

# Synthesis and Properties of Electrically-Sensitive Poly(acrylic acid-*co*-acetoacetoxy ethyl methacrylate) Gels

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Received 30 October 2007; accepted 4 July 2008

DOI 10.1002/app.28982

Published online 17 September 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of electric field sensitive copolymer P(AA-*co*-AAEM) gels of acrylic acid (AA) with acetoacetoxy ethyl methacrylate (AAEM) were prepared by free-radical copolymerization, with *N,N'*-methylene bisacrylamide (MBAAm) and ammonium persulfate (APS) as crosslinking agent and initiator, respectively. The structures and properties of the gels were tunable by changing the monomer feed weighty ratio ( $R$ ) ( $R = W_{AAEM}/(W_{AAEM} + W_{AA})$ ) of AAEM and AA. The influences of the NaCl concentration and pH buffer solutions on the equilibrium swelling ratios of the gels were studied in detail. It is shown that both NaCl concentration and pH value of the buffer solution affect the

swelling properties of the P(AA-*co*-AAEM) gels greatly. Moreover, the gel deswelling behavior induced by a direct current electric field was investigated and an excellent electric-sensitivity was found. Among all the samples, the gel with monomer feed weighty ratio ( $R$ ) = 0.1479 showed the best electrical contraction properties. On the basis of the experimental results, the mechanism of the electricity-induced deswelling behavior was presented. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3690–3696, 2008

**Key words:** electrically-sensitive; gel; acrylic acid; acetoacetoxy ethyl methacrylate; deswelling

## INTRODUCTION

“Smart” polymeric gels are such gels that the size, structure, or viscoelastic properties etc. can exhibit reversible and discontinuous (or continuous) changes in response to the external stimulus. The stimuli-responsive properties, implying a kind of intelligence, offer the possibility of the gel-based technology.

Electrically sensitive gel is an important member in the family of the “smart gels.” Most of the electrically sensitive gels are polyelectrolytes. Hamlen et al.<sup>1</sup> firstly reported the electric field-induced deformation of polyelectrolyte gels in 1965. In the later 1970s' Tanaka et al.<sup>2</sup> reported the phenomena of the volume phase transitions of gels. In fact, as earlier in 1950s' Flory<sup>3</sup> has theoretically predicted the volume phase transition of gels. In 1982, Tanaka et al.<sup>4</sup> described an electric field-induced phase transition of a partially hydrolyzed polyacrylamide (PAAm)

gel in a mixed solvent of 50/50 (v/v) acetone and water. Tanaka's discovery aroused great research interests in the field of smart gels. Hirotsu<sup>5</sup> observed a shrinking of ionic gel beads near the phase transition point under DC (direct current electric field) and AC (alternating current electric field) excitations. Shiga and Kurauchi<sup>6</sup> found that the deformation of the PAANA gel in NaOH solution in an electric field is strongly affected by the concentration of NaOH solution. Ire<sup>7</sup> prepared a PAAm gel containing triphenylmethane leuco derivatives, and observed the bending deformation of the gel under electric and light field together. Osada et al.<sup>8</sup> investigated the bending deformation of the gel in surfactant solution. In 1993, a fast-responsive gel was synthesized by Nanavati and Fernandez.<sup>9</sup> Liu et al.<sup>10</sup> studied the responsive behavior of the gelatin hydrogel under DC stimulus. Yan et al.<sup>11</sup> investigated the stimuli-response of the hydrophobic pH-sensitive gels in the direct current electric field. Recently, the applications of the electrical sensitive gels mainly aims to the potential applications in the field of membranes and drug delivery systems,<sup>12–14</sup> artificial muscle,<sup>1,15–17</sup> biomimetic actuator,<sup>6</sup> and vibration isolator<sup>18</sup> etc. For these applications, a fast response speed of hydrogel to the external stimuli is crucial. To increase this response rate, preparing the gel samples with dangling chains or submicrometer particle size, as well as macroporous structures proves to be effective.<sup>19</sup>

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Contract grant sponsor: The National Natural Science Foundation of China; contract grant numbers: 20606010, 20736002.

