



## Study on the Sensitive Property of Poly (AMPS-co-DMAEMA) Hydrogel under Electric Stimulation

Liewen Liao

School of Materials Science and Engineering

Northwestern Polytechnical University

Xi'an 710072, China

Institute of Green Chemical Engineering

ZhongKai University of Agriculture and Engineering

Guangzhou 510225, China

Zhengtang Liu

School of Materials Science and Engineering

Northwestern Polytechnical University

Xi'an 710072, China

Hangbo Yue & Yingde Cui

Institute of Green Chemical Engineering

ZhongKai University of Agriculture and Engineering

Guangzhou 510225, China

Tel: 86-20-8901-3955 E-mail: liaolw@163.com

*The research is financed by the National Natural Science Foundation of China (No. 20176007 & No. 20376087). (Sponsoring information)*

### Abstract

Taking 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and 2-dimethylamino ethyl methacrylate (DMAEMA) as monomers, taking N,N'-methylenebis acrylamide as the cross linker, and taking the ammonium persulfate and sodium bisulfite as the redox initiators, we adopted the aqueous polymerization to prepare the Poly(AMPS-co-DMAEMA) hydrogel and studied the shrinking and bending behaviors of hydrogel under exterior DC electric field stimulation. The result indicated that the DMAEMA monomer content and the pressure could significantly influence the electric sensitivity of hydrogel. With the increase of the DMAEMA content and the non-contract electric field, the Poly(AMPS-co-DMAEMA) hydrogel first bended toward the cathode and then bended toward the anode.

**Keywords:** Hydrogel, Electric stimulation response, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 2-dimethylamino ethyl methacrylate (DMAEMA)

According to the response of hydrogel to the exterior stimulation, the hydrogel can be divided into traditional hydrogel and intelligent hydrogel, and the intelligent hydrogel can perceive exterior tiny physically chemical stimulations such as temperature, electric field, magnetic field, light, pH, ion strength and pressure, and show significant expansions or responses in the response process. We can utilize this characteristic to apply the intelligent hydrogel into the medicine controlled release, chemical convertor, memory component switch, artificial muscle and many domains (He, 1997, P.118-127, Moschou, 2004, P.499-502, Hamlem, 1965, P.1149-1150).

The DMAEMA molecule contains alkaline tertiary amine which can be turned into protons and presents characteristic of positive ion in the acidic medium (Huang, 2003, P.177-182). The sulfoacid group in the AMPS molecule has high charge density, and it is easy to be dissociated as sulfoacid ion and presents the characteristic of negative ion. In this article, we took the N,N'-methylenebis acrylamide as the cross linker, took the ammonium persulfate and sodium bisulfite as the redox initiators, and adopted the free radical polymerization process to prepare the Poly(AMPS-co-DMAEMA) hydrogel, and studied the sensitivity under the 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), DMAEMA (industrial class, made by Guangzhou Shuangjian Trading Co., Ltd), N,N'-methylenebis acrylamide (MBAAm) (analytical pure, made by Tianjin Kermel Chemical Reagent Co., Ltd), ammonium persulfate (analytical pure, made by Tianjin Kermel Chemical Reagent Co., Ltd), sodium bisulfite (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 Spectrum 2000 Fourier Transform Infrared Spectrometer (Pekin-Elmer, USA), 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, DMAEMA and cross linker MBAAm according to Table 1, added proper quantitative distilled water to make it dissolved, and added quantitative ammonium persulfate and sodium bisulfite, mixed up and encased miscible liquids into the plastic pipe (which diameter was 6mm and the length was 20cm) and pressurized it, and put it in the constant temperature water bath of 50°C and produced the hydrogel. Marinate the hydrogel into the deionized water for three days, and changed water twice one day to eliminate the monomers which didn't react. Finally, put the hydrogels into the vacuum drying oven to dry until constant weight, and the drying hydrogel could be used in the infrared spectrum test.

### 1.3 Infrared spectrum token of hydrogel

Made the infrared spectrum test to the hydrogel sample by the Spectrum 2000 Fourier Transform Infrared Spectrometer (Pekin-Elmer, USA), and the scanning range was 500~4000cm<sup>-1</sup>, and the resolution was 4cm<sup>-1</sup>.

### 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 (the bottom diameter was 8mm, and the altitude was 10mm), 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 supply, and took out the dehydrated gelatin, absorbed the surface water and measured them again. Computed the mass maintenance rate ( $R_m$ ) according to the formula (1).

$$R_m (\%) = m_t / m_f \times 100 \quad (1)$$

Where,  $m_t$  was the mass of the gelatin through electrification of  $t$  time (g), and  $m_f$  was the mass of the hydrogel before electrification (g).

