

# PVA/PAA Thermo-Induced Hydrogel Fiber: Preparation and pH-Sensitive Behavior in Electrolyte Solution

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**ABSTRACT:** The preparation of thermo-induced hydrogel fibers composed of poly(vinyl alcohol) and poly(acrylic acid) is presented. The hydrogel fiber was prepared by extruding the spinning dope from *in situ* polymerization of acrylic acid in the presence of PVA into a coagulating bath of saturated ammonium sulfate aqueous solution. The network was formed by thermally heating the dried fibers under vacuum. The final hydrogel fibers exhibit pH-sensitive behavior and show a hysteresis loop in the pH range from 3.0 to 12.0. The pH value, at which the swelling elongation ratio of the fiber had a jump, shifted to a lower value with increasing PAA content within the network. Increasing the heating temperature and time for the fibers, decreased the swelling elongation ratio, and the jump point pH shifted to higher pH value. The oscillatory swelling/contracting behavior of the hydrogel fiber exhibited a good reversible pH-responsive property. Transmission Electron Microscopy (TEM) showed that PVA and PAA have good compatibility and give a relative independent interpenetrating network. Scanning Electron Microscopy (SEM) showed that in the surface of the fibers there were microholes and ditches due to some diffusion of PAA into the coagulating solution. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2423–2430, 2002

**Key words:** fibers; hydrogels; networks; stimuli-sensitive polymers; swelling

## INTRODUCTION

Polyelectrolyte gels change their conformation with the degree of dissociation, which is a function of quantities such as pH value, polarity of the solvent, ionic strength, and temperature of the external environment solution.<sup>1–7</sup> Katchalsky<sup>8</sup> created the first responsive polymer gel by crosslinking water-soluble polyelectrolyte to form gel, which swelled and shrank in response to the change in solution pH. He and his coworkers<sup>9</sup> also created machines powered by gels responsive to pH and ionic strength. The fundamental swelling behavior of the hydrogels has been investigated

extensively since Tanaka<sup>10</sup> suggested the swelling theory, with respect to the change in pH. Numerous attempts to control the swelling changes in hydrogels through external modulation by pH stimuli have also been reported.

One of the simplest pH-sensitive hydrogels can be prepared by crosslinking a blend of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA). There are several ways to prepare such a network. First,<sup>11–13</sup> it is possible to prepare porous gels by repetitive freezing and thawing cycles of a watery solution of PVA/PAA. It is assumed that an entanglement network with a high concentration of PVA and PAA chains in the physical junctions is formed. Second,<sup>3–4,6</sup> the pH-sensitive network of PVA and PAA can be formed by crosslinking polymerization of acrylic acid in the presence of PVA followed by crosslinking PVA. The interpenetrat-

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ing network is pH and temperature sensitive, depending on the molecular structure. The third method<sup>14–19</sup> is simply heating the PVA/PAA blend and placing the system into water, which leads also to a crosslinked hydrogel. It is assumed that the crosslinking of the completely miscible blend system occurs via dehydration between the—COOH<sup>−</sup> groups, esterification, and strong hydrogen bonding during the thermal treatment.<sup>14,15</sup>

Numerous studies and applications for PVA/PAA hydrogels using the above methods have been reported, such as artificial muscle,<sup>20,21</sup> sensor and chemomechanical systems,<sup>22,23</sup> drug delivery systems,<sup>24–27</sup> etc. However, from the viewpoint of the material preparation, the reported hydrogel systems were all prepared in molds or as films. There are few studies giving a systematic report on the PVA/PAA hydrogel in fibrous form prepared by the traditional wet-spinning technique. For this work we adopted three steps for a novel PVA/PAA hydrogel of fibrous form. The first step was to prepare the PVA/PAA blend solution as the spinning dope via *in situ* polymerization of AA monomer in the presence of PVA. The second step was to spin the dope into a PVA/PAA composite hydrogel fiber using the gelation property of the PVA in the presence of dense salt solution. The third one was thermally heating the above hydrogel fiber to reduce the solubility of the fiber such that it may function as a responsive hydrogel. The swelling behavior of the final hydrogel fibers in various pH environmental solutions was then investigated. Considering the double diffusion during the process of the wet-spinning the good compatibility of PVA and PAA may be somewhat impaired because of the difference in hydrophilic properties of PVA and PAA in the presence of ammonium sulfate. Thus, the internal texture and the surface morphology of PVA/PAA hydrogel fibers were also investigated using TEM and SEM imaging.

