 S II BROMMA Corp.). The standard sample was dextran which was obtained from Pharmacia Biotech Corp.

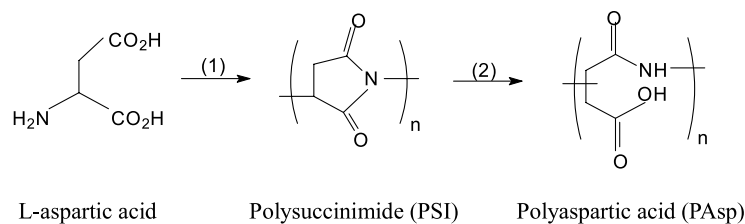
2.3. Preparation of PSI and PAsp with high molecular weight

L-Aspartic acid powder (2 kg) and 1.474 kg of 85% phosphoric acid were put into a blender (Oster (USA) Osterizer) with a capacity of 5 l. The reaction was carried out for 4.5 h at 200 °C under a reduced pressure of 0.09 Mpa. The product was washed several times with methanol and water until it was neutral and then dried at 85 °C under a vacuum condition. Finally, the yellowish powder of PSI product was obtained. This thermal polycondensation reaction was shown in Scheme 1 (1).

The hydrolysis of PSI was performed in an ice bath by adding 2 g of PSI, 1.5 g of sodium hydroxide and 10 ml of deionized water into a 100 ml beaker with a magnetic stirring bar. The mixture of PSI, sodium hydroxide and deionized water was stirred for 1 h. After the hydrolytic reaction, the pH of the solution was adjusted to be neutral by adding 35% HCl solution. Then, 70 ml methanol which was saturated with NaCl was poured into the beaker, and the precipitate was recovered by a filtration and dried at 40 °C under a vacuum condition. The molecular weight of the obtained PAsp was 199,500 [18]. This ring opening reaction was shown in Scheme 1 (2).

2.4. Preparation of PAsp resin

PAsp resin has been prepared from PSI with molecular weight 199,500 which was synthesized by thermal polycondensation of L-aspartic acid [18]. One gram of PSI was dissolved in 32 ml of organic aprotic polar solvent such as *N,N*-dimethylformamide (DMF) in a beaker with a magnetic stirring bar. Ten milliliters of deionized water as a dispersant was added into the beaker. The mixture containing PSI, DMF and deionized water was stirred for 0.5 h, then 0.08 g of the cross-linking agent was added into the beaker, and the cross-linking reaction was carried out for 2 h at 40 °C, so that the cross-linked polymer has formed. Next,



Scheme 1. Chemical structure of Asp, PSI and PAsp, and reaction scheme of PAsp (1) is the thermal polycondensation reaction (2) is the ring opening reaction.

the imide ring of the cross-linked polymer was subjected to hydrolyze with NaOH solution at 40 °C until pH=8 and 10. This pH is defined as terminal pH, and it means the pH of reaction solution at the end of the hydrolytic reaction. In this experiment, the terminal pHs of two products were 8 and 10, respectively. Then methanol was poured into the solution, and the precipitate was recovered by a filtration and dried at 40 °C under a vacuum condition. Thereby a cross-linked PAsp resin as a super-absorbent polymer was obtained.

2.5. The swelling of PAsp resin at room temperature

The swelling ratio is the criterion of describing water absorption capacity. The measurement of the swelling ratio of PAsp resin was conducted at 22 °C by the tea-bag method, and using deionized water, physiological saline, chloride and sulfate solution with different concentrations as liquids to be absorbed. The physiological saline was a 0.9 wt/wt% NaCl aqueous solution. The tea bags used in the method were made of 300 meshes nylon net and 40 cm in diameter. The weight of the wet nylon net was measured and marked as W_n . The weight of dry PAsp resin was marked as W_o . The test sample of PAsp resin, after measured, was placed into the tea-bag and then the tea-bag with sample inside was suspended and fully immersed into liquids to be absorbed at 22 °C. After 24 h, the tea bag was hung in the air for 15 min, and then the weight of the tea bag including swollen resin was measured and marked as W_t . The swelling ratio of PAsp resin was calculated as:

$$\text{Swelling ratio (g/g)} = \frac{(W_t - W_o - W_n)}{W_o} \quad (1)$$

2.6. Swelling in buffer solutions

Buffer solutions with pH 1–14 were used to study of pH-sensitivity of PAsp hydrogel. The desired basic and acidic pHs were adjusted by NaOH and HCl solutions, respectively. The pH values were precisely checked by a pH-meter (Leici/E-201-C, accuracy ± 0.01). Then, 0.20 g of dried sample was used for the swelling measurements in buffers according to the above mentioned method [2].