Contract grant sponsor: The Ministry of Education of China; contract grant number: 20050251004.

*Journal of Applied Polymer Science*, Vol. 110, 3690–3696 (2008)  
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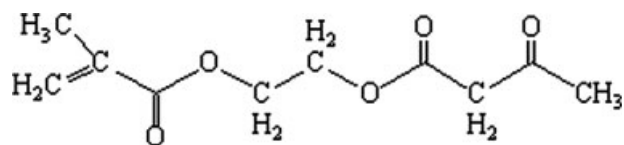


Figure 1 The structure of AAEM monomer.

In this work, using *N,N'*-methylene bisacrylamide and ammonium persulfate as crosslinking agent and initiator respectively, acetoacetoxy ethyl methacrylate (AAEM) and acrylic acid (AA) were chosen to prepare a series of electric field sensitive gels by free-radical copolymerization. The inspiration to employ AAEM lies in its specific structure (as shown in Fig. 1) with a long chain connected with the C=C, the copolymer of which endows the gel with the possible excellent electric sensitivity. Although the side chain brought by the AAEM into the gel is not as long as the dangling chain which has studied by the literatures,<sup>20,21</sup> it is hopeful to improve the electrical sensitivity of the hydrogel. This idea has been supported by our former study.<sup>22</sup> In this work, the hydrogels with various AAEM content were prepared, and both the swelling and electric-sensitive properties were investigated.

## EXPERIMENTAL

### Materials

Acrylic acid (AA: CP,  $\geq 98$  wt %) and ammonium peroxydisulfate (APS: AR,  $\geq 98$  wt %) were purchased from Lingfeng chemical reagent (Shanghai, China); Acetoacetoxy ethyl methacrylate (AAEM,  $\geq 95$  wt %) was provided by CHARNA chemicals and pharmaceuticals (Shanghai, China); *N,N'*-methylenebisacrylamide (MBAAm: CP,  $\geq 98$  wt %) was the product of Sinopharm Chemical Reagent (Shanghai, China). NaCl, NaOH, H<sub>3</sub>BO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, and CH<sub>3</sub>COOH were all AR grade. Monomer AA was purified by vacuum distillation; other reagents were used as received.

### Preparation of the copolymer hydrogels

The typical manipulation for the free radical copolymerization of AA and AAEM was as follows: 2 g mixture of monomers AA and AAEM with various monomer feed weighty ratios ( $R$ ) ( $R = W_{AAEM} / (W_{AA} + W_{AAEM})$ ,  $W_{AAEM}$  and  $W_{AA}$  is the weight of AAEM and AA, respectively), 0.014 g MBAAm (0.7 wt % of total monomers), and 0.06 g APS (3 wt % of total monomers) were together dissolved in 18 mL deionized water. After the complete dissolution, the mixture solution was sealed into a polyethylene tube. Copolymerization was performed for 6 h at 60°C, until the solution changed into gel. The gel matrix was washed with deionized water several times to remove any residual low molecular weight materials and the water-soluble linear polymers. In this work, only the feed weighty ratio ( $R$ ) was changed, while the dosage of other reactants was constant and the total percentage of the monomers in the reaction solution was kept at 10% by weight, aiming to investigating the impact of various  $R$  on the hydrogels properties. The feed dosage of the reactants is listed in Table I.

### Fourier transform infrared spectroscopy

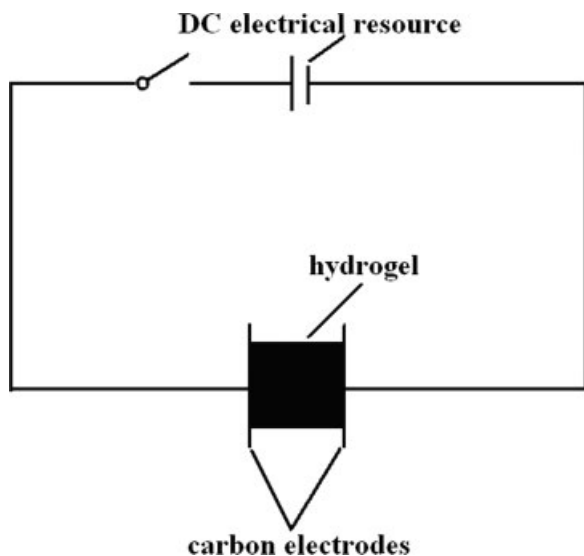
The Fourier transform infrared (FTIR) spectra of the gels were obtained using the attenuated total reflection FTIR spectroscopy (NICOLET 6700). To avoid the interference of water, the gels were dealt with freeze drying.