## EXPERIMENTAL

### Materials

PVA supplied by Jinsan Petrochemical Co. Ltd. (Shanghai, China) had a DP = 1750, with a degree of saponification of 99.5%. AA monomer obtained from Feida Chemical Co. Ltd. (Shanghai, China) was distilled under vacuum before use to remove the inhibitor. Ammonium persulfate

**Table I** Sample Preparation and Designation of PVA/PAA Blend

Sample	Weight Ratio of AA/PVA	Mass of AA (g)	Mass of APS (g)	Mass of TEMED (g)
No. 1	7:3	10.5	0.05	0.05
No. 2	6:4	9.0	0.045	0.045
No. 3	5:5	7.5	0.0375	0.0375
No. 4	4:6	6.0	0.0300	0.0300
No. 5	3:7	4.5	0.0225	0.0225

(APS) was of analysis grade from Shanghai Qianjin Chemical Plant. *N,N,N',N'*-Tetraethylmethylenediammine (TEMED), ammonium sulfate and all other chemicals were chemically pure from a local source. Deionized water was used for all experiments.

### Preparation of the PVA/PAA Blending Solution

A definite amount of PVA was dissolved in deionized water at 98°C for 2 h to prepare the preassigned weight concentration solution. AA aqueous solution containing the initiator APS and activator TEMED (each at 0.5% weights with respect to AA monomer) was mixed with PVA aqueous solution for 1 h under N<sub>2</sub>, bubbling to eliminate oxygen. Then the mixed blend in which weight percent of AA plus PVA to total components was always 15% was sealed in a flask. The polymerization was carried out at 50°C in a water bath for 5 h, resulting in a transparent PVA/PAA blending solution. The feed composition and the designation of the PVA/PAA blending solutions are listed in Table I. The real composition could be slightly different from the feed one because the samples were subsequently washed by water to remove residual AA monomer before further testing.

### Preparation of the PVA/PAA Hydrogel Fiber

The PVA/PAA blending solution was poured into a syringe and then was extruded into saturated ammonium sulfate aqueous solution bath under a suitable nitrogen pressure. The syringe was immersed in the coagulation bath at 25°C. The diameter of the needle hole was 1.0 mm. The extruded filament was immersed in the coagulation bath for 15 min, and then the gelling fibers were kept in air for the following procedure.

### Preparation of Thermo-Induced PVA/PAA Hydrogel Fibers

The above hydrogel fibers were dried first at 50°C for 24 h and then at 100°C in vacuum for 1 h.

Finally, after heat treatment at the preassigned temperature for the preassigned time, thermo-induced PVA/PAA hydrogel fibers were obtained.

### Measurement of Elongation/Contraction Behavior

The pH value of the environmental solution was monitored with a PHS-3C meter (Shanghai, China), and HCl and NaOH were added in turn to maintain the desired pH value. Also, the hydrogel fibers were periodically placed in fresh solution to avoid the buildup of an undesired ionic strength of the solution, which would affect the hydrogel fiber's swelling elongation ratio. Experiments were carried out entirely in a glovebox under nitrogen. The swelling elongation ratio of the PVA/PAA hydrogel fiber specimens were evaluated by the following expression:

$$\text{Swelling Elongation Ratio (\%)} = 100(L_s - L_d)/L_d$$

where  $L_d$  is the initial length of the sample at the beginning of swelling and  $L_s$  is the final length value when the specimen reached an equilibrium swelling state in the preassigned pH medium.