2.7. Swelling in salt solutions

Water absorbent capacity of PAsp resin was determined

in 0.9 wt/wt% solutions of NaCl and CaCl₂ according to the above method described in Section 2.5 [2].

2.8. Swelling kinetics

PAsp resin samples (0.20 g) were poured into numbers of weighed tea bags and immersed in 2000 ml deionized water. At certain time intervals, the swelling ratio of the samples was measured according to Eq. (1). The measurement condition is the same as Section 2.5 [2].

2.9. Temperature-sensitive properties of PAsp hydrogel

The temperature-sensitive properties of the hydrogels at both terminal pH 8 and 10 were studied in deionized water in term of swelling ratio as a function of temperature. Two water bathes were prepared, where samples were immersed and observed. When swelling was measured in one bath, temperature of the other bath was rising. The temperature in the bath was gradually increased with step about 5 °C, and the hydrogels were allowed to adjust equilibrium for 30 min at each experimental point before the measurement [19].

2.10. Kinetics of deswelling

The kinetics of deswelling of PAsp hydrogels were also followed gravimetrically, in a constant temperature water bath (60 °C). Swollen hydrogels equilibrated in the tea bag was firstly hung in the air for 15 min in order to remove any surplus water at room temperature (22 °C) rapidly. The samples were then transferred quickly to a constant temperature water bath (60 °C). Zero time of deswelling was thus defined precisely at the moment at which the swollen hydrogel was placed in the water bath of water at 60 °C. After every 30 min, hydrogels were surface dried through hanging in the air for 15 min. The mass of hydrogels were recorded during the course of deswelling at these time intervals and marked as m_t . The percentage water retention (W_r)(%) is calculated as follows:

$$W_r = \left(\frac{m_t}{m_e} \right) \times 100\% \quad (2)$$

where m_e is the mass of the hydrogel at swelling equilibrium at room temperature (22 °C) [20].

2.11. Microscope observation

The surface of dry PAsp resin sample was determined using a scanning electron microscope (Hitachi S-570). Dry PAsp resin sample was grounded into powder, and mounted on metal stub, and coated with gold, subsequently, its surface was observed and photographed by SEM (scanning electron microscope).

3. Results and discussion

3.1. Effect of PSI concentration on swelling capacity

In the experiment, 1 g of PSI was dissolved in 12, 16, 20, 24, 28 and 32 ml of *N,N*-dimethylformamide (DMF) in a beaker. The swelling ratio of PAsp resin prepared with various concentrations of PSI, is shown in Fig. 1. The results indicated that the higher the concentration of PSI, the lower the water absorbency was.

When terminal pH was 8 in the hydrolysis reaction, a high swelling capacity is obtained with low concentration of PSI. This kind of PAsp resin, however, was less sensitive to the PSI concentration (lower sloped curve). Since pH of the emulsion was adjusted to 10 after the crosslink reaction, the super-absorbency of polyaspartic acid resin attributes to both functional groups of ionic carboxylate (from neutralized PAsp) and non-ionic carboxamide (from PSI). The increasing swelling results from the presence of the ionic groups in polymer chains because the ionic groups are more strongly solvated rather than non-ionic groups in the aqueous medium. When the cross-linked polymer was hydrolyzed by NaOH solution more completely (i.e. terminal pH was 10), higher water absorbent capacities are obtained from employing lower initial concentration of PSI. Based on our experience, when the PSI concentration was fewer, the hydrolysis reaction was completed more easily at the same terminal pH. Therefore, the enhanced swelling versus lower PSI concentration is due to the formation of high carboxylate groups. In these hydrolyzed

