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Jinyue Song<sup>a</sup>; Genqi Liu<sup>a</sup>; Shiwen Yang<sup>a</sup>

<sup>a</sup> Department of Applied Chemistry, Northwestern Polytechnical University, Xi'an, P. R. China

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# Electroresponsive Behavior of 2-Hydroxypropyltrimethyl Ammonium Chloride Chitosan Hydrogel Under DC Electric Field

JINYUE SONG, GENQI LIU\* and SHIWEN YANG

Department of Applied Chemistry, Northwestern Polytechnical University, Chang'an District, Xi'an, P. R. China

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A novel polycationic chitosan hydrogel, 2-hydroxypropyltrimethyl ammonium chloride chitosan hydrogel (HACC hydrogel), was prepared by the introduction of quaternized groups with glycidyltrimethylammonium chloride (GTMAC) and epichlorohydrin as crosslinker, and its swelling properties and electroresponsive behavior in aqueous NaCl solutions were studied. The results indicated that the water uptake ability of the hydrogel decreased with the increasing ionic strength of aqueous NaCl solution. The hydrogel swollen in the NaCl solution bent toward the anode under the non-contact dc electric fields, and its bending speed and equilibrium strain increased with the increasing of applied voltage. The electroresponsive behavior of the hydrogel was also affected by the electrolyte concentration of external NaCl solution, and there is a critical ionic strength of 0.15 where the maximum equilibrium strain of the hydrogel occurs. By changing the direction of the applied potential cyclically, the hydrogel exhibited good reversible bending behavior.

**Keywords:** 2-Hydroxypropyltrimethyl ammonium chloride chitosan, hydrogel, electroresponsive behavior, swelling, bending

## 1 Introduction

A hydrogel is a three-dimensional network of hydrophilic polymers that can swell in water and aqueous solution and hold a large amount of water while maintaining the structure. Intelligent hydrogels can change their volume and shape reversibly depending on external stimuli, such as changes in pH (1–3), solvent composition (4,5), temperature (6–8), light (9) and electric field (10–14), etc. As the electric field is the most conventional and convenient stimulus from the point of signal control, the electroresponsive hydrogel has become the research focus recently. The electroresponsive hydrogels, which can directly transform the electrical energy into mechanical work have many potential applications in the field of smart gel-based devices, such as sensors (15,16), actuators (17,18), artificial muscles (19,20), and drug delivery systems (21,22).

However, the current preparation materials of electroresponsive hydrogels are mostly synthetic polymers, and only a few of them are about natural polymers materials (23–25). It is well known that natural polymers have better biocom-

patibility and a less latent toxic effect than most synthetic polymers, so natural polymer-based hydrogels would be more suitable for applications in some fields. Chitosan (CS) is a deacetylation product of chitin, which has good biocompatibility, biodegradability, nontoxicity, and easy availability. Sun et al. (26) prepared CS/poly(ethylene glycol) composite hydrogel fibers, but only the CS/PEG gel was immersed in 0.1% HCL, it had a response to the electric field, which causes many inconveniences for its application. Shang et al. (25) reported an electric-sensitive hydrogel film, and studied its bending behavior in the electric field, however, the response speed and bending angle are still to be raised.

In this paper, a novel polycationic chitosan hydrogel (HACC hydrogel), crosslinked with epichlorohydrin in alkaline conditions was prepared by the quaternization of chitosan, and its swelling properties and electroresponsive behavior in NaCl solutions were studied. The results indicated that the HACC hydrogel has excellent electroresponsive properties.

## 2 Experimental

### 2.1 Materials

Chitosan (CS) (deacetylation degree = 95.4%) was purchased from Jinhu Crust Product Co., Ltd. (Shandong,

\*Address correspondence to: Genqi Liu, Department of Applied Chemistry, Northwestern Polytechnical University, Xi'an 710129, P. R. China. Tel: +86-13991869386; E-mail: liugenqi@nwpu.edu.cn

China). Glycidyltrimethylammonium chloride (GTMAC) was purchased from Shandong Guofeng Fine Chemical Co., Ltd (Shandong, China). Sodium chloride was purchased from Tianjin Chemical Factory (Tianjin, China). Potassium hydroxide was purchased from Tianjin Chemical Reagent Factory (Tianjin, China). Perchloric acid was purchased from Tianjin Xinyuan Chemical Co., Ltd. (Tianjin, China). Absolute ethanol was purchased from Tianjin Hongda Chemical Reagent Factory (Tianjin, China). Epichlorohydrin was purchased from Tianjin Bodi Chemical Co., Ltd. (Tianjin, China). All the materials were used without further purification.