### Electron Microscopy

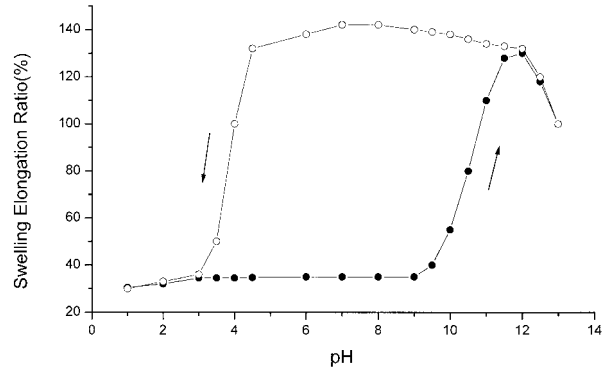
To examine the surface of the PVA/PAA hydrogel fibers, SEM was performed using a HITACHI-800 scanning electron microscope with the accelerating voltage at 35 kV and via the secondary electron image. The fiber samples for SEM were coated with gold using the sputtering technique.

The internal texture of the composite hydrogel fibers was observed using a HITACHI-800 transmission electron microscope with the accelerating voltage at 200 kV. TEM samples were prepared as follows: mixing the dried hydrogel fibers with epoxy resin, putting the mixture in gelatin capsules, and hardening them for 3 h at 90°C, the hardened resins were ultrathin sliced with a glass knife in a microtome, and the sliced samples for TEM scooped up on copper meshes and used.

## RESULTS AND DISCUSSION

### pH-Stimulated Elongation/Contraction Behavior

Figure 1 shows the equilibrium swelling elongation ratio of the thermo-induced hydrogel fiber as a function of pH value of the environmental solution. With increasing pH from 1.0 to 13.0, the fibers roughly maintained a constant length in



**Figure 1** Equilibrium swelling elongation ratio of thermo-induced PVA/PAA hydrogel fiber as a function of pH. The solid symbols represent the trace from acidic to basic medium and the open symbols represent the opposite trace. The PAA/PVA weight ratio was 7/3 and the fiber was heated at 150°C for 60 min.

the pH range from 1.0 to 10.0 and then abruptly elongated at about pH 10.0 and reached a maximum value at pH 12.0. When the pH value was greater than 12.0, the fibers contracted gradually. On the other hand, when decreasing pH from 13.0 to 1.0, the gel fiber elongated gradually in the pH range from 13.0 to 12.0 and roughly maintained a constant length from pH 12.0 to 4.0. At about pH 3.5 the swollen gel fibers contracted suddenly and then roughly maintained a constant length below pH 3.0. An hysteresis loop occurs between pH 3.0 and 12.0. The elongation/contraction behavior of the PVA/PAA hydrogel fiber can be divided into three pH regions: no hysteresis is found in region I (pH = 1.0 to 3.0) and region III (pH = 12.0 to 13.0), and a large hysteresis loop appears in region II (pH = 3.0 to 12.0).

### Hysteresis on Elongation/Contraction Behavior

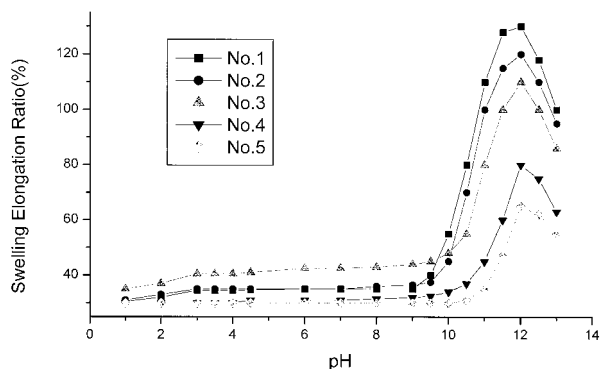
Umemoto<sup>28</sup> et al. reported that such hysteresis behavior was present in the PAN hydrogel fibers as an amphoteric gel but was not present in monopolar cationic or anionic gel. Tanaka et al.<sup>29</sup> presented a quantitative interpretation of Donnan theory for swelling in weakly charged gels as a function of ionic composition of the solvent. The balance of the osmotic pressure of free ions in the gel and environmental solution, the dissociation state of attached ionic groups in the gel, and the contractile force of the network play important roles in swelling of the gel. However, the hysteresis loop in the gel cannot be predicted in the above theory.