### 1.5 Electric stimulation bending performance of hydrogel

First, expanded the hydrogel in the NaCl liquor with 0.8% of mass concentration, and chopped the expanded hydrogel into the gelatin bars (20mm×2mm×1mm), and put them into the culture dish with a few NaCl solution and lucid bottom. Vertically put two parallel electric characteristic which interval was 20mm in the culture dish, and made the gelatin bars vertical to the direction of the two electric characteristic and in the middle position of two electric characteristic, and fixed one end of the gelatin bars, and put the angle measurement equipment on the bottom of the culture dish. Threw pressure to the gelatin, and measured the curve degree of the gelatin through reading the angle deviation of the gelatin on the angle measurement equipment. When the gelatin bar achieved the maximum curve angle under the electric stimulation, cut off the power supply and read the number, and regulated that when the gelatin bended toward the cathode, the curve angle was positive, and when the gelatin bended toward the anode, the curve angle was negative.

## 2. Results and discussions

### 2.1 Infrared spectrum analysis of Poly(AMPS-co-DMAEMA) hydrogel

Figure 1 was the infrared spectrum of the Poly(AMPS-co-DMAEMA) hydrogel, and the flexing libration absorption apex of the amido group in the AMPS molecule occurred at 1665 cm<sup>-1</sup>, and the flexing libration absorption apex of the ester group in the DMAEMA molecule occurred at 1730 cm<sup>-1</sup>. But characteristic absorption apex (at about 1640 cm<sup>-1</sup>) of the unsaturated double-linkage didn't exist, which indicated that two sorts of monomers have produced the polymerization reaction.

### 2.2 Electric stimulation deswelling behavior of hydrogel

#### 2.2.1 Hydrogel deswelling kinetics under constant pressure

The change of the mass maintenance rate of expanded Poly (AMPS-co-DMAEMA) hydrogel under the 15V contact pressure stimulation with the time was seen in Figure 2.

From Figure 2, under the situation that the pressure kept at 15V, with the delay of electrification time, the  $R_m$  value of the hydrogel would decrease gradually. With the increase of the DMAEMA content in the copolymer, the  $R_m$  value of the hydrogel also decreased in turn.

The reason might be that acidic sulfonic group and alkali tertiary amine existed in the Poly(AMPS-co-DMAEMA) hydrogel network. A90D10 hydrogel contained more AMPS main chain, and when the content of the side chain sulfonic group was more, the hydrophilicity and the conductivity were better. DMAEMA molecule in the A50D50 hydrogel contained hydrophobic ester group, and the hydrophobic side groups on the macromolecule chain would assemble and form hydrophobic micelles, and the macromolecule chain would present austere conformation (Zhang, 2002, P.25-29), so the expansion change degree of the hydrogel with much DMAEMA would decrease.

### 2.2.2 Influence of pressure on the hydrogel shrinking behavior

The hydrogel shrinking influence result under different DC pressure stimulation was seen in Figure 3. From Figure 3, when the electrification time kept 30min, with the increase of pressure, the  $R_m$  value would gradually decrease. And with the increase of the DMAEMA content in the copolymer, the shrinking degree of the gelatin volume would be delayed.

For general polyelectrolyte hydrogel, under the function of electric field, the transfer speed of the movable counterion was related with the electric field tension except for the character of the ion (ion radius and charges) (Ma, 2002). With the increase of the pressure, the transfer speed of the charged ion increased. With the transfer of the ions with different electric characteristic in the gelatin network, because of the function of electrostatic attraction, part of charges on the poly ion group in the gelatin network would be shielded, the decrease of the charged poly ion quantity would reduce the "distracting" function of the gelatin to the water, and the moisture would be exuded into the gelatin network. For the Poly(AMPS-co-DMAEMA) gelatin with different matching ratios, with the increase of the voltage, the  $R_m$  value would gradually decrease.

### 2.3 Electric simulation bending behavior of hydrogel

The influencing result of the pressure to the bending behavior of gelatin is seen in Figure 4, and the exterior pressure would act on the hydrogels with different components through the NaCl solution with 0.8% of mass concentration.

From Figure 4, under the stimulation of non-contact DC pressure, A90D10 hydrogel bended toward cathode, and A50D50 hydrogel bended toward anode, and A70D30 hydrogel first bended toward cathode and then bended toward anode and with the increase of pressure, the curve angle of the gelatin would increase with it.