### XRD determination

The crystallinity of the gels was studied with an X-ray diffraction (XRD) instrument (D/MAX 2550 VB/PC, RIGAKU). The swollen gels were mashed into small pieces, and then were freeze-dried to afford powder, which were used for the XRD study.

TABLE I  
The Feed Dosage of Reactants and Solvent

Gels	AA (mol/L)	AAEM (mol/L)	R	MBAAm (mol/L)	APS (mol/L)	H <sub>2</sub> O (mL)
CG1	1.4599	0	0	0.0045	0.0131	18.0
CG2	1.4453	0.0056	0.0115	0.0045	0.0131	18.0
CG3	1.4234	0.0125	0.0254	0.0045	0.0131	18.0
CG4	1.4088	0.0172	0.0349	0.0045	0.0131	18.0
CG5	1.3869	0.0258	0.0525	0.0045	0.0131	18.0
CG6	1.3650	0.0330	0.0670	0.0045	0.0131	18.0
CG7	1.3504	0.0412	0.0831	0.0045	0.0131	18.0
CG8	1.3139	0.0499	0.1015	0.0045	0.0131	18.0
CG9	1.3139	0.0521	0.1054	0.0045	0.0131	18.0
CG10	1.2409	0.0725	0.1479	0.0045	0.0131	18.0



**Figure 2** Apparatus scheme for the electric response measurements.

### SEM observation

Scanning electron microscope [SEM (JSM-6360LV, JEOL)] was used to observe the pore structure of the hydrogels (operating voltage was 15 kV). The gel samples were prepared by freeze-drying the swollen hydrogels. Before SEM-observation, the surfaces of the gels were coated with gold using a sputter-coater.

### Swelling ratio measurements

The equilibrium swelling ratio of P(AA-co-AAEM) gel was calculated according to the measured weight of the swollen gel ( $W_s$ ) and that of dried gel ( $W_d$ ),

$$\text{Swelling ratio (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

In this work, deionized water, NaCl aq. with various concentrations from 0.005 to 0.30 mol/L, and buffer solutions (prepared with NaOH,  $H_3BO_3$ ,  $H_3PO_4$ , and  $CH_3COOH$ ) with pH between 2.02 and 11.9, were used as the different medium respectively. The swollen process of gel continued for 3 days to ensure the swelling equilibrium. After the excessive water on the gel surface was carefully removed by filter paper, the swollen gel was weighted as  $W_s$ . The  $W_d$  value was determined by drying the swollen gel in an oven at 120°C for 24 h.

### Contraction of the gels in DC electric field

The apparatus used to determine the electric sensitivity of the gels is shown in Figure 2. Two parallel

carbon electrodes were fixed on two organic glass flats with a distance of 1.2 cm. The gels were cut into  $2 \times 1.2 \times 1.2 \text{ cm}^3$  trips and put between the two electrodes after being weighed. Then a 20 V of voltage was applied. Under the stimulus of the electric field, the gels began to contract. After a period of electric stimulus, the contracted gels were taken out and weighed. The deswelling ratio of the gels can be calculated by

$$\text{Deswelling ratio (\%)} = \frac{W_0 - W_t}{W_0} \times 100 \quad (2)$$

where,  $W_0$  and  $W_t$  is the mass of the gel before and after contraction, respectively.