The  $pK_a$  of PAA is 4.28.<sup>30,31</sup> When the pH is less than the  $pK_a$ , the  $H^+$  ionic strength is very high. This effectively suppressed the ionization of the polycarboxylic groups. The gel is neutral, and the flexibility of the polymeric chain is rather low. Polycarboxylic groups within the network ionize and attract cations into the gel to replace the  $H^+$  ions as the pH of the environmental solution rises above its  $pK_a$ . This effectively raises the concentration of free ions inside the gel. Thus, the ionic swelling pressure will increase and so does the swelling. Additionally, the gel tends to expand to minimize the repulsion between the ionized polycarboxylic groups.

With increasing pH the polymeric network becomes more hydrophilic as the degree of ionization increases. However, as the pH increases still further, the ionic strength also increases. The osmotic pressure difference of free ions between the internal and external solution decreases and the gel tends to deswell. Also, the free cations at a higher concentration cause shielding on polycarboxylate groups, and this can cause the hydrogel to deswell. Thus, when the polycarboxylic groups were fully ionized, the effect of electrostatic repulsion between the carboxylate groups played a dominant role and the gel rapidly expanded at about pH 10.0. When the pH value exceeded 12.0, the effect of ionic strength surpassed the effect of the electrostatic repulsion between the polycarboxylate groups and played a dominant role. The gel deswells as shown in the curve of Figure 1. The swelling elongation ratio of the fiber decreases monotonously with further increasing of pH.

The swelling elongation ratio of the fiber has a jump at about pH 10.0, much higher than the  $pK_a$  of polycarboxylic groups. The authors think this is mainly due to the effect of network elasticity of the hydrogel limiting the swelling of the fiber. TEM (Fig. 6) shows that PVA and PAA are not completely compatible, and PVA has a continuous network. The changes of pH and ionic strength had little effect on the PVA network because of its acid and basic stability. This may be also the reason why the hysteresis loop of the PVA/PAA hydrogel fiber does not disappear, but it does disappear in the case of PAN hydrogel fiber via controlling ionic strength. Only when the swelling force of the PAA network surpasses the contracting force of the PVA network does the gel fiber swell abruptly.

During the pH decreasing process, when the pH changed from 13.0 to 12.0, the shielding effect



**Figure 2** Effects of blend composition and solution pH on the swelling elongation ratio of the PVA/PAA hydrogel fibers. Curves of No. 1 to No. 5 correspond to the fibers with weight ratio of AA/PVA weight ratio in polymerization preparation 7/3, 6/4, 5/5, 4/6, and 3/7, respectively. All fibers were heated at 150°C for 60 min.

on the completely ionized polycarboxylate groups, caused by high ionic strength, played a dominant role in the swelling of the gel fiber. In the pH range from 3.0 to 1.0, the polycarboxylic groups were nonionized, and the high  $H^+$  concentration also decreased the osmotic pressure of the gel. In the pH range from 12.0 to 3.5, the electrostatic repulsion between the polycarboxylate groups within the network became dominant because of the decreasing ionic strength, and the fiber's swelling exhibited hysteretic behavior. The hydrogel fiber's swelling elongation ratio reached a maximum value limited by network elasticity at its maximum ionized state. When the pH was lower than the  $pK_a$ , the electrostatic repulsion between the polyolycarboxylate groups within the network disappeared and then the network collapsed. There was a contraction jump in the curve at about pH 3.5. Thus, there occurred a great hysteresis loop in the pH range from 3.0 to 12.0.