The reason might be that the electric characteristic of the poly ion group in the sample gelatin network were different. For A90D10 hydrogel, the poly ion group in the gelatin network presented the characteristic of negative ion. For A50D50 hydrogel, the poly ion group presented certain characteristic of positive ion. With the increase of pressure, the poly ion group in the A70D30 hydrogel network changed from the characteristic of negative ion to the characteristic of positive ion, so it first bended toward the cathode and then bended toward the anode, and the function of the osmotic pressure might influence the electrode change of the poly ion group, and the electric stimulation response mechanism should be further studied by scholars. Through adjusting the pressure, the bending direction of Poly(AMPS-co-DMAEMA) hydrogel could be controlled, which indicated that this sort of hydrogel material possessed potential application foreground in many domains such as bionic material and chemical valve.

## 3. Conclusions

In this article, we prepared the Poly(AMPS-co-DMAEMA) hydrogel through the aqueous solution polymerization method, and measured the sensitivity under the simulation of the electric field. The results included (1) under the direct contact pressure stimulation, the mass maintenance rates of A90D10, A70D30 and A50D50 decreased in turn under same condition, and with the increase of the pressure, the shrinking phenomena of hydrogel were more and more obvious, (2) under the non-contact electric field stimulation, A90D10 hydrogel bended toward cathode, A50D50 hydrogel bended toward anode, and A70D30 first bended toward cathode and then bended toward anode with the increase of pressure.

## References

- Hamlem R P, Kent C E & Shafer S N. (1965). Electrolytically Activated Contractile Polymers. *Nature*. No.206. P.1149-1150.
- Heqing & Shengjing. (1997). Response Hydrogel and Its Application in Medicine Controlled Release. *Journal of Functional Polymers*. No.10(1). P.118-127.
- Huangyi, Fan, Xiaodong & Huhui et al. (2003). Synthesis and Characterization of Novel Hydrogels of Poly(DMAEMA-co- $\beta$ -Cyclodextrin Acrylate). *Acta Polymerica Sinica*. No.2. P.177-182.
- Ma, Xinglan & Xue, Shuiqiang. (2002). *Physical Chemistry*. Xuzhou: China University of Mining and Technology

Press.

Moschou E A, Peteu S F, Bachas L G, et al. (2004). Artificial muscle material with fast electro actuation under neutral pH conditions. *Chemistry of Materials*. No.16(12). P.499-502.

Zhang, Jianhe & Yang, Yajiang. (2002). Stimuli-Response of Hydrophilic-Hydrophobic Semi-IPN Hydrogels under DC Electric Field. *Acta Polymerica Sinica*. No.1. P.25-29.

Table 1. Feed composition of Poly(AMPS-co-DMAEMA) hydrogel<sup>a</sup>

Hydrogel <sup>b</sup>	AMPS (mol %)	DMAEMA (mol %)	Crosslink agent (mol %)	Initiator (mol %)	Total concentration of monomer (mol/L)
A90D10	90	10			
A70D30	70	30	1	1	1
A50D50	50	50			

Note: <sup>a</sup>: The amount of crosslink agent or initiator is mole percent (mol %) of total monomer content.

<sup>b</sup>: The A90D10, A70D30 and A50D50 hydrogels respectively denote n(AMPS):n(DMAEMA)=9:1, 7:3, 5:5.

