Preparation and pH-Sensitivity of Polyacrylonitrile (PAN) Based Porous Hollow Gel Fibers

Xinyuan Shen, Yali Ji, Jue Wang

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 200051, People's Republic of China

ABSTRACT: Polyacrylonitrile based porous hollow gel fibers were prepared from PAN hollow fibers by oxidation and subsequent alkaline treatment. Fourier-transform infrared (FTIR), X-ray diffraction, and scanning electron microscope (SEM) analyses showed that the PAN porous hollow gel fiber was a kind of amphoteric fiber due to the combination of cationic groups of pyridyl and anionic groups of carboxyl; after gelation the hollow channel and finger-like pores on the fiber walls were conserved. The effects of cyclization reaction degree, alkaline solution concentration, and alkaline treatment time on the mechanical properties or pH-sensitive behavior of the porous hollow gel fibers were investigated. The elongation/contraction behavior was studied in detail. It was found that the gel fiber exhibited a large swelling in an alkaline solution and contracting in an acid solution; the swelling change in length was above 90%; the responsive time of elongation/contraction was less than 20 s; the maximum contraction force was 20 N/cm^2; and pH-sensitivity was reversible. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 313–320, 2008

Key words: hollow gel fibers; hydrogels; polyacrylonitrile; porous; stimuli-sensitive polymer

INTRODUCTION

pH-sensitive hydrogels have attracted much attention due to their promising applications in drug delivery devices, separation processes, sensors and many other fields.[1-3] As early as 1950, Katchalsky and coworkers[4] had created the first pH responsive polymer gel, poly(acrylic acid) (PAA), which swelled and shrank in response to the change of pH in the solutions, and directly transformed chemical energy into mechanical work in a reversible manner. Such smart hydrogels have been extensively investigated since the swelling theory was established by Tanaka et al.[5] Previous studies on hydrogels were mainly focused on three-dimensional bulk samples, of which the responsive rate to external stimulus was not rapid enough in that the time required for a gel to shrink or expand was proportional to the square of its linear dimension.[6] Such low responsive rate of

bulk samples will restrict their applications in some fields, such as artificial muscles. To overcome this disadvantage, some efforts were made continually. Suzuki[7] improved responsive rate by constructing the micropore structure in the PVA-PAA hydrogel. Umemoto et al.[6] used PAN fibers to prepare pH-responsive gel fibers by preoxidation and subsequent saponification. Compared with bulk samples, the responsive rate of fibrous samples was highly improved. If taking into consideration hollow-typed fibers, one may choose to direct the flow of stimulus medium through the hollow channel and achieve contraction or elongation with these fibers by varying the stimulus medium, which may be adaptively applied in artificial muscles. It is analogous to the neural system sending out signals to control muscular motion. Thus, to design such porous hollow gel fibers is quite significant.

In this article, we used PAN hollow fibers as protofilament to prepare porous hollow gel fibers by oxidation treatment and subsequent saponification reaction. With the combination of hollow channel and innumerous micropores on the fiber walls, the gel fibers not only possessed on-off switch property like pH-responsive polymers, but also possessed permeaselectivity like common polymeric membranes. With such unique properties they could be potentially used either as drug delivery carrier or as switch membrane. Here, we discussed the preparation technology of PAN porous hollow gel fibers and its pH-sensitive behavior.

EXPERIMENTAL

Preparation and characterization

The PAN hollow fibers used as precursor were prepared according to our previous work.[8] The PAN porous hollow gel fiber was prepared as follows: the PAN hollow fiber with a constant length was mounted on an aluminum frame, then placed in a thermostat drier for annealing with an operation step as such: below 190°C, for each 10°C rise in temperature, kept the constant temperature for 10 min; over 190°C, for each 10°C rise in temperature, kept the constant temperature for 20 min. Subsequently, the preoxide fiber was immersed in NaOH solutions with different concentrations, and boiled for a series of fixed times, then well washed with distilled water, and finally dried in vacuum.