## 2.2 Preparation of HACC Hydrogel

2 g of CS was dispersed in 60 g deionized water and then 60 drops of perchloric acid was added with stirring at room temperature. After CS dissolved completely, the temperature rose to 60°C. Subsequently, 31 g 35.5 wt% GTMAC aqueous solution was added to the chitosan solution slowly. Then the temperature rose to 85°C and the reaction was carried out under continuous stirring for 10 h. The resultant was poured into absolute ethanol and a precipitate of 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC) was obtained. The precipitate was filtered, washed with absolute ethanol and dried at 60°C.

2.0 Wt% solution was prepared by dissolving a certain amount of HACC in deionized water. Then, the HACC solution was poured into a plexiglass case and dried into the membrane. The dry HACC membrane was peeled off the plexiglass case and immersed in a reaction solution of pH 13 at 50°C, which contained 0.74 wt% of epichlorohydrin, 4.22 wt% of water in ethanol. After the crosslinking reaction for 8 h, the crosslinked HACC hydrogel membrane was synthesized. Subsequently it was taken out, washed thoroughly with deionized water and immersed in deionized water for 24 h. During that time, the water was changed once every 8 h, then the hydrogel was dried in vacuum oven at 50°C until a constant weight was obtained and used for studying the swelling properties and electroresponsive behaviors under DC electrical fields.

## 2.3 IR Analysis

IR spectra of the CS, HACC and HACC hydrogel samples were recorded on a NICOLET IS10 IR spectrometer (Thermo Fisher Scientific, USA), using a KBr pellet technique.

## 2.4 Swelling Properties of HACC Hydrogel

Pre-weighed dry samples of the hydrogels were immersed in aqueous NaCl solutions of different ionic strength at room temperature until the samples reached their equilibrium swelling states. After the removal of the excess surface water by filter paper, the weights of the swollen hydrogel samples

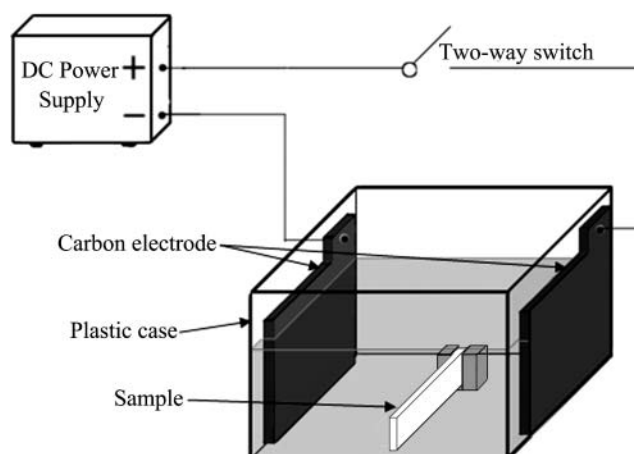


Fig. 1. Self-made equipment of measurement under DC electric field.

were measured. The equilibrium swelling ratio ( $E_{SW}$ ) was determined according to the following equation:

$$E_{SW} = \frac{W_e - W_d}{W_d} \quad (1)$$

Where  $W_e$  and  $W_d$  were the weights of samples at equilibrium swollen state and in the dry state, respectively.

## 2.5 Bending Behavior of HACC Hydrogel under DC Electric Fields

The aqueous NaCl solution was poured into a plastic case equipped with two parallel carbon electrodes (Fig. 1). The distance between them was 30mm. The HACC hydrogel was fully swollen in aqueous NaCl solutions at room temperature, and cut into 13 mm long  $\times$  2 mm wide  $\times$  0.16 mm thick strips. One end of the sample was fixed and the hydrogel was placed in the center of the case. The electroresponsive behavior of the hydrogel was investigated by measuring the displacement of its free end, that is, the deflection of bending ( $Y$ ) before and after applied electric field. The sign of the deflection is defined positive when a hydrogel bends to the anode. The strain of bending ( $\varepsilon$ ) is calculated by the following Equation 2 (27):

$$\varepsilon = \frac{6DY}{L^2} \quad (2)$$

Where  $Y$  is the deflection of bending,  $D$  is the thickness of the hydrogel and  $L$  is the original length of the hydrogel before application of an electric field.

To test the reversible bending behavior of the hydrogel strips, the polarity of the electric field was altered every 20 seconds by changing a two-way switch.