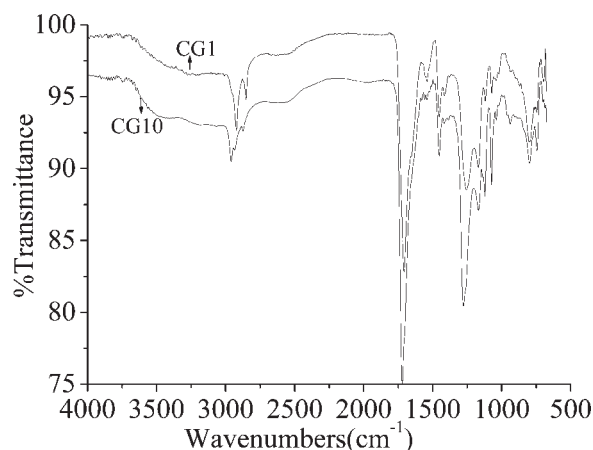
## RESULTS AND DISCUSSION

### FTIR spectra of the gels

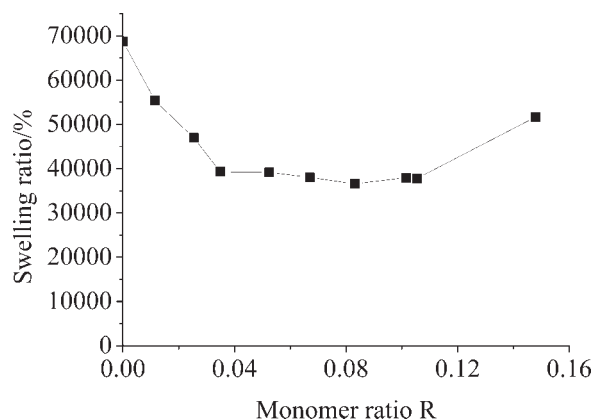
Figure 3 shows the FTIR spectra of CG1 (without AAEM) and CG10 (with AAEM :  $R = 0.1479$ ). The evidence for the existence of AAEM in gel is the absorbance peak of sample CG10 in the region of 2800–3000  $\text{cm}^{-1}$ , that is, CG10 has both the  $\nu_{C-H}$  of  $-CH_3$  (2962.17 and 2979.25  $\text{cm}^{-1}$ ) and  $-CH_2-$  (2846.74 and 2858.03  $\text{cm}^{-1}$ ), whereas, there is only the  $\nu_{C-H}$  of  $-CH_2-$  (2827.46 and 2854.18  $\text{cm}^{-1}$ ) in CG1, due to the absence of  $-CH_3$ . Besides, there is no vibration absorbance of  $\nu_{C=C}$  near 1650  $\text{cm}^{-1}$ , proving that the unreacted monomers has been completely removed from resulted gels. On the basis of the aforementioned analysis, we can conclude that CG1 is the polymer gel of AA, and CG10 is the copolymer gel of AA and AAEM.

### Swelling properties of the gel in deionized water

The monomers AA and AAEM in P(AA-co-AAEM) hydrogels exhibit markedly different structure and



**Figure 3** FTIR spectra of CG1 and CG10 ( $R = 0.1479$ ).



**Figure 4** Equilibrium swelling ratio of the P(AA-co-AAEM) gels in deionized water.

properties. The solubility of AAEM is much weaker than that of AA, which means AAEM is a relatively hydrophobic monomer. Moreover, there is a long group connected to the C=C in AAEM. Hence, gels with different properties and appearance can be obtained by tuning the monomer feed weighty ratio ( $R$ ). Our experimental results showed that when increasing the AAEM concentration, the gels changed from transparent to white, indicating the gel matrix changed from homogeneous to heterogeneous state. When the monomer feed weighty ratio ( $R$ ) increased to a specific value, the solubility of AAEM in water becomes saturated; moreover, the strength of the gels obtained proves to be very weak. Herein, to acquire the gel with qualified strength, we only changed the monomer feed weighty ratio ( $R$ ) between 0–0.1479, here  $W_{AAEM}$  and  $W_{AA}$  is the weight of AAEM and AA, respectively.