The chemical structure was studied by FTIR spectroscopy (Perkin–Elmer,) with KBr pellets. The morphologies of the PAN porous hollow gel fibers were examined by SEM observation (Can-Scan-4). The samples were cryogenically fractured in liquid nitrogen and then coated with gold. The wide angle X-ray diffraction (WAXD) measurement was performed on a Rigaku D-Max-B diffractometer to study the crystallization structure of PAN porous hollow gel fibers.

Measurement of mechanical property

Stress–strain measurements of the PAN porous hollow gel fibers were performed on an AGS-500ND tensile testing machine at a testing length of 1 cm.

Measurement of elongation/contraction behavior

A series of aqueous solutions with different pH values were obtained by adjusting NaOH and HCl contents. pH value was monitored by a pHS-25 m. The fibers were placed in an aqueous solution for a fixed time until the change in length reached a maximum, which was regarded as an equilibrium length le. Thus, the change in length is calculated as follows: $\Delta le = le - l_0$, where l_0 is the initial length. According to the relationship of Δle and pH value, the pH-sensitive curve of PAN porous hollow gel fibers was obtained.

Measurement of contraction force

The dynamical properties of generating contraction force of PAN hollow gel fibers in isometric state were studied through measurements of the stress change when the fibers were immersed in 1M HCl solution from 1M NaOH.[6]
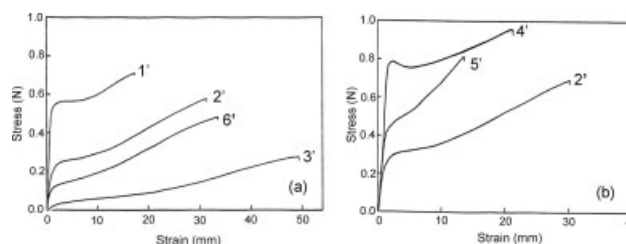
Figure 1 Stress–strain curves of the PAN porous hollow gel fibers. 1'- oxidation temperature = 220°C, oxidation time = 30 min, alkaline concentration = 0.5M, alkaline treatment time = 10 min; 2'- oxidation temperature = 220°C, oxidation time = 30 min, alkaline concentration = 0.5M, alkaline treatment time = 20 min; 3'- oxidation temperature = 220°C, oxidation time = 30 min, alkaline concentration = 0.5M, alkaline treatment time = 30 min; 4'-oxidation temperature = 200°C, oxidation time = 30 min, alkaline concentration = 0.5M, alkaline treatment time = 20 min; 5'- oxidation temperature = 230°C, oxidation time = 30 min, alkaline concentration = 0.5M, alkaline treatment time = 20 min; 6'- oxidation temperature = 220°C, oxidation time = 30 min, alkaline concentration = 0.7M, alkaline treatment time = 20 min.

Measurement of pH responsive rate

The fibers were immersed in a 1M NaOH aqueous solution for 10 s, and immediately put into a 1M HCl aqueous solution. The ratio of length change is calculated as follows: $\varepsilon = (l_t - l_0)/l_0$, where l_t is the length at time t.

RESULTS AND DISCUSSION

Effects of preparation conditions on mechanical properties

In our previous work, it was found that the alkaline-resistance of PAN hollow fibers was improved after oxidation treatment. However, hydrolytic reaction still occurred and made fibers gelate due to the existence of free —CN groups that uncyclized during oxidation reaction. Thus, to get high quality of PAN porous hollow gel fibers, it is a key to choose suitable preparation condition.

