

Study on the Swelling, Shrinking and Bending Behavior of Electric Sensitive Poly (2-acrylamido-2-methylpropane sulfonic acid) Hydrogel

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Abstract

Taking 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as monomer, taking N,N'-methylenebis acrylamide as the cross linker, and taking the potassium persulfate as the initiators, we adopted the aqueous polymerization to prepare the PAMPS hydrogel and studied the swelling kinetics and electric sensitive properties of the hydrogel. The results indicated that, the swelling process of PAMPS in deionized water exhibited a non-Fickian diffusion model. Applying 15 V contact voltage for 30 minutes, the minimum of mass maintenance rate of PAMPS was 36.82 %. Under noncontact continuous 15 V voltage applied periodically, the PAMPS showed a favorable reversible bending behavior.

Keywords: Hydrogel, Swelling, Electric stimulation response, 2-acrylamido-2-methylpropane sulfonic acid (AMPS)

Environmental sensitive hydrogel also known as intelligent hydrogel which can response exterior environment stimulus such as temperature, electric field, pH degree, ionic strength, concentration of organic compound in water, light, pressure, etc. The most outstanding feature of intelligent hydrogel is that gel volume will occur discrete changes when the external stimulus reaching to a critical region. In addition, intelligent hydrogel enjoys advantages of response, drive and information processing features (Bashir, 2002, P.3091-3093, Gerlach, 2005, P.555-561). Among all types of stimulus, since electric field enjoys easily operating and regulating conveniently, the electric-field-sensitive hydrogel (EFSH) has more broad prospects than other sensitive hydrogels. Under electric stimulation, EFSH exhibits volume or shape changes like gel swelling, shrinking and bending behavior. It is possible for EFSH to transform from electric energy to mechanical energy. Therefore, EFSH plays a role in areas of energy exchange devices (Gong, 1994,

P.9583-9587, Osada, 1992, P.242-244). Scholars have contributed greatly to EFSH in many domains such as medicine control-release system (He, 1997, P.118-127), chemical convertor, memory component switch and artificial muscle (Moschou, 2004, P.499-502). AMPS received attention in recent years due to its strongly ionizable sulfonate group, which has a high charge density, and it is easy to be dissociated as sulfoacid ion and presents the characteristic of negative ion. Therefore, great importance has been attached to the EFSH based on AMPS. We studied the swelling kinetics of PAMPS in deionized water and the sensitivity under stimulation of the electric field.

1. Experiment

1.1 Main reagents and apparatus

The main reagents in the experiment included AMPS (industrial class, made by Guangzhou Shuangjian Trading Co.,Ltd), N,N'-methylenebis acrylamide (MBAAm) (analytical pure, made by Tianjin Kermel Chemical Reagent Co., Ltd), potassium persulfate (analytical pure, made by Tianjin Kermel Chemical Reagent Co., Ltd) and other reagents which were general analytic pure and didn't be treated before using.

The apparatus in the experiment included JY600 Electrophoresis Apparatus Trophoresis Power Supply (made by Beijing Junyi Dongfang Electrophoresis Equipment Co., Ltd), 902C Platinum Electrode and Electric Heat Constant Temperature Water Bath.

1.2 Preparation of hydrogel

Weighed certain quantitative monomeric AMPS and cross linker MBAAm (the amount was 4 wt% of monomer content), added proper quantitative distilled water to make it dissolved, and added quantitative potassium persulfate (the amount was 5 wt% of monomer content), mixed up and encased miscible liquids into the plastic pipe (which diameter was 6 mm and the length was 20 cm) and pressurized it, and put it in the constant temperature water bath of 50 $^{\circ}$ C and produced the hydrogel. Marinate the hydrogel into the deionized water for three days, and changed water twice one day to eliminate the monomer which didn't react. Finally, put the hydrogel into the vacuum drying oven to dry until constant weight, and the drying hydrogel could be used in the following test.

1.3 Swelling properties of hydrogel

To measure the swelling ratio, preweighed dry sample was immersed in deionized water. After excessive surface water was removed with filter paper, the swollen sample was weighted at various time intervals. This procedure was repeated until there was no further weight increases. The swelling ratio was determined according to the formula (1).

Swelling ratio
$$(g/g) = (W_s - W_d) / W_d$$
 (1)

where W_s and W_d denote the weights of swollen and dry samples (g), respectively.

1.4 Electric stimulation shrinking behavior of hydrogel

First, made the hydrogel expand in the distilled water, and chopped the expanded hydrogel into column forms, and put them into the measurement equipment, and put a pair of platinum electric characteristic into the hydrogel along the horizontal directions from two sides. Connected the power supple, and took out the dehydrated gel, absorbed the surface water and measured them again. Computed the mass maintenance rate (Rm) according to the formula (2).

$$R_m(\%) = m_t / m_f \times 100$$
⁽²⁾

Where, m_t is the weight of the gel through electrification of t time (g), and m_f is the weight of the hydrogel before electrification (g).

1.5 Electric stimulation bending performance of hydrogel

First, expanded the hydrogel in the NaCl liquor with various mass concentration, and chopped the expanded hydrogel into the gel bars ($20 \text{ mm} \times 2 \text{ mm} \times 1 \text{ mm}$), and put them into the culture dish with a few NaCl solution and lucid bottom. Vertically put two parallel electrodes which interval was 20 mm in the culture dish, and made the gel bars vertical to the direction of the two electrodes and in the middle position of two electrodes, and fixed one end of the gelatin bars, and put the angle measurement equipment on the bottom of the culture dish. Threw electricity to the gel, and measured the bend degree of the gel through reading the angle deviation of the gel on the angle measurement equipment.