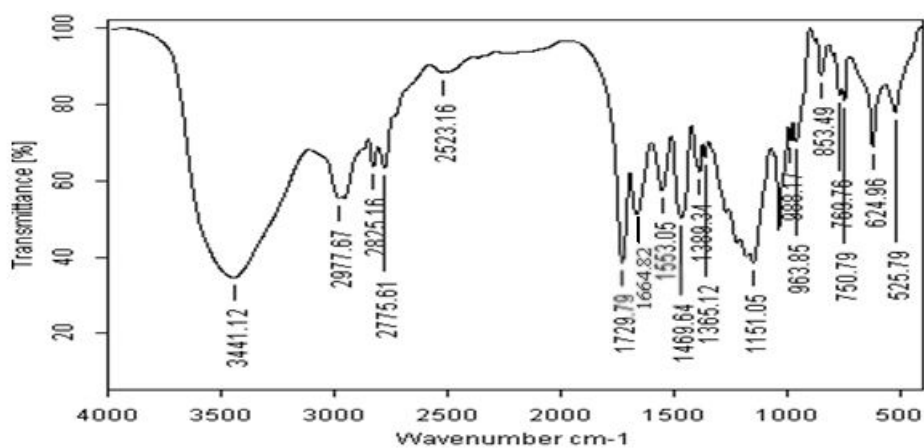


Figure 1. FTIR Spectrum of Poly(AMPS-co-DMAEMA) Hydrogel

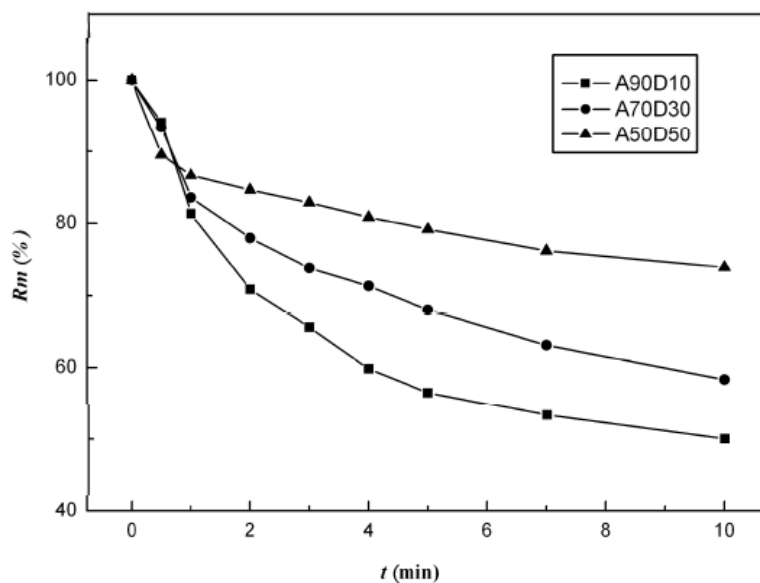


Figure 2. Shrinking Behavior of Poly(AMPS-co-DMAEMA) Hydrogel under 15V Electrical Stimulation

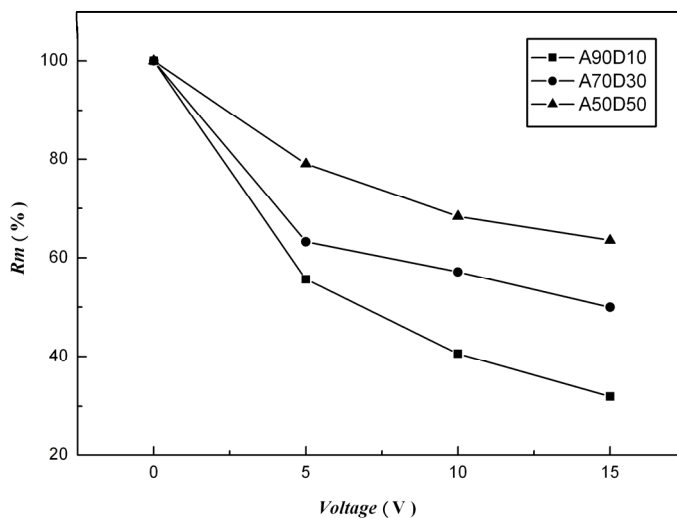


Figure 3. Shrinking Behavior of Poly(AMPS-co-DMAEMA) Hydrogel under Electrical Stimulation for 30min

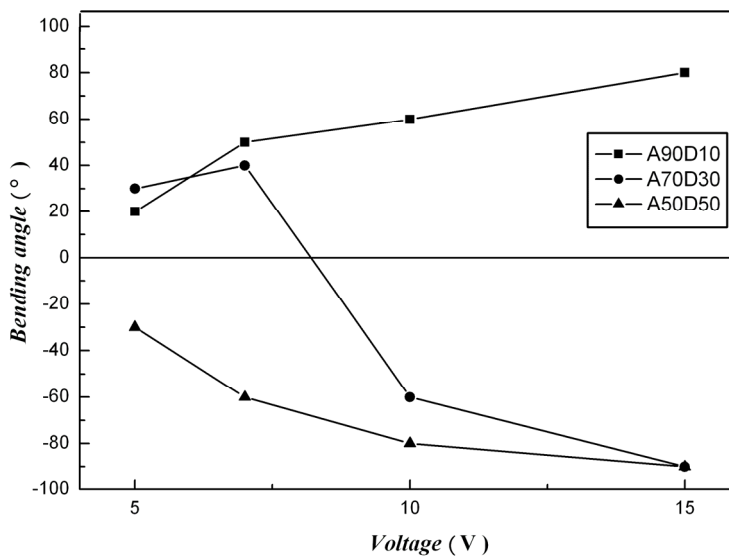


Figure 4. The Effects of the Applied Voltage on the Bending Angle of Poly(AMPS-co-DMAEMA) Hydrogel in 0.8wt% NaCl aqueous solution