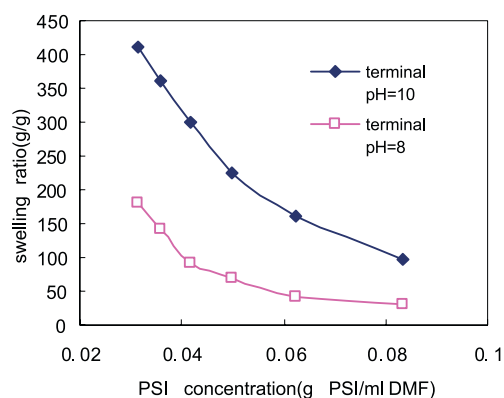


Fig. 1. Effect of PSI concentration on swelling capacity of polyaspartic acid resin. Their terminal pHs were 8 (□) and 10 (◆), respectively.

more completely samples, the carboxylate groups in network increased appreciably and higher swelling capacity is obtained [2]. Its water absorbent capacity was enhanced due to electrostatic repulsion from these carboxylate groups as the main driving forces.

3.2. Swelling in salt solution

Polyaspartic acid super-absorbents are ionized hydrogels that their swelling capacity depends on the properties of the physical and chemical structure and the medium. Generally, the extent to that the hydrogel swells at equilibrium increases with more functional ionizable groups on the network. However, it decreases with higher extent of cross-linking occurred during the synthetic step(s). The swelling of PAsp resin in saline solutions was appreciably reduced comparing to the values measured in deionized water. This well-known phenomenon, commonly observed in the swelling of ionic hydrogels [21], often results from a charge screening effect of the additional cations causing a non-perfect anion–anion electrostatic repulsion, led to a decreased osmotic pressure (ionic pressure) difference between the polymer network and the external solution. Fig. 2 exhibits relationship between swelling and NaCl concentration. It shows that changing the NaCl concentration higher than about 0.5 wt% has no appreciable influence on water absorbent capacity of polyaspartic acid resin [2].

The swelling data obtained from the various chloride and sulfate salt concentrations were given in Figs. 3 and 4. The swelling capacity decreased with high charge of the cation (multivalent < univalent). It may be explained by complexing ability arising from the coordination of the multivalent cations with polyaspartic acid groups. This ionic cross-linking mainly occurs at surface of particles. It is found that hydrogels are rubbery and very hard when they swell in Ca^{2+} or Mg^{2+} solution. In contrast, PAsp hydrogels swollen in univalent cation solutions exhibit lower strength [2]. On the other hand, we found that the less the radius of

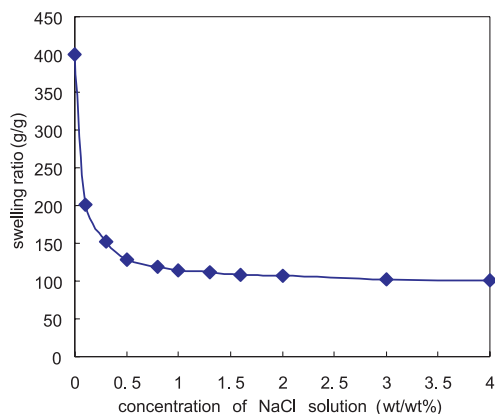


Fig. 2. Swelling capacity variation of polyaspartic acid resin in various concentrations of NaCl solutions. The terminal pH of sample had been adjusted at 10.

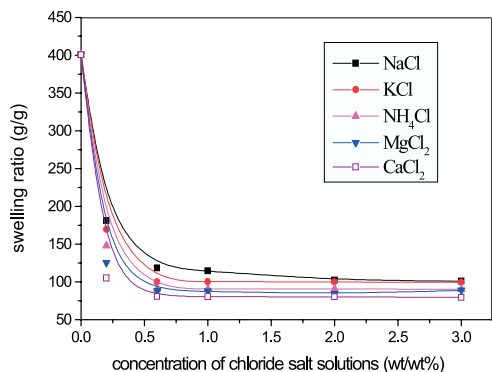


Fig. 3. Swelling capacity variation of polyaspartic acid hydrogel in various chloride salt solutions. The terminal pH of sample had been adjusted at 10.