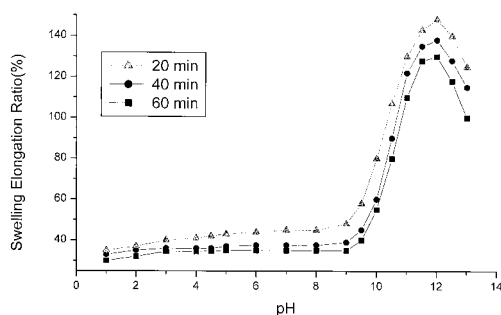
#### Effect of PAA Content on pH-Sensitive Behavior

Figure 2 shows the dependence of the swelling elongation ratio of thermo-induced hydrogel fibers with different PAA contents during the increasing pH of environmental solution. Each curve shows a jump pH value in the range of 10 to 12; the higher the PAA content of the hydrogel, the lower the jump point pH value. Above the jump point pH value the swelling elongation ratio of the hydrogel fibers increases with the increase of PAA content of the gel. When the pH was higher than the  $pK_a$  of the polycarboxylic groups, electrostatic repulsion between the ionized poly-

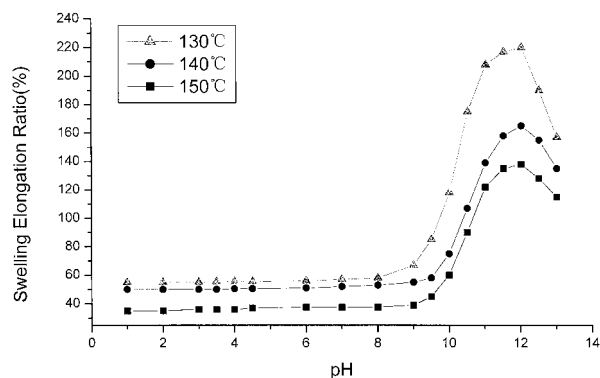
carboxylic groups occurred; the higher the PAA content, the stronger the electrostatic repulsion. For the hydrogel fibers of higher PAA contents, the electrostatic repulsion can overcome the elasticity force of the networks at comparatively low pH values and change the conformation of the network. However, at pH lower than the jump point pH values, the swelling elongation ratio of the fibers exhibited nonmonotonous behavior with the increase of the PAA contents of the gel. This may be caused by intermolecular isobutyric–anhydride crosslinkages, which raise the elasticity of the network, and intramolecular glutaric–anhydrides, which decrease the hydrophilic property of the network. The higher the PAA content of the gel the more pronounced are the above two kinds of reactions,<sup>15,16</sup> both of which result in decreasing swelling elongation of the hydrogel fibers in water.

#### Effect of Heating Time on pH-Sensitive Behavior

Figure 3 shows the dependence of the swelling elongation ratio of the thermo-induced PVA/PAA hydrogel fibers at various heating times with increasing pH of the environmental solution. Increasing the heating time for the fibers, the swelling elongation ratio decreased and the jump point pH value shifted to higher pH values. This is the result of the following factors: esterification reaction between the —OH and —COOH groups of the polymeric chains, intermolecular isobutyric–anhydrides between the —COOH groups of the PAA polymeric chains, and intramolecular glutaric–anhydrides of adjacent —COOH groups along the PAA polymeric chains. The longer the



**Figure 3** Effects of heating time at 150°C and solution pH on the swelling elongation ratio of the PVA/PAA hydrogel fibers. Weight ratio of AA/PVA is 7/3 in polymerization preparation. Curves correspond to the hydrogel fibers heated for 60, 40, and 20 min, respectively.



**Figure 4** Effects of heating temperatures for 40 min and environmental solution pH on the swelling elongation ratio of the PVA/PAA hydrogel fibers. Weight ratio of AA/PVA is 7/3 in polymerization preparation. Curves correspond to the hydrogel fibers heated at temperatures of 130, 140, and 150°C, respectively.

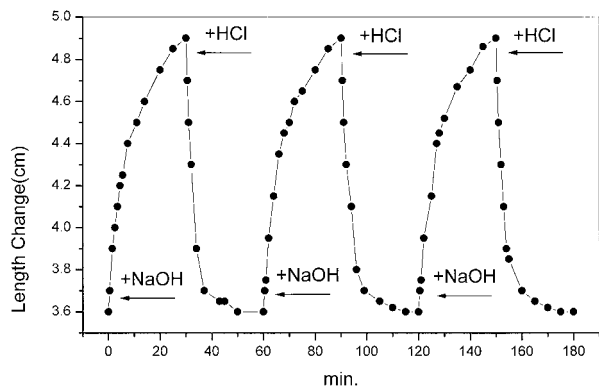
heating time, the more extensive are the above chemical reactions.