Figure 1 shows the stress–strain curves of the PAN porous hollow gel fibers affected by oxidation temperature, alkaline treatment concentration and alkaline treatment time. When the oxidation temperature was as low as 200°C, there coexisted a yield point and an obvious platform in the stress–strain curve, which was a typical C-type stress–strain curve. Furthermore, its initial modulus and fracture strength were high, indicating the porous hollow gel fiber prepared under such a technological condition belonged to a kind of hard-tough material. When the oxidation temperature increased to 220°C, some changes had been found in the stress–strain curve:
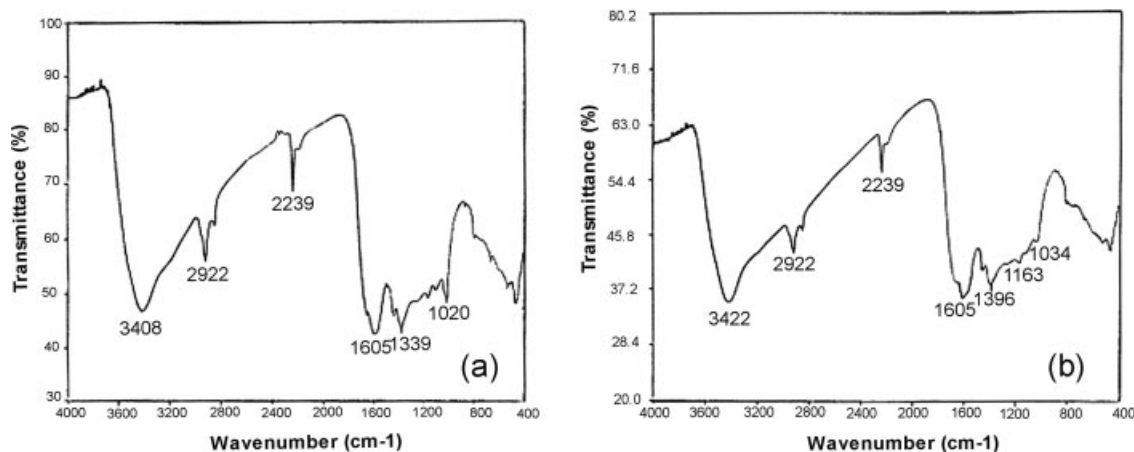
Figure 2 The FTIR spectra of PAN porous hollow gel fibers. Oxidation temperature = 220°C, oxidation time = 30 min, alkaline concentration = 0.5M. (a) Alkaline treatment time = 20 min; (b) alkaline treatment time = 30 min.

the yield was not obvious, and both the fracture strength and initial modulus decreased, while, the rapture elongation increased. All these phenomena represented the characteristic of soft-tough materials. It is considered that there are two factors affecting the mechanical property of PAN porous hollow gel fibers: one is an attractive power between polar cyano-groups, and the other is crosslinking density of cyano-groups and pyridyl-groups. When the crosslinking density is low, the former is the main factor affecting mechanical property; when the crosslinking density is high, the latter is the main factor affecting mechanical property. With the increase of oxidation temperature, the cyclization degree of PAN hollow fibers increased, thus resulting in a high crosslinking density of cyano-groups and pyridyl-groups and few free cyano-groups existence. After alkaline treatment, the cohesive energy among macromolecular chains decreased, and the force needed to overcome cohesive energy decreased relevantly, leading to the decrease of the fracture strength and increase of the rapture elongation. However, when the oxidation temperature increased to 230°C, the gel fibers exhibited a high fracture strength, a high initial modulus, and a low rapture elongation, which was the characteristic of hard-strong materials. Such a phenomenon was due to the limitation of chain flexibility from the network structure formed from the high crosslinking density of cyano-groups and pyridyl-groups.

Figure 1 also shows that with the increase of alkaline treatment time (see sample 1′, 2′ and 3′), the fracture strength decreases and the rapture elongation intensely increases, thus resulting in the increase of the fracture work and so the toughness. Such results also originated from the decrease of the crosslinking density of cyano-groups and pyridyl-groups with the increase of alkaline treatment time.

When the alkaline treatment time was up to 30 min, a violent decrease of fracture strength was observed (see sample 3′). That is because a trapezoidal frame was formed during oxidation, and the macromolecular chains would be broken only in the case that the two bonds in one trapezoidal frame were broken simultaneously. The longer alkaline treatment time could make more macromolecular chains broken, causing the relative movement of molecules more easily at the stretching state, and finally, irreversible viscose flow occurred. Thus the sample 3′ had a high rapture elongation. Furthermore, with the increase of alkaline solution concentration, the gel fibers displayed a good toughness, owing to the decreased crosslinking density of cyano-groups and pyridyl-groups at a high alkaline solution concentration.