the same valent monatomic cation, the more the water absorption capacity was ($\text{Na}^+ > \text{K}^+$ and $\text{Mg}^{2+} > \text{Ca}^{2+}$), and that the swelling ratio decreased with high number of atom of the univalent cation (polyatomic < monatomic). The radius of the same valent monatomic cation means the radius of atom of the same valent monatomic cation (i.e. the radius of atom is $\text{Na} < \text{K}$ and $\text{Mg} < \text{Ca}$, so the radius of ion is $\text{Na}^+ < \text{K}^+$ and $\text{Mg}^{2+} < \text{Ca}^{2+}$). According to above three aspects, therefore, the chief trend is that the swelling ratios were, in chloride salt solutions, $\text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$, and in sulfate salt solutions: $\text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Mg}^{2+}$. The variety of swelling ratio was irrelevant to the kind and valence of anion (Cl^- and SO_4^{2-}) basically [22].

3.3. Swelling kinetics

A preliminary study was conducted on the hydrogel swelling kinetics. Fig. 5 illustrates the dynamic swelling behavior of the polyaspartic acid super-absorbent sample in deionized water. Initially, the rate of water absorption abruptly rose and then began to level off. The saturated swelling was obtained after 8 h. The swelling trend line of polyaspartic acid hydrogel can express as Voigt-based equation (Eq. (3)) [23].

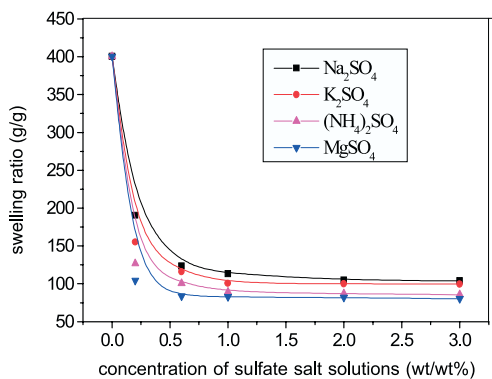


Fig. 4. Swelling capacity variation of polyaspartic acid hydrogel in various sulfate salt solutions. The terminal pH of sample had been adjusted at 10.

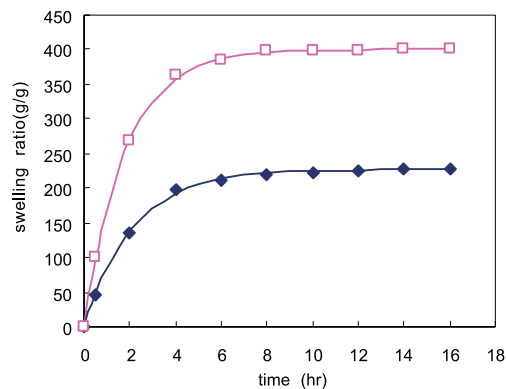


Fig. 5. Swelling ratio as a function of time for polyaspartic acid hydrogel. Their terminal pHs were 8(♦) and 10(□), respectively.

$$S_t = S_e(1 - e^{-t/\tau}) \quad (3)$$

Where S_t is swelling at time t (g/g), S_e is equilibrium swelling ('power parameter', g/g), t is time (h) for swelling S_t , and τ stands for the 'rate parameter' (h).

It is found that the rate parameters for the hydrogels at terminal pH 8 and 10 are 2.13 and 1.76 h, respectively. Based on the smaller τ value of the latter, it swells faster than the former. This difference may result from more hydrophilic and ionic groups (COO^-) in hydrogel at terminal pH 10. It is the most important factor. Because swelling properties of cross-linked hydrophilic poly electrolytes in aqueous solutions are determined by several chemical and structural factors, and the hydrophilicity of polymer backbone and degree of ionization and amount of ionic groups have significant impacts on the swelling behaviour that make hydrogels so fundamentally interesting and technologically important [3,24–26]. On the other hand, it may also be originated from porosity of resin particles obtained from the drying process. The fast water extraction during drying procedure induced the high and connected pores in the product at terminal pH 10, which result in large specific surface area to absorb lots of water in short time [3,25]. The porosity leads to faster water diffusion into the polymer network and higher swelling rate. In addition, in the course of hydrolysis, the reaction emulsion becomes viscous state that prevents removing the evolved NH_3 and water vapor from this viscous medium, so the removed vapor creates fewer pores in the viscous emulsion [2]. However, this mechanism is the least important, so that it cannot be relied upon for controlling the degree of swelling.