#### Effect of Heating Temperature on pH-Sensitive Behavior

Figure 4 shows the dependence of the swelling elongation ratio of the thermo-induced PVA/PAA hydrogel fibers upon the various heating temperatures during to the increasing pH change of the environmental solution. Compared with Figure 2 the curves show similar shapes and show typical time–temperature equivalent relationships. As the heating temperature increased, the swelling elongation ratio of the fibers decreased and the jump point pH shifted to a higher pH value. This may be caused by the above-mentioned reactions such as the crosslinking and anhydride formation, which increased the network elasticity and decreased the hydrophilic property of the fibers, respectively.

#### Oscillatory Swelling/Shrinking Behavior

The PVA/PAA hydrogel fiber elongated (swelled) in basic and contracted in acidic solutions. Figure 5 shows the time dependence of the change in length of the PVA/PAA hydrogel fiber during the pH change of the environmental solution. The elongating process (from pH 1.0 going immediately to 13.0) took place much slower than did the contracting process (from pH = 13.0 immediately to 1.0). From the beginning of elongating/contracting until the equilibrium length of the fiber



**Figure 5** Dynamic change in length of the PVA/PAA hydrogel fiber heated at 150°C for 60 min (sample No. 3). The solution was exchanged from  $S_1$  to  $S_2$  (elongation) and  $S_2$  to  $S_1$  (contraction). Here,  $S_1$  is the acidic solution (pH = 1.0) and  $S_2$  is the basic solution (pH = 13.0).

was reached, the time difference between the both processes differed by 10 min in their rates.