The structure of PAN porous hollow gel fibers

Fanta et al.[9] reported that cyano-groups in the PAN fibers could be transformed into carboxyl-groups during alkaline treatment. It was found that the FTIR spectra of PAN porous hollow gel fibers were different from that of PAN oxidation fibers. The intensity of characteristic absorbing band of —CN at 2239 cm^{-1} in the gel fibers was further weakened, and C=N band at 1600 cm^{-1} still conserved, in the meanwhile, two new bands appeared at 1020 and 3408 cm^{-1}, representing —CO and —OH characteristic bands, respectively. All above indicated that the pyridyl-group was conserved and a new group of carboxyl was formed because of the hydrolysis of the residue cyano-groups during alkaline treatment. Thus, the PAN porous hollow gel fiber we prepared was a kind of amphoteric gel fiber, in which the cationic groups of pyridyl and anionic groups of carboxyl coexisted. Figure 2(b) shows that the intensity
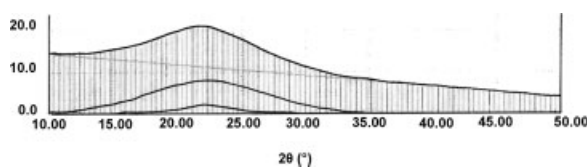
Figure 3 WAXD spectra of PAN porous hollow gel fibers. Oxidation temperature = 220°C, oxidation time = 30 min, alkaline concentration = 0.5*M*, alkaline treatment time = 20 min.

of —CN band becomes weak and the intensity of —CO and —OH bands becomes strong with the increase of alkaline treatment time, which further confirms that the hydrolysis degree of free cyano-groups increases with the increase of alkaline treatment time, thus causing the crosslinking density of cyano-groups and pyridyl-groups decrease accordingly.

Figure 3 shows no diffraction peaks at $2\theta = 17°$, $28°$, and $25°$ appear, indicating the crystal structure of the PAN porous hollow gel fibers is damaged, and a planar network structure formed from the crosslinking of cyano-groups and pyridyl-groups is decomposed due to the hydrolysis of the residual free cyano-groups. From the above analysis, it can be concluded the structural transformation during alkaline treatment as depicted in Figure 4.

Figure 5 displays the SEM observation of the PAN fiber. Compared with the PAN porous hollow oxidation fibers [see Fig. 5(1)], the morphology of the PAN porous hollow gel fibers [see Fig. 5(2)] changed remarkably. Innumerable irregular grooves appeared on the surface of the fiber due to the etching of alkaline solution. And both the aperture size of the longitudinal channel in the center of the fiber and the aperture size of the horizontal finger-like pores reduced apparently as a result of the swelling of the oxidation fiber during alkaline treatment. However, the reserved channel aperture could still realize the changes of species, composition and concentration of stimulant medium. Furthermore, the micropores on the fiber walls could be used as switch membranes.

### pH-sensitive behavior of the PAN porous hollow gel fibers

pH-stimulated elongation/contraction behavior

Figure 6 shows the equilibrium swelling elongation ratio of the PAN porous hollow gel fibers as a function of pH value of environmental solutions. With the increase of pH from 1.0 to 14.0, the fiber roughly maintained a constant length in the pH range from 1.0 to 12.0, then abruptly elongated at pH = 12.0, and finally reached a maximum value at pH = 13.0. When the pH value was greater than 13.0, the fiber