3.4. Temperature sensitivity and response of PAsp hydrogel

It is well-known that the hydrogels with suitable hydrophilic–hydrophobic balance may exhibit thermo-sensitivity, i.e. sharp decrease in volume in aqueous environment with high temperature. Presumably this occurs due to the enhanced intramolecular hydrophobic interaction as well as the deterioration of the H-bonding with water [19].

Fig. 6 illustrates the temperature-dependant swelling of PAsp hydrogels when the temperature of the aqueous media increased from 25 to 60 °C. As clearly seen, swelling ratio decreased with the increasing temperature in the region of 35–60 °C. The temperature sensitivity of PAsp hydrogels was dependent on the porosity. In this case, more pore enhanced the uptake of water during swelling and deswelling when compared with less porous hydrogel (terminal pH 8) [27]. The fact was shown in SEM images (Figs. 8 and 9).

From above results, we choose 60 °C to carry out below response test. Fig. 7 illustrates the temperature response kinetics of hydrogels at terminal pH 8 and 10 after the swollen hydrogel samples at room temperature (22 °C) were quickly transferred to a hot water bath of 60 °C [28]. This figure shows that the deswelling of hydrogel at terminal pH 10 is much faster than that of hydrogel at terminal pH 8. In particular, hydrogel at terminal pH 10 loses about 30% water in 30 min and loses over 70% water within 270 min, compared to a loss of 35% water in 270 min for hydrogel at terminal pH 8. The results can be ascribed to the more porous structure of hydrogel at terminal pH 10 that allows facile water desorption and hence faster shrinking. The deswelling rate of the hydrogel at terminal pH 8 is seen to be slower than that of the terminal pH 10 hydrogel; this result again indicates the reasonable conversion is essential to both swelling/deswelling rates [20].

In regard to the deswelling kinetics, during the initial deswelling course, the conventional hydrogels undergo phase separation and shrink in surface area. A dense layer forms on the surface and entraps water inside the hydrogel, preventing heat and mass transfer from the aqueous medium to the inner part of the hydrogel [29]. However, in the case of the porous hydrogels, it is possible for the water molecules to rapidly transfer through the macropores into the innermost matrix, even though phase separation has occurred on the surface, which leads to a rapid deswelling [27].

It is found that dry resin at terminal pH 8 and 10 exhibited distinct surface. The surface of the former is

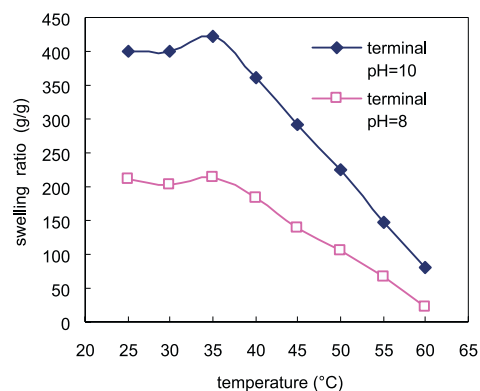


Fig. 6. Thermo-induced swelling ratio changes of PAsp hydrogels. Their terminal pHs were 8(□) and 10(◆), respectively.

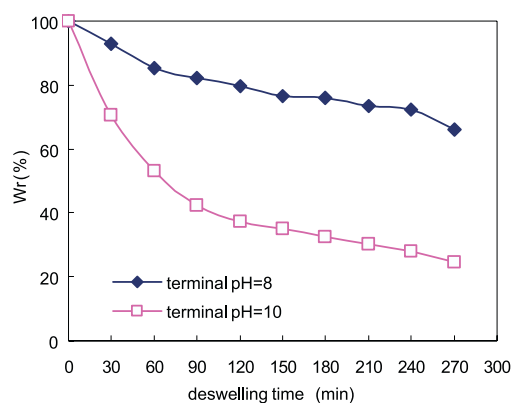


Fig. 7. Temperature response kinetics for polyaspartic acid hydrogels in water at 60 °C. Their terminal pHs were 8(◆) and 10(□), respectively.