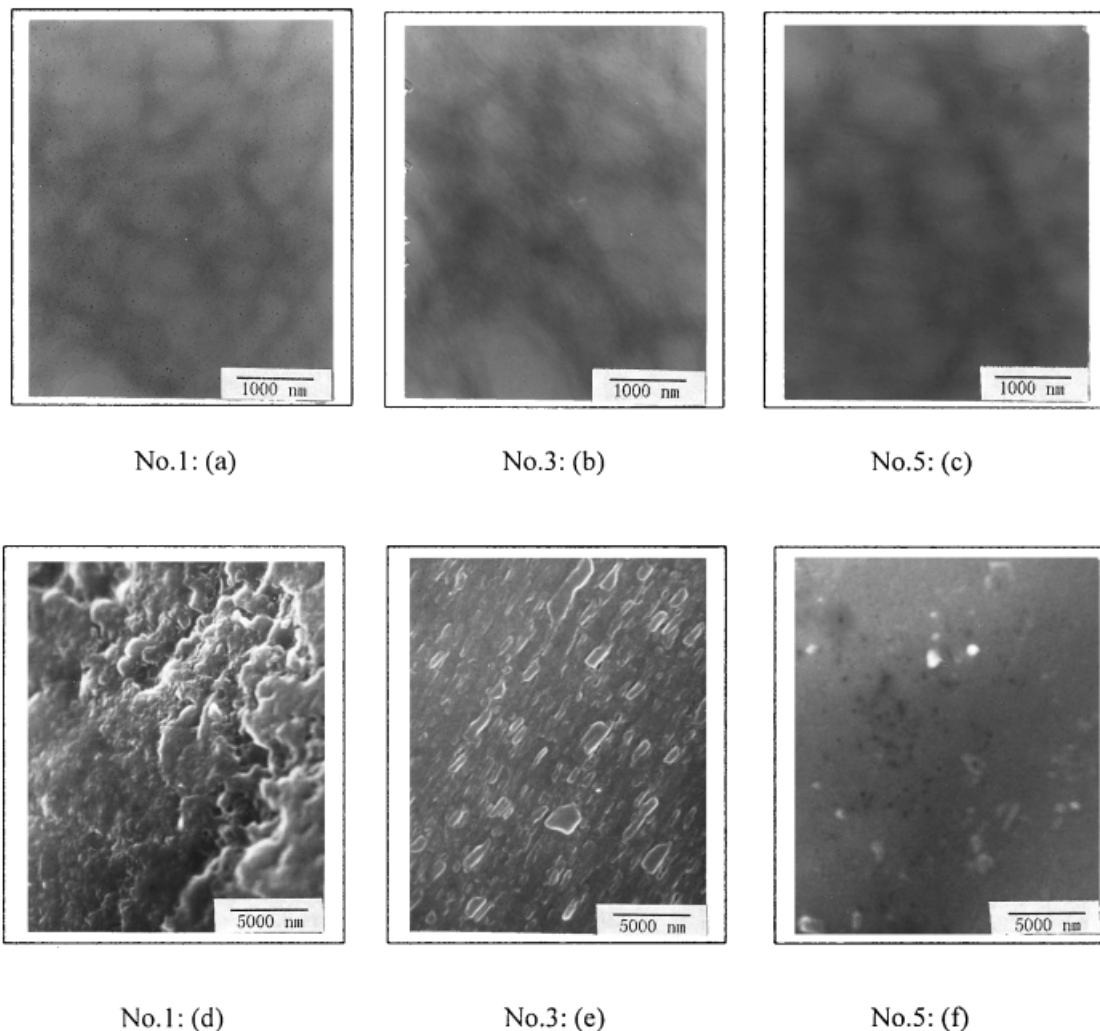
During the contracting process the  $H^+$  ions diffuse into the hydrogel and neutralize the negative charged polycarboxylate groups. A neutral layer of the polymer that contracted was formed around the inner part of the polymer, which was still ionized and swollen. When diffusing into the gel network,  $H^+$  can be rapidly captured by the  $RCOO^-$  groups. A moving front separating a non-ionic shell from an ionized core will develop. Because the shell was nonionic,  $H^+$  can readily diffuse into the shell while  $Na^+$  diffuses out. On the other hand, during the swelling process the hydrogel was initially in its nonionic  $-ROOH$  form, and was then converted to the ionized state form upon immersion in NaOH solution.  $OH^-$  initially diffused easily into the gel. However, reaction with the polycarboxylic groups soon ionized the hydrogel, and an ionized shell was formed around the nonionized core. A Donnan potential quickly built up, inhibiting the  $OH^-$  from further penetrating the shell, which was now also anionic.<sup>32</sup> Thus, the kinetics of the ion exchange dominated the kinetics of the volume change even though the ion exchange reactions are usually fast. According to Figure 5, both the extent and the rate of elongating/contracting of the hydrogel fiber were well reproducible. Even when the hydrogel was elongated/contracted repeatedly, it returned to almost the same degree of elongation/contraction with which it began. In fact, the fiber's diameter can be readily adjusted by changing the needle hole and other spinning conditions, and the smaller the

fiber's diameter, the faster the responsive rate to environmental solution.<sup>32</sup> Thus, this hydrogel fiber with pH-sensitive properties shows enormous potential for application in many fields such as artificial muscle, sensors, chemomechanical system, etc.

### TEM and SEM Observation

To examine the compatibility between the two polymers we used TEM and SEM to observe the internal texture and the surface morphology of the PVA/PAA hydrogel fibers, which were wet-spun into a coagulating bath of ammonium sulfate saturated aqueous solution. Figure 6 shows the TEM images of the fibers with different PAA contents. The matrix is the PVA phase and the disperse phase is PAA. There are no distinct interfaces between the two polymers, showing that the two polymers have good compatibility. However, the domains of the two polymers were much larger than those reported in other work,<sup>16–18</sup> which studied the compatibility between the two polymers by solid<sup>13</sup> C-NMR. It seems that during the process of extruding the dope into a coagulating bath phase separation occurs. As the increase of the PAA content, the interfaces become more ambiguous and the domains almost cannot be distinguished in the image of the fiber with AA/PVA weight ratio 7/3. This shows that, with the increase of the PAA content, the compatibility becomes better. From the images it can be seen that the interpenetrating network can be formed in the fiber with higher PAA/PVA weight ratio 7/3. However, for the fiber with lower PAA/PVA weight ratio there are two obvious phases in which PVA is the continuous phase. In this article, PVA is always the continuous phase and the network structure.