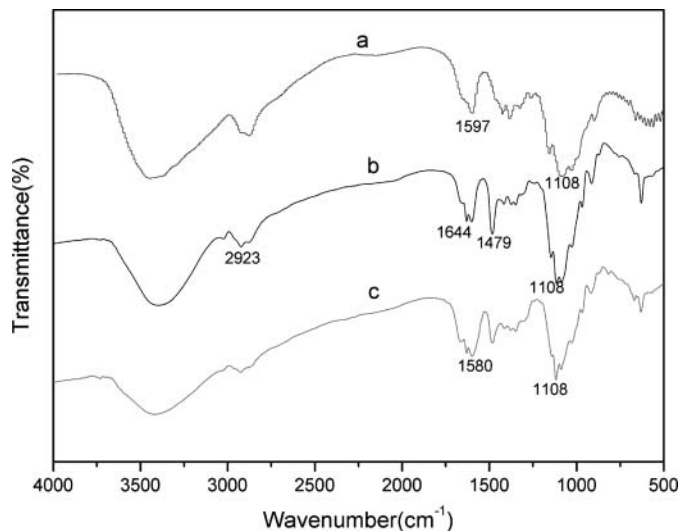


Fig. 2. IR spectra of (a) CS, (b) HACC, and (c) HACC hydrogel.

### 3 Results and Discussion

#### 3.1 IR Analysis

The IR spectra of the CS, HACC and the HACC hydrogel are shown in Figure 2. Figure 2(a) showed that there are two characteristic peaks at  $1597\text{ cm}^{-1}$  (bending vibration band of  $-\text{NH}_2$ ), and  $1108\text{ cm}^{-1}$  (stretching vibration band of  $\text{C}-\text{O}-\text{C}$ ) in the IR spectra of CS. Comparing with Figure 2(a), the new absorption bands at  $2923\text{ cm}^{-1}$  (stretching vibration band of  $-\text{CH}_3$ ) and  $1644\text{ cm}^{-1}$ ,  $1479\text{ cm}^{-1}$  (bending vibration band of  $-\text{CH}_3$ ) appeared in the IR spectra of HACC (Fig. 2(b)), which indicated that the  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}(\text{CH}_3)_3\text{Cl}$  groups were successfully introduced into the CS. A comparison of the IR spectra of HACC and HACC hydrogel shows that there was an obvious absorption band at  $1580\text{ cm}^{-1}$  (bending vibration band of  $-\text{NH}-$ ) in the IR spectrum of the HACC hydrogel, which indicated that the  $-\text{NH}_2$  crosslinked with the epoxy group of epichlorohydrin. The absorption bands at  $1108\text{ cm}^{-1}$  (stretching vibration band of  $\text{C}-\text{O}-\text{C}$ ) became sharp, which indicated the  $-\text{OH}$  crosslinked with the epoxy group of epichlorohydrin.

#### 3.2 Swelling Properties of HACC Hydrogel

Figure 3 shows the equilibrium swelling ratio of the HACC hydrogel in different ionic strength of the aqueous NaCl solution. The equilibrium swelling ratio was shown to decrease with increasing concentration of the NaCl solution. This can be explained by the fact that with the increasing concentration of the NaCl solution, the shielding effect caused by the counterions in the electrolytic solution would occur, leading to a reduction in the electrostatic repulsion of the polyions and a decrease of equilibrium swelling ratio of the hydrogel.