smooth, tight and forms a dense layer. In contrast, the latter is rough, loose and like a dry sponge without any surface layer. And the observation for the latter is consistent with a more open and porous structure [20]. The swelling process is complicated and involves three successive steps [28,30–32]: (a) the diffusion of water molecules into a polymer system, (b) the subsequent relaxation of hydrated polymer chains, and (c) the expansion of polymer network into aqueous solution. Because the dense layer is formed on the surface of dry resin at terminal pH 8, the diffusion of free water into the polymeric network is blocked, and hence water in the network was insufficient in quantity. During deswelling process of PAsp hydrogel, it is well recognized that shrinking rate of a temperature-sensitive hydrogel also depends on the water-diffusing rate. A faster response rate could be achieved, if entrapped water within a hydrogel could quickly diffuse out. Thus, in addition to the hydrophilic/hydrophobic balance in the PAsp segments, the characteristic of the dense surface layer must also be considered as another possible factor that could influence the deswelling rate [28,33–36]. So the relatively slower rate of swelling or deswelling may be attributed to the existence of denser surface layer.

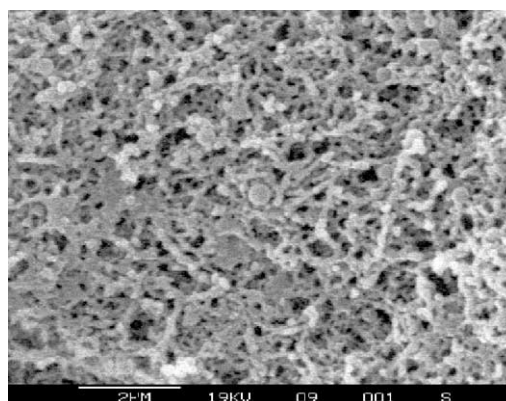


Fig. 8. The SEM micrograph of sample at terminal pH 10.

3.5. SEM studies

Figs. 8 and 9 illustrate the cross-sectional views of the scanning electron microscopic images of dry resin at terminal pH 10 and 8, respectively. The dry resin at terminal pH 10 shows a more open and porous channel structure, which is well consistent with the phenomena above. These results support the fact that dry resin at terminal pH 10 is more porous, and thus exhibits a faster swelling or deswelling response rate. In contrast, the structure of at terminal pH 8 is rough, of irregular cross-section and less pores than another sample. This scanning electron microscopic image explains the slower response rate.

3.6. pH-Dependent swelling of the hydrolyzed hydrogel

According to higher swelling of resin at terminal pH 10, it is chosen to carry out the pH-sensitivity test. Firstly, the swelling of this hydrogel is investigated at various pHs ranged from 1.0 to 14.0. The result is shown in Fig. 10. Through buffer, there are no additional ions in medium for setting pH. It is ascribed to water absorbent capacity of a super-absorbent is strongly influenced by ionic strength [2,21]. Therefore, the desired basic and acidic pHs were adjusted by NaOH and HCl solutions, respectively. Fig. 10 indicated that this PAsp resin did not possess the maximum of swelling ratio at pH 7, and this was different from the cross-linked polyacrylic acid resin that was researched most universally. Maybe it is due to following reasons. PAsp resin is a kind of high molecular polymer, which was synthesized from L-aspartic acid. And L-aspartic acid is a kind of amino acid, which is an ampholyte and partially acidic. The two sharp water absorbent peak can be ascribed to high repulsion of $-\text{NH}_2^+$ and $-\text{NH}_3^+$ groups in acidic media and $-\text{COO}^-$ groups in basic media. Of course, the secondary amine groups ($-\text{NH}_2^+$) exert the main effect, and the $-\text{NH}_3^+$ groups which indicate the amine of N-term in PAsp do not exert enough repulsion force on hydrogel swelling. However, at very acidic condition ($\text{pH} \leq 3$), a