2. Results and discussions

2.1 The swelling kinetics of PAMP hydrogel

As far as swelling of a dried gel in water was concerned, Yoshida proposed the following three steps to occur in succession (Yoshida, 1994, P.97-102): (1) water molecules diffuse into the polymer network; (2) the hydrated polymer chains relax; (3) the polymer network expands into the surrounding liquid. The swelling process of PAMPS hydrogel in deionized water was illustrated in Figure 1. To obtain a more quantitative understanding of the nature of the transport kinetic in the hydrogel, the swelling ratio is analyzed as a function of the time for $0 \le (M_t/M_{\infty}) \le 0.6$. The data were fitted to the equation (3).

(3)

where M_t and M_{∞} are the weight of water absorbed by the hydrogel at time t and at the equilibrium swollen state, respectively. k is a characteristic constant related to the structure of the hydrogel network, and n is a swelling exponent. The n and k would be calculated from the slope and intercept of the plot of $\ln(M_t/M_{\infty})$ against lnt, respectively. There are three models, which describe the diverse range of responses of hydrophilic polymer networks to the presence of water. These models are based on the relative rates of penetrant diffusion and polymer chain relaxation (Alfrey, 1966, P.249-261): (a) Fickian diffusion (n=0.5), also known as Case I diffusion, occurs when the rate of diffusion is significantly slower than the rate of relaxation of the polymer chains. (b) Case II transport (n=1) arises when the rate of diffusion (0.5<n<1) occurs when the rates of diffusion and polymerrelaxation are comparable and is connected with the transition region between the two limiting cases of Case I and Case II. As seen in Figure 2, the corresponding value for n was 0.64 499, which indicated that the swelling mechanism of PAMPS hydrogel would be non-Fickian transport.

2.2 Electric simulation deswelling behavior of hydrogel

The changes of the mass maintenance rate of expanded PAMPS hydrogel under 5 V, 10 V, 15 V DC electric stimulation were seen in Figure 3. From Figure 3, when the electrification time kept 30min, with the increase of voltage, the R_m value would gradually decrease. And with the delay of electrification time, the shrinking degree of the gel volume also would be delayed. For general polyelectrolyte hydrogel, the contractile behavior of the hydrogel in an electric field is due to voltage-induced motion of ions. Theories, such as electrodiffusion, electrophoresis, electro-osmosis and local pH profiles caused by water electrolysis can explain the mechanism of stimulus response in DC electric fields for normal polyelectrolyte gels (Kim, 2003, P.1-5).

2.3 Electric simulation bending behavior of hydrogel

When a noncontact electric field was applied to PAMPS gel strip, in aqueous NaCl solution, it showed significant and quick bending towards the cathode. When the electrical stimulus was removed, the gel returned gradually to its original position. It was thought that the bending behavior of hydrogel under an electric field was due to the voltage-induced motion of ions, and the concomitant expansion of one side of the hydrogel and the contraction of the other. (Kim, 2004, P.1456-1460).

The influence of the medium ionic concentration on the bending behavior of the PAMPS hydrogel in response to an electric stimulation by varying the concentration of the NaCl solution from 0.1 to 1.2 wt% was examined. As shown in Figure 4, the equilibrium bending angle increased with the concentration of NaCl solution when the concentration was less than 0.6 wt%, while the bending angle decreased with the concentration greater than 0.6 wt%. An increase of electrolyte concentration in a solution induces an increase of free ions moving from solution into the PAMPS hydrogel, as a result, the bending degree of the hydrogel could increase. However, if the concentration is greater than its critical concentration, the shielding effect of the polyions by the ions in the electrolytic solute occurs, leading to a reduction in the electrostatic repulsion of the polyions and a decrease in the degree of bending angle. (Sun, 2001, P.236-246).

The effects of the applied voltage on the bending angle were shown in Figure 5. From Figure 5, the bending angle and bending speed increased with an increase of the applied voltage. Also, from figure 6, the PAMPS hydrogel strip showed a reversible bending behavior. With a voltage of 15 V applied periodically for 10 min, the number of reversible bends up to more 20 times, indicating the PAMPS hydrogel material possesses potential application foreground in bionic materials and artificial organ components.

3. Conclusions

In this article, we prepared the PAMPShydrogel through the aqueous solution polymerization method, and studied the swelling kinetics of sample hydrogel, and measured the sensitivity under the simulation of the electric field. The results included (1) Swelling kinetics mechanism of the hydrogel could be non-Fickian diffusion model, (2) With the increase of direct contact electric stimulation, the mass maintenance rates would gradually decrease. And with the delay of electrification time, the shrinking degree of the gel volume also would be delayed. The contractile behavior of the hydrogel in electric field is due to voltage-induced motion of ions, (3) Under the noncontact electric field stimulation, the PAMPS hydrogel strip showed a favorable bending angle, bending speed and a reversible bending behavior, which indicated the hydrogel materials possess potential application in bionic sensor and actuator materials.

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Figure 1. The swelling kinetics of PAMP hydrogel



Figure 2. The fitting plot of $\ln(M_t/M_{\infty})$ against ln t



Figure 3. The deswelling kinetics of the PAMPS hydrogel as a function of the applied voltage



Figure 4. The effect of medium ionic concentration on the equilibrium bending angle of the PAMPS hydrogel at 15 V constant voltage



Figure 5. The bending kinetics of the PAMPS hydrogel in aqueous 0.4 wt% NaCl solution



Figure 6. The reversible bending behavior of the PAMPS hydrogel in 0.4 wt% NaCl solution due to switching the electric field (15 V) on and off