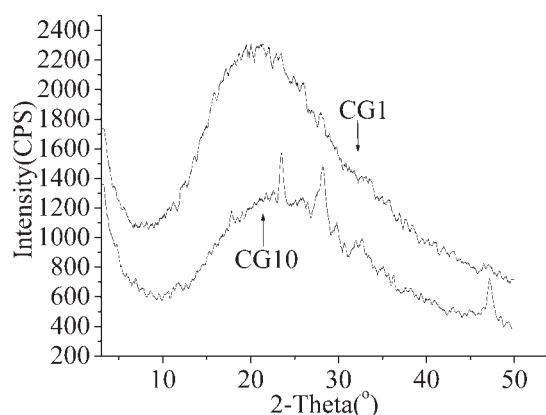
Figure 4 shows the equilibrium swelling ratio of P(AA-co-AAEM) gels in deionized water, which decrease first, and then increase with increasing the feed monomer weighty ratio ( $R$ ). The equilibrium swelling ratios almost keep constant in the range of  $R = 0.035$ – $0.11$ , probably attributing to the combinational effect of both hydrophilicity and side chains in AAEM units. On one side, it is obvious that the hydrophilicity of the P(AA-co-AAEM) gels will decrease with increase in the content of the hydrophobic AAEM segment. On the other hand, however, the AAEM brings P(AA-co-AAEM) gels the side chains, whose steric hindrance can increase the space in the gel network, which is helpful for the water to enter into the gel network. When the feed monomer weighty ratio ( $R$ ) is lower than 0.035, the hydrophobic effect of AAEM plays a dominant role, and hence proves negative for increasing the swelling ratio of gels. When  $R$  is between 0.11 and 0.1479, the effect of steric hindrance becomes stronger and consequently benefits for promoting the swelling ratio. At the same time, when  $R \geq 0.11$ ,

there were dendritic microdomains distributing evenly in the gel (observed with optical microscope) which was not found in the gels  $R < 0.11$ . With the increasing  $R$ , the dendritic microdomains became more obvious. This could be another important factor which influences the swelling properties of the gel markedly. Anyway, the mechanism of the change of equilibrium swelling ratio of P(AA-co-AAEM) gels with the  $R$  is very complicated.

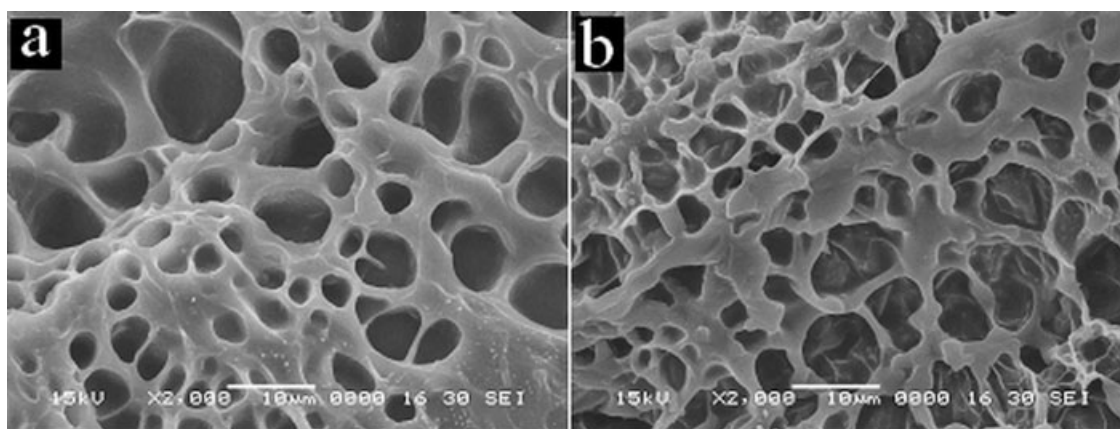
The XRD (Fig. 5) and SEM (Fig. 6) characterization can provide some information of the effect of AAEM on the structure of the gels. There are three peaks in the XRD curve of CG10 which represents the existence of crystallinity, while peak is absent in the XRD curve of CG1, proving that CG1 is amorphous. The SEM images shown in Figure 6 indicate that the shape and depth of the pores in CG10 and CG1 are different. Therefore, the presence of AAEM also changed the crystallinity and physical structure of the copolymer gel, which could induce the change of the macroscopic properties of the gel.