contracted gradually. However, when the pH was decreased from 14.0 to 1.0, the gel fibers elongated gradually in the pH range from 14.0 to 11.0, and roughly maintained a constant length from pH 11.0 to 2.0. As the pH value was lower than 2.0, the fiber contracted suddenly. The elongation/contraction behavior of the PAN porous hollow gel fiber could be divided into three pH regions. In region 1 (pH < 2), the specimen was in a shrinking state, and no hysteresis was found. Increasing the environmental pH, i.e., decreasing HCl concentration or ionic strength, widened the differential concentration of H^+ ions between inside and outside gel fibers, thus resulting in a little increase of osmotic pressure and swelling ratio. In this region, the electrostatic repulsion nearly made no contribution to swelling due to the low degree of dissociation. In region 2 (pH = 2.0 to 12.0), a large hysteresis appeared. With increasing pH to 12, Na^+ ions in the environment diffused into gel fibers and exchanged with H^+ ions, thus rapidly increasing the dissociation degree of networks, and causing the macromolecular chains negatively charged. Consequently, the electrostatic repulsion among COO^- groups was enhanced. On the other hand, when the environmental pH decreased to two inversely, H^+ ions in the environment exchanged with Na^+ ions inside gel fibers and neutralized the electronegativity of macromolecular chains, resulting in the decrease of dissociation degree, the attenuation of electrostatic repulsion and so the shrinkage of macromolecular chain. The occurrence of hysteresis indicated the PAN porous hollow gel fibers were a kind of amphoteric gel fiber.[6] In region 3 (pH > 12), the very high ionic strength made the electro-
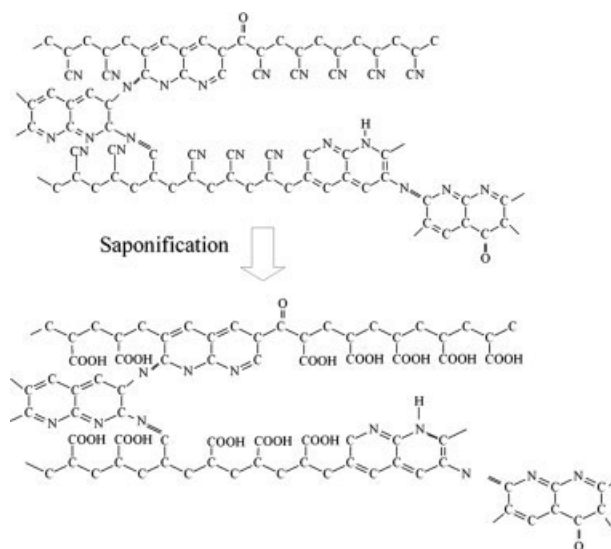
Figure 4 Schematic of structural transformation during alkaline treatment.
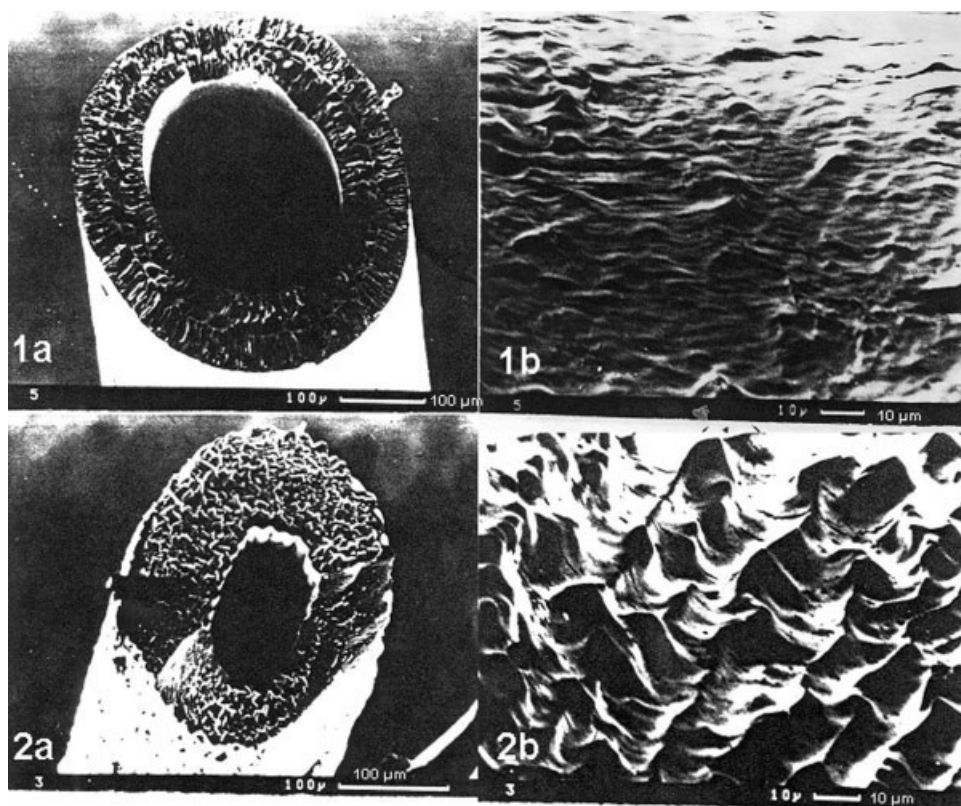
Figure 5 SEM images of the PAN hollow oxidation fiber (1) and the PAN porous hollow gel fibrous membranes (2). Oxidation temperature = 220°C, oxidation time = 30 min, alkaline concentration = 0.5*M*, alkaline treatment time = 20 min. (a) Cross section; (b) surface.