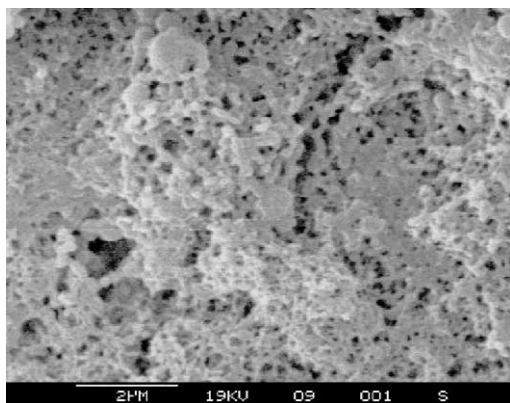


Fig. 9. The SEM micrograph of sample at terminal pH 8.

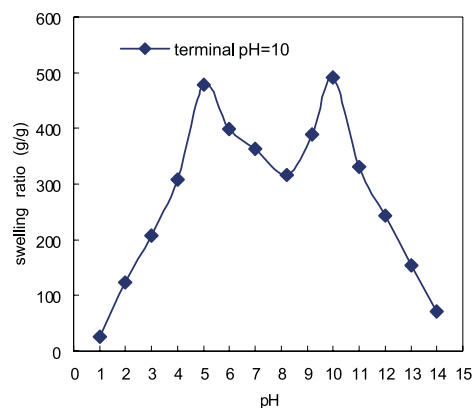


Fig. 10. Effect of pH on swelling absorbency of polyaspartic acid resin. The terminal pH of sample had been adjusted at 10.

screening effect of the counter ions, i.e. Cl^- , shields the charge of the cations ($-\text{NH}_2^+$ and $-\text{NH}_3^+$) and prevents an efficient repulsion [2]. Therefore, an obviously reduced final absorbency appears. And under this acidic condition, anionic carboxylate groups are protonated, so the polymeric network collapsed. At around pH 3, the carboxylic acid component comes into action as well. Since the pK_a of the amino acid monomer is about 2.09–3.86, its ionization occurs above this value. That may enhance absorbency [2]. However, in certain pH range 6–8 which is close to neutrality, most base and acid groups are non-ionization, so H-bonding between amine and carboxylic acid or carboxamide groups may result in a kind of cross-linking followed by a decreased swelling. Latest analogous viewpoints are reported in the case of an interpenetrating network composed of poly(*N*-isopropylacrylamide)–poly(acrylic acid) [37] and chitosan-*g*-poly(AA-*co*-AAm) [2]. With farther increase of pH, ionization of carboxylic acid groups happens, and the electrostatic repulsive force between the $-\text{COO}^-$ groups leads to high swelling. However, when pH achieves above 10, a screening effect of the counter ions (Na^+) hinders the swelling at pH 10–12 and opposed the swelling at $\text{pH} > 13$. As a result, the polymeric network of hydrogel totally collapses at pH 14. A similar behavior has been recently reported in the case of chitosan-*g*-poly(AA-*co*-AAm) [2] and copolymeric gels from acrylic acid (the anionic constituent) and methacrylamidopropyl trimethyl ammonium chloride (the cationic constituent) [38]. In such system, in a word, H-bonding and a combination of attractive or repulsive electrostatic interactions are main causes for appearance of several phases obtained in different pH conditions.

On the other hand, since hydrogel swells differently in media with different pHs, reversible pH-responsiveness of PAsp hydrogel was studied in buffer of pH 5 and 12, respectively. However, there is higher ionic strength in this buffer, so that it is found that the ultimate water absorbencies are much lower than those in the non-buffered media. According to the synthetic materials, there are both amine (carboxamide) and carboxylate functional groups in

the structure of polyaspartic acid resin. The protonation of secondary amine groups ($-\text{NH}_2^+$) and carboxylic groups occurs at $\text{pH} < \text{p}K_1$, as a result, $-\text{NH}-$ groups turn into $-\text{NH}_2^+$. However, with increase of pH, the carboxylic functional groups are converted to $-\text{COO}^-$ at $\text{pH} > \text{p}K_2$. Either protonated ($-\text{NH}_2^+$) or deprotonated ($-\text{COO}^-$) groups increase charge density on the polymer causing a higher osmotic pressure inside hydrogel on account of the electrostatic repulsion between $\text{NH}_2^+-\text{NH}_2^+$ or $\text{COO}^- - \text{COO}^-$ [2]. The swelling of super-absorbent results from a balance of osmotic pressure between the internal and external medium of the polymeric network.