#### The equilibrium swelling ratio of the gels in NaCl solutions

Figure 7 shows the equilibrium swelling ratio of the gels in aqueous solutions of NaCl with various concentrations. Here, CG1–CG10 represent the gels with different monomer feed weighty ratio ( $R$ ) between 0 and 0.1479 in turn. Figure 7 illustrates that the equilibrium swelling ratios of all the gel samples decreased obviously with the increase of NaCl concentration. The swelling ratio decreased very quickly at first, then slows down, and finally became almost constant. The decreased swelling ratio of gels in NaCl solution is due to the shielding effect of  $Na^+$  ions, as well as the osmotic pressure. As a polyanion gel, the repulsive interaction between the carboxyl anions ( $COO^-$ ) in P(AA-co-AAEM) gel is a crucial driving force helpful for the gel swelling. But the counter ion ( $Na^+$ ), an easily movable small ion in



**Figure 5** The XRD patterns of two of the hydrogels.



**Figure 6** The SEM images of two of the hydrogels, CG1 (a) and CG10 (b).

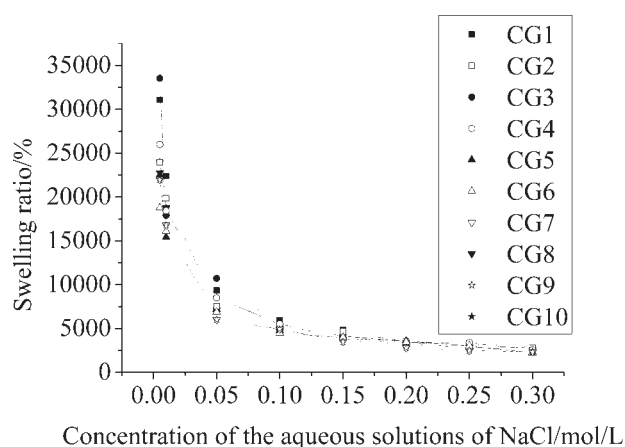
the network, impacts a shielding effect on the polyanions, which will certainly weaken the repulsion interaction between  $\text{COO}^-$  groups. Moreover, according to the Donnan equilibrium, an increase of the movable counter ions in a solution leads to a decrease in the osmotic pressure within the gel, and causes the gel to shrink consequently.

#### The equilibrium swelling ratio of the gels in pH buffer solutions

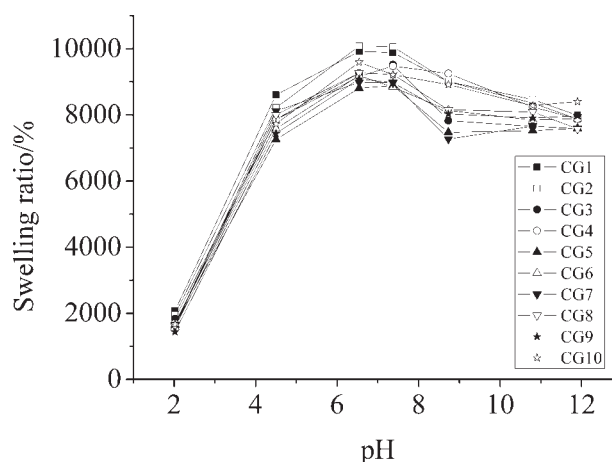
As a polyanionic gel, the ionization degree of carboxyl groups in P(AA-co-AAEM) gel is certainly affected by solution pH. Figure 8 illustrates the impact of pH value on the swelling ratio of gel samples with various  $R$ . It is obvious that the swelling ratio of each sample increases with increasing pH when the pH is lower than 6.5, but decreases at a higher pH beyond 7.5. All the gels exhibit the maximum swelling ratios at pH = 6.5–7.5. Generally, the swelling ratio of P(AA-co-AAEM) hydrogels

depends on the combinational effect of the ionic groups within the polymer, as well as on the affinity of the network for water. Under an extremely low pH, the hydrophilic group in the gel exists mainly in the form of  $-\text{COOH}$  groups. With increasing the surrounding pH,  $-\text{COOH}$  groups are gradually ionized to anionic  $-\text{COO}^-$ , which itself has a better hydrophilicity than  $-\text{COOH}$ , and also imposes a positive effect on the gel swelling due to the repulsive interaction. It should be pointed out that there is also  $\text{Na}^+$  ion in the pH buffer solution, which counteracts the swelling of the gels. The  $\text{Na}^+$  concentration in pH buffer solutions increases with the pH increase. This is somehow responsible for the decreased swelling ratio with pH higher than 7.5.