static repulsion reduce. Besides, the conformation entropy was decreased due to the stretch of molecular chains between the crosslinking points, which caused the network attempt to shrink. At this time, the dissociation degree of networks drove to 1, and the osmotic pressure of free ions inside and outside gel fibers also drove to 0. The specimen exhibited a little shrinkage.

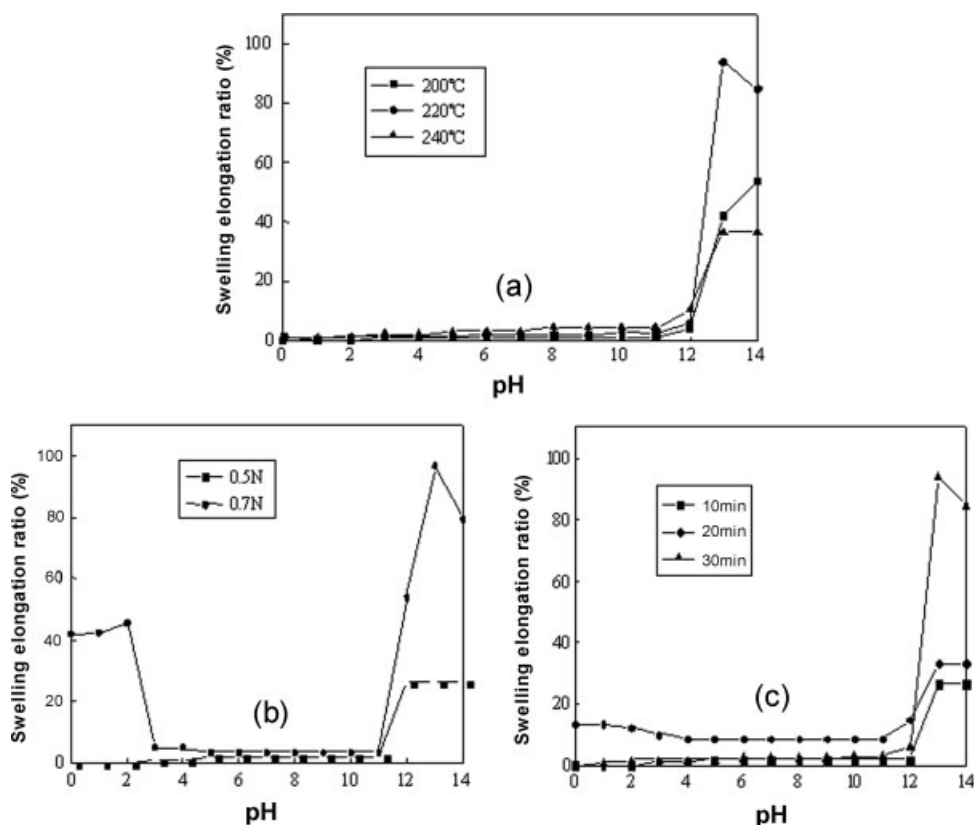### Effects of preparation condition on pH-sensitive behavior

Figure 7(a) depicts the effects of oxidation treatment temperature on pH-sensitive behavior of the PAN porous hollow gel fibers. At the oxidation temperature of 220°C, the PAN porous hollow gel fibers obtained had a high swelling degree in alkaline medium. It was because that the higher oxidation temperature led to the higher crosslinking density of cyano-groups and pyridyl-groups, which raising the elasticity of the network. But when the oxidation temperature was up to 240°C, the number of pyridyl-group increased, while, the number of free cyano-group decreased, thus resulting in the decrease of crosslinking density. Furthermore, the number of carboxyl-group decreased with the decrease of the number of free cyano-group, thus the electrostatic repul-

sion among carboxyl-groups attenuated, and eventually swelling became more difficult.