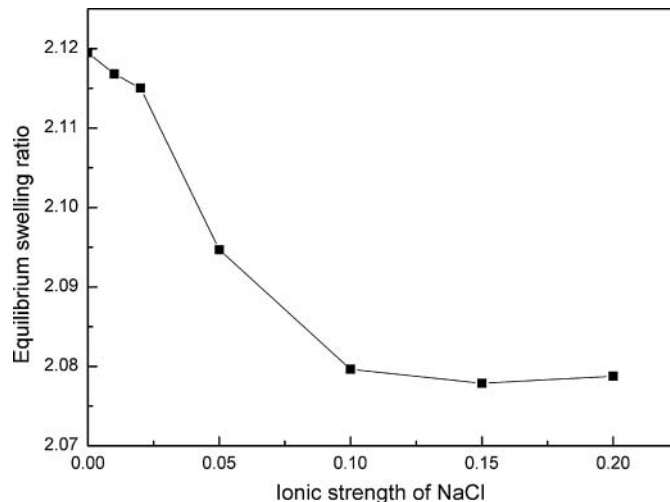


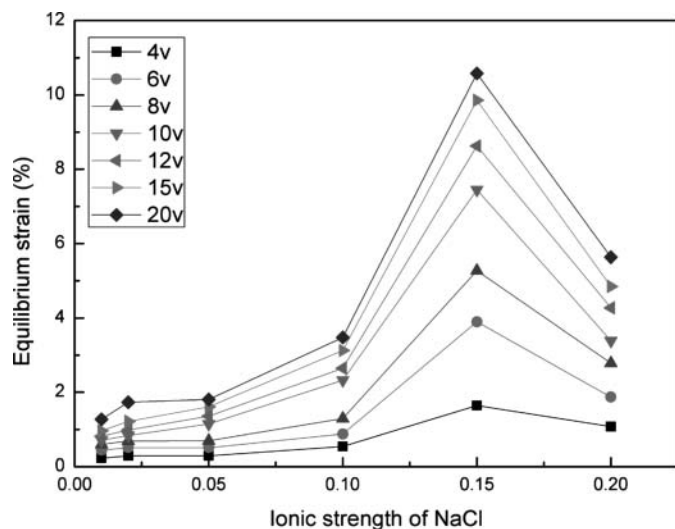
Fig. 3. Equilibrium swelling ratio of HACC hydrogel in different ionic strength of the aqueous NaCl solution.

#### 3.3 Bending Behavior of HACC Hydrogel under DC Electric Fields

When the HACC hydrogel stripe swollen in the aqueous NaCl solution was subjected to a DC electric field, it bent toward the anode. When the polarity of electric field was changed, the hydrogel stripe first became straight and then bent in the opposite direction.

The  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}(\text{CH}_3)_3\text{Cl}$  group is a strong electrolyte group, so the HACC hydrogel is a polycationic hydrogel. When an electric field is applied on the polycationic hydrogel in the aqueous solution, the counterion of the polyion moves toward the negative electrode, and the polyion remains immobile. Also, the free ions in the surrounding solution move toward their counter-electrodes and come into the hydrogel. Thus, the osmotic pressure of the hydrogel polymer network near the negative electrode increases and becomes larger than that of the positive electrode side. Consequently, the osmotic pressure difference occurs within the hydrogel, and it is the driving force of bending toward the positive electrode.

The electroresponsive behavior of the hydrogel was also affected by the ionic strength of aqueous NaCl solution. Figure 4 shows the correlation between the equilibrium strain and ionic strength of aqueous NaCl solution under different voltages at room temperature. It shows that with the increasing of ionic strength of aqueous NaCl solution, the equilibrium strain increased first and then decreased gradually. The maximum equilibrium strain occurs when the ionic strength of aqueous NaCl solution is 0.15. As described above, an increase in the electrolyte concentration of a solution induces an increase in the free ions moving from the surrounding solution toward their counter electrodes, and into the hydrogel itself. As a result, the strain of the hydrogel increases. However, if the ionic strength of the NaCl solution is greater than its critical ionic strength of

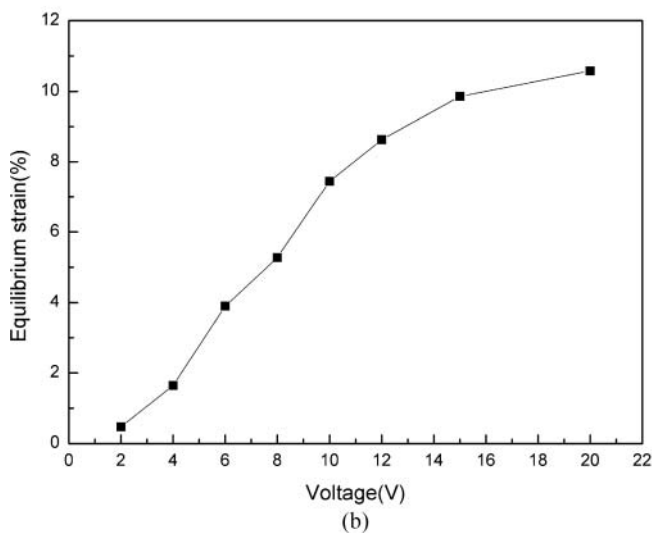
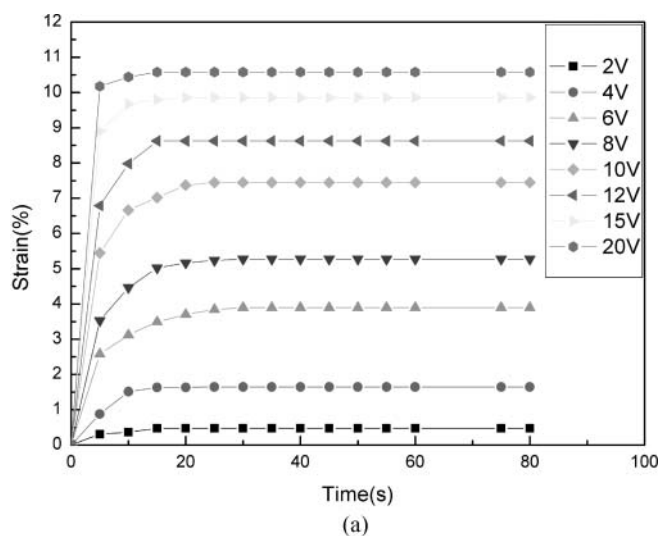


**Fig. 4.** Effect of ionic strength of the aqueous NaCl solution on the equilibrium strain under different applied voltages.