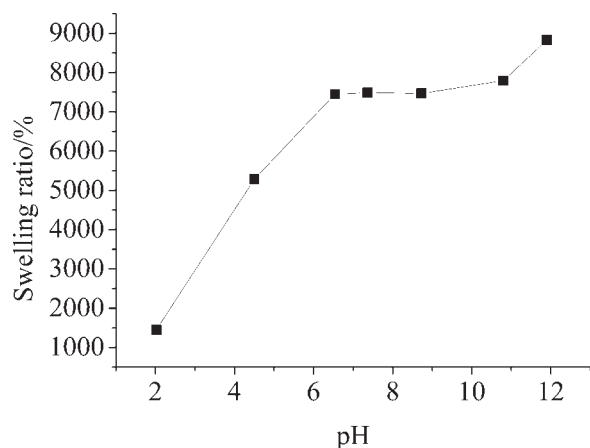
To better understand the influence of solution pH on swelling ratio of the gels, different pH buffer solutions with same  $\text{Na}^+$  concentration are used to determine the swelling ratio. The results are shown in Figure 9, which shows that swelling ratio under the same  $\text{Na}^+$  concentration increases with the



**Figure 7** Equilibrium swelling ratio of P(AA-co-AAEM) gels as a function of NaCl concentration.



**Figure 8** Equilibrium swelling ratio of P(AA-co-AAEM) gels in pH buffer solutions.



**Figure 9** Equilibrium swelling ratio of P(AA-co-AAEM) gels in pH buffer solutions with the same concentration of  $\text{Na}^+$ .

increase of pH, providing a supporting evidence for the abovementioned interpretation.

#### The contraction of P(AA-co-AAem) gels under the stimulus of DC electric field

Figure 10 describes the deswelling kinetics of the P(AA-co-AAEM) gels under DC electric field. It is apparent that the gels have an excellent sensitivity to the DC stimulus. They release water out from gel network at a high speed at first, and then at a relatively slower speed. Almost 40% of the water is released in the first 5 min, but no significant change occurs in the deswelling curves 30 min later. Figure 10 indicates that, the gel with  $R = 0.1479$  (sample CG10) has the best electric sensitivity, which has the fastest stimuli-responsive speed ( $\sim 74\%$  of deswelling ratio in 20 min) and the highest deswelling ratio (81.7%) in 60 min. Comparing with the sample CG1 without AAEM ( $R = 0$ ), CG10 exhibits a lower swelling ratio, but a better electric sensitivity, attributing to the effect of the side chains brought by AAEM segment.

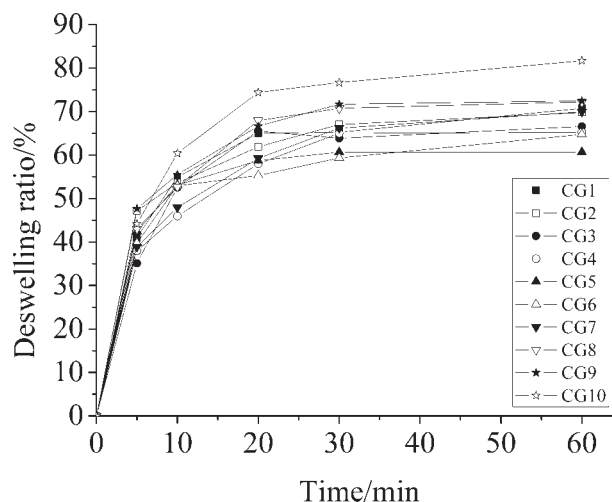
Comparing with the deswelling behavior introduced by some literatures, CG10 also exhibits the better electric-sensitivity including a higher deswelling ratio and a faster responsive speed. For example, Yang et al. synthesized the polysoap hydrogels and found that these gels lose about 60% of water in 60 min in a 20 V of DC electric field stimulus.<sup>23</sup> An IPN gel composed of sodium alginate and poly(diallyldimethylammonium chloride), synthesized by Kim et al. can lose 40% of its weight in 60 min.<sup>24</sup> Also studied by this group is the electrical sensitive behavior of a polyelectrolyte complex composed of chitosan/hyaluronic acid, which will deswell only 30% in 60 min under the stimulus of 15 V of DC electric field.<sup>25</sup> Compared with the aforementioned