Figure 7(b,c) show the effects of alkaline concentration and alkaline treatment time on pH-sensitive
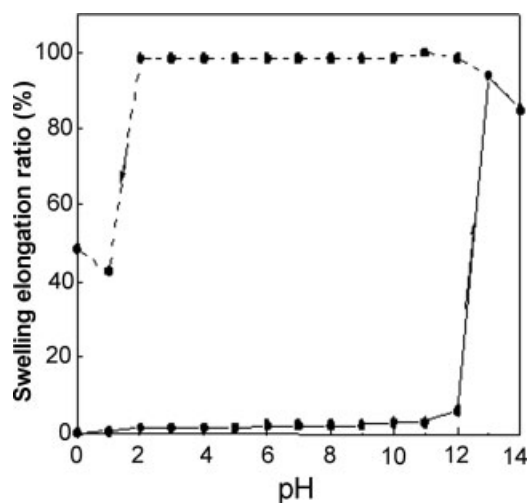
Figure 6 Equilibrium swelling elongation ratio of the PAN porous hollow gel fibers as a function of pH. The solid line represents the trace from acidic to basic medium and dash line represents the opposite trace. Oxidation temperature = 220°C, oxidation time = 30 min, alkaline concentration = 0.5*M*, alkaline treatment time = 20 min.

Figure 7 Effects of preparation condition on pH-sensitive behavior. (a) oxidation treatment temperature; (b) alkaline concentration; (c) alkaline treatment time.

behavior of the PAN porous hollow gel fibers, respectively. With the increase of alkaline concentration and alkaline treatment time, the swelling elongation ratio increased. Especially, the high alkaline concentration even caused the swelling elongation ratio rise from 26.5% to 96.6%. It was presumed that with the increase of alkaline concentration and alkaline treatment time, on the one hand, the number of —COO transformed from —CN increased and led to the higher electrostatic repulsion among carboxyl-groups, thus the higher swelling degree occurred; on the other hand, more macromolecular chains would break in the high alkaline concentration and long alkaline treatment time, causing intermolecular force decrease and molecule's movement easily happen, in the end, accelerating the swelling of the gel fibers.

It can be seen from above figures the elongation ratio of the PAN based porous hollow gel fibers could amount to over 90%, and the maximum was 96.6%, which was much higher than that of PAN based solid gel fibers. That's because the hollow fibers were more easily permeated by alkaline solution, thus improving the accessibility of alkaline and resulting in a large deformation ratio within the same alkaline treatment time.

Contraction force of the PAN porous hollow gel fibers

Figure 8 shows the contraction force of the PAN porous hollow gel fibers increases with measurement time, and reaches an equilibrium state within 20 s. When the test specimen was immersed into $1M$ HCl solution from $1M$ NaOH solution, the H^+ ions diffused into the gel fibers and neutralized the nega-
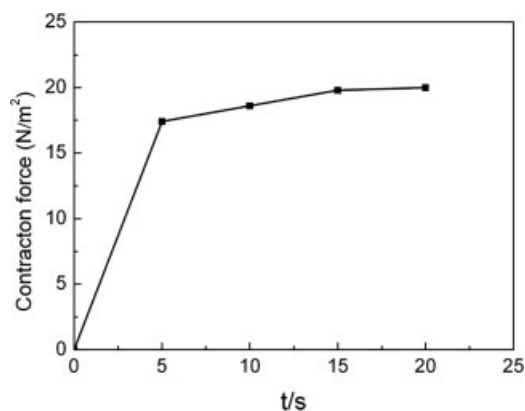
Figure 8 Contraction force of the PAN porous hollow gel fibers as a function of time.
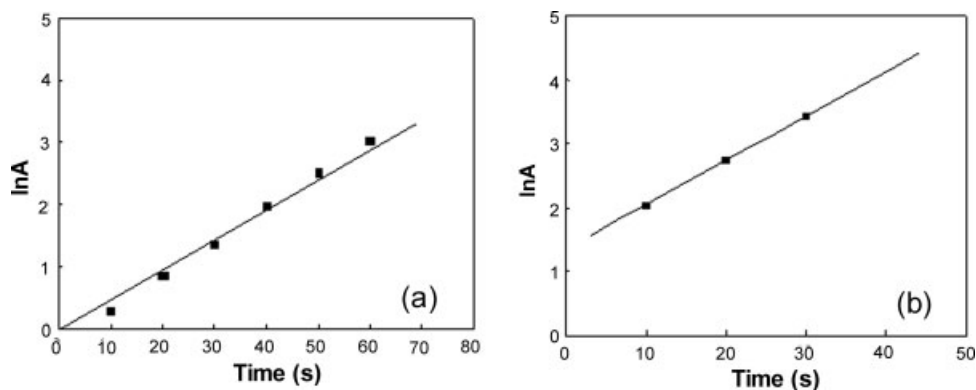
Figure 9 Length changes of the PAN porous hollow gel fiber with time. (a) elongation process; (b) contraction process.