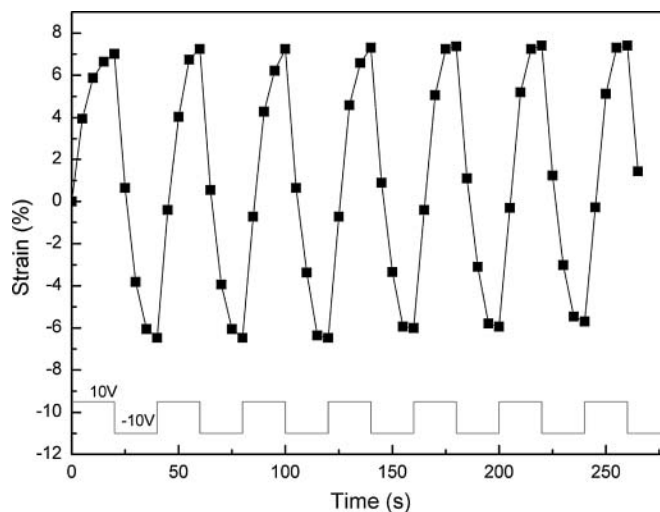
0.15, the shielding effect of the polyions caused by the counterions in the electrolytic solution would occur, leading to a reduction in the electrostatic repulsion of the polyions and a decrease in the equilibrium strain (28).

Figure 5 shows the bending kinetic curves and equilibrium strain of the HACC hydrogel under different applied voltages in ionic strength of aqueous NaCl solution of 0.15. As shown in Figure 5(a), the gradient slope in the plot of the strain of bending vs. time became steeper with the increasing of applied voltages and then leveled off at a steady state. Note that the bending speed and equilibrium strain increase with the applied voltage increasing, which could be explained by the fact that there was an enhancement in the transfer rate of the counterions of the immobile quaternary ammonium groups on the hydrogel network from the hydrogel to the external solution and the free ions moved from the external solution into the hydrogel as the potential gradient in the electric field is increased. Further analysis of the relationship between the voltage amplitude and the equilibrium strain showed a linear correlation between them when the voltages are smaller than 12V (Fig. 5(b)). When the voltages are larger than 12V, the increasing speed of equilibrium strain slowed down with the increasing of applied voltages. These quantitative relationships could be useful in the design of actuator devices.

In addition, the reversible bending behavior of the hydrogel depending on the electric stimulus was examined. When an electric field was applied, the strip of hydrogel bent toward the positive electrode. When the electric stimulus was removed, the gel was gradually displaced to its original position. Also, if the polarity of the electric field was altered, the hydrogel bent toward the opposite direction. When a cycle electric field (the electric field direction changes every time 20s) was applied, with the reverse of electric field direction, the hydrogel bends quickly to the



**Fig. 5.** Bending kinetic curves (a) and equilibrium strain (b) of HACC hydrogel under different applied voltages in 0.15mol/L NaCl solution.



**Fig. 6.** Response of bending for HACC hydrogel under a cyclically varying electric field from 10V to  $-10V$  every 20 sec ( $I = 0.15$ ).

opposite direction without hysteresis. Figure 6 indicated that the HACC hydrogel exhibited good reversible bending behaviors under a cyclically varying electric field from 10V to  $-10V$  every 20 seconds.

#### 4 Conclusions

A novel polycationic chitosan hydrogel (HACC hydrogel) was prepared by the introduction of quaternized groups. The water uptake ability of the hydrogel increased with the decreasing of ionic strength of aqueous NaCl solution. Under a non-contact dc electric field, the hydrogel stripe shows electroresponsive behavior. The bending behavior can be adjusted via voltage of the applied electric field and the ionic strength of the electrolyte. By changing the direction of the applied potential repeatedly, the hydrogel stripe exhibited good reversible bending behaviors. The hydrogel may have potential applications in the high-tech fields, such as artificial muscles, actuators, electric current modulated drug delivery systems, etc.

#### Acknowledgements

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