literature results, the gels prepared in our lab had a better deswelling ratio under the DC stimulus.

#### Mechanism of the P(AA-co-AAem) gels under the DC field stimulus

For the possible mechanism of the gels contraction under electric stimulus, many authors brought forward different interpretations. Tanaka et al.<sup>4</sup> suggested that the electric-responsive deswelling of gels is induced by the establishment of a stress gradient in the gel. De Rossi et al.<sup>17</sup> considered that the electrically induced changes in the local pH at the electrodes were caused by the electrolysis of water as a mechanism of anisotropic gel deswelling. Electro-osmosis and electrophoresis of water, was also suggested as a mechanism of anisotropic gel deswelling.<sup>17,26,27</sup> Shiga and Kurauchi<sup>6</sup> proposed that the swelling deformation of a PAANA gel is qualitatively induced by a change in the osmotic pressure based upon the difference in mobile ion concentrations between the inside and the outside of a gel.

In this work, the electric sensitivity of the P(AA-co-AAEM) gels mainly derives from the change of the state of the  $-\text{COOH}$  and the attraction of the anode to the gel. When the gels are applied with DC electric field, the water near the electrodes is electrolyzed, which produces  $\text{H}^+$  and  $\text{OH}^-$  in the area around the anode and cathode respectively. Accordingly, the local pH value at anode will be lowered, and the negatively charged  $-\text{COO}^-$  groups in anionic polymer network are neutralized. As a result, the charge density and the electrostatic repulsion in gel networks, as well as the hydration extent of polymer, is significantly reduced, leading to the gel deswelled at the periphery of anode. The P(AA-co-



**Figure 10** The deswelling kinetics of the P(AA-co-AAEM) gels under DC electric field.

AAEM) gel was a polyanionic gel, so the anode had an attraction to the gel. The deswelled part of the gel near the anode, together with the attraction of the anode to the gel network made P(AA-co-AAEM) gel move forward the anode, which made the medium where the gels exist more acidic, then the deswelling of whole gel happened. It should be noted that AAEM segment itself in P(AAEM-co-AA) gel is not the cause of the electrical-responsive deswelling, which, however, significantly imposed an impact on the gel electric-sensitivity. The possible reason we deduce is that the introduction of AAEM monomer brings side chains into P(AAEM-co-AA) gel, which changes the structure and physical properties of polymer, increasing the internal space of gel network and decreasing the —COOH content and hydrophilicity of the resulted gel. The dendritic microdomains in the gel could be another important factor improving the electrosensitivity of the copolymer gel, which will be studied in the later work.

### CONCLUSIONS

Electrical sensitive P(AA-co-AAEM) gels were synthesized by free radical copolymerization. These gels had good swelling properties in water, but exhibited a decreased swelling ratio when increasing the NaCl concentration. Keeping the same Na<sup>+</sup> concentration in the pH buffer solutions, the gels swelling ratio increased with the increase of pH value. The P(AA-co-AAEM) gels also had excellent response to the stimulus from DC electric field. The gel obtained with  $R = W_{AAEM}/(W_{AAEM} + W_{AA})$  of 0.1479 (sample CG10) has the best electric sensitivity, probably due to the fact that the AAEM content in gel markedly changes the structure and physical properties of the gel. The results of this work supported the idea that the side chains not as long as the dangling chain introduced in the literatures also can improve the electrical sensitivity of the hydrogels. This kind of gel is promising to be used in the field of drug

delivery, membrane separation, artificial muscle, and biomimetic actuator.

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