The domains in the images shown are larger than those of most literature using NMR.<sup>16–18</sup> This may be caused by the double diffusion in the wet-spinning process. PVA is solidified readily by saturated ammonium sulfate aqueous solution. The PVA macromolecules assemble to form large domains. PAA in the surface layer of the dope can diffuse into the coagulating solvent, and PAA inside the gel may be bounded by the continuous PVA network to form a dispersed phase. With increasing PVA content within the gel the domains of both the continuous phase and the dispersed become large, whereas at lower PVA content the domains of the two phases become small and the interfaces become ambiguous and exhibit an interpenetrating network. Figure 6 shows the



**Figure 6** TEM (a,b,c) and SEM (d,e,f) images of the PVA/PAA hydrogel fibers heated at 150°C for 60 min. Sample numbers No. 1, No. 3, and No. 5 represent the weight ratio of PAA/PVA in polymerization preparation 7/3, 5/5, and 3/7, respectively.

SEM photographs of fibers with different PAA contents. With the increase of PAA content the fiber's surface becomes rough. Conversely for higher PVA content the fiber's surface becomes smooth. For fibers with higher PAA contents the surfaces have large amounts of microholes and ditches. These may be the result of the above description. Why the hysteresis depicted in this paper did not disappear under higher ionic strength may be related to the relative mutually independent interpenetrating network structure.

## CONCLUSIONS

The thermo-induced PVA/PAA hydrogel fibers were prepared by a three-step method. In the first

step, the spinning dope of PVA/PAA blend solution was prepared by *in situ* polymerization of AA in presence of PVA aqueous solution. Second, the hydrogel fibers were prepared by extruding the dope into saturated ammonium sulfate aqueous solution as the coagulating bath. In the third step, the solidified and dried fibers were further crosslinked by thermally heating under vacuum.

The hydrogel fibers exhibited pH-sensitive properties under electrolyte solution. During the cycle of pH increasing and decreasing of the environmental solution the swelling elongation ratio of the hydrogel fiber exhibited a large hysteresis loop in the pH region 3.0 to 12.0 and no hysteresis loop appeared in the pH region 1.0 to 3.0 and 12.0 to 13.0.

The swelling elongation ratio of the hydrogel fiber had a jump corresponding to a specific pH value. At pH values lower than the pH jump point the elongation ratio of the fibers had no monotonous relation to the PAA contents of the hydrogel fibers. Above the pH jump point, the swelling elongation ratio of the hydrogel fibers increased abruptly, and showed a maximum value at pH 12.0 and then decreased gradually. The higher the PAA content of the gel, the lower the pH jump point value and the greater was the swelling elongation ratio of the fibers above the pH jump point. With increasing heating time, the swelling elongation ratio of the hydrogel fibers decreased and the pH jump point shifted to higher values. The temperature had a similar effect.

The hydrogel fibers exhibited good reversible oscillatory swelling/contracting behavior. By controlling the spinning conditions the indicated hydrogel fibers can be prepared easily and this promises significant applications.

TEM and SEM images showed that the fibers were heterogeneous PVA/PAA blend polymers. The ambiguous interface showed that the two polymers have good compatibility. PVA always existed as a continuous network, and the PAA existed as a dispersed phase. With the increase of PAA content within the gel the PAA phase became continuous and the domain size became smaller showing an interpenetrating network for the fiber with a higher PAA/PVA weight ratio such as 7/3. In the process of wet-spinning phase separation appeared. PAA in the surface layer of the filaments can diffuse into the coagulating solution. The surface of the hydrogel fibers became smoother with increasing PVA content within the gel.

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