3.7. Salt-sensitivity of PAsp hydrogel

Because carboxylate groups exist in polyaspartic acid network, water absorbent capacities show variety in various electrolyte solutions with the same concentration. These different swelling capacities result from valency change of electrolyte. Cations can interact with the networks with carboxylate groups. According to Figs. 3 and 4, the swelling ratio in Ca^{2+} solution is lower than that in Na^+ solutions. Because of existence of the bivalent Ca^{2+} , the crosslinking density enhances. It is due to the double interaction of Ca^{2+} with carboxylate groups resulting in ‘ionic crosslinking’. The swelling and deswelling process of hydrogel at terminal pH 10 in NaCl and CaCl_2 solutions is shown in Fig. 11. In NaCl solution, water absorbent capacity of PAsp resin enhances with increase of time. When hydrogel is transferred into CaCl_2 solution, its swelling reduces on account of the increasing cross-linking density. Then, after the deswollen hydrogel is diverted into sodium chloride solution again, the sodium ions substitute calcium ions [2] into the polymeric network once more. The previous ionic crosslinks are destroyed by this ion exchange, leading to swelling enhancement. Therefore, when swelling of PAsp

resin is measured alternatively in NaCl and CaCl_2 solutions with equal concentration, the reversible cation-response of polyaspartic acid hydrogel is validated. The ion exchange ability of carboxylate groups results in this chemical behavior of PAsp hydrogel.

4. Conclusion

Polyaspartic acid resin was synthesized by polysuccinimide (PSI), through chemical crosslinking using the cross-linking agent (diamine). Water absorbent capacity of PAsp resin is influenced strongly by PSI concentration and terminal pH. The swelling reduced with increasing the PSI concentration. However, swelling capacity raised by enhancing the terminal pH. It can be ascribed to more carboxylate groups in sample at high terminal pH. On the other hand, high terminal pH is able to enhance the swelling/deswelling response rate and temperature-sensitive properties. These response kinetics are affected by a dense surface layer and the porosity of the network. A dense surface layer is a smooth and tight layer on the surface of resin. The dense surface layer and the low and unconnected microporosity induced by the slow water extraction during the drying process result in very low water swelling capacity. The swelling capacity of PAsp hydrogel shows high sensitivity to pH. Effect of H^+/OH^- concentration at various pHs leads to several large changes of swelling capacity. The reversible pH-responsiveness make this intelligent polymer had wider applications. We can consider the ionic repulsion between charge-groups incorporated in the polymeric network by an external pH modulation as the main driving force responsible for this sharp change of water absorbency. The swelling capacity reduces with increasing valency of cation (univalent > multivalent). A high ability of ion exchange of the carboxylate groups leads to the cycle between swelling and deswelling of hydrogel at terminal pH 10 alternatively immersed in CaCl_2 and NaCl solutions.

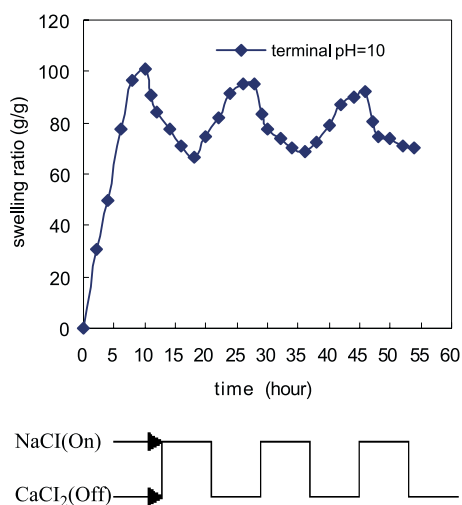


Fig. 11. Reversible cation-sensitivity of polyaspartic acid hydrogel. The terminal pH of sample had been adjusted at 10.

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