tively charged macromolecular chains, leading to the decrease of the dissociation degree and electrostatic repulsion force, thus, macromolecular chains began to coil. With the time elapsing, the degree of coiling increased, resulting in the increase of the contraction force of the PAN porous hollow gel fibers. In 20 s, the dissociation degree of networks drove to a constant, meaning the contraction force of the test specimen reached an equilibrium state. The maximum contraction force was as large as 20 N/cm^2, which showed much potential application in artificial muscles, for the driving force of biologic skeletal muscle was merely $4 \sim 10$ N/cm^2.

pH responsive rate of the PAN porous hollow gel fibers

As to a common relaxation process, slack time τ is used to describe the rate of behavior change. τ represents the time from one equilibrium state to another equilibrium state. It's determined by materials' property. The elongation of the PAN porous hollow gel fibers in alkaline medium is also a relaxation process, and the length change of gel fibers is time-dependent. Thus, during a swelling process, the relationship between fiber length and time can be expressed as follows:

$$L_\infty - L = (L_\infty - L_0)\exp\left(-\frac{t}{\tau}\right) \qquad (1)$$

where L_∞ is equilibrium length, L is the length at time t, L_0 is the initial length, and τ is slack time. If

$$A = \frac{L_\infty - L_0}{L_\infty - L} \qquad (2)$$

Then

$$\ln A = (1/\tau)t \qquad (3)$$

During the contraction process in an acidic medium, the above-mentioned expressions need to be modified in that gel fibers cannot completely return to the initial length. The correction is as follows:

$$L_\infty - L = (L_\infty - L_0)\exp\left(C - \frac{t}{\tau}\right) + \Delta \qquad (4)$$

where Δ is an irreversible deformation and C is a constant.

Now,

$$A = \frac{L_\infty - L_0}{L_\infty - L - \Delta} \qquad (5)$$

From Figure 9(a,b), the slack times during swelling process in 1M NaOH and contraction process in 1M HCl were calculated as 18.4 s and 14.4 s, respectively. Both were less than 20 s, indicating that although the protofilament size of the PAN porous hollow gel fibers (external diameter, 400 μm) was much larger than that of the solid PAN fiber (external diameter, 25 μm), they had nearly the same
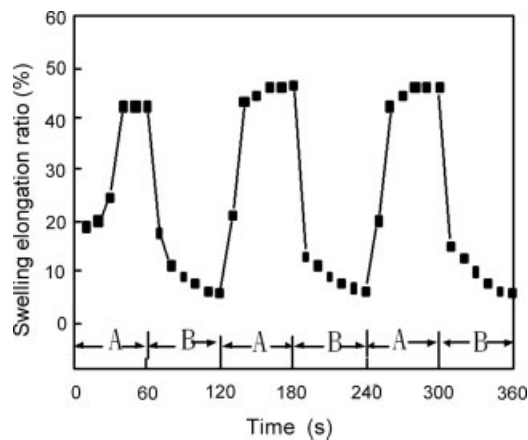

Figure 10 Dynamic changes in length of the PAN porous hollow gel fibers. The solution was exchanged from A to B (elongation) and B to A (contraction). Here, A is 1M NaOH solution and B is 1M HCl solution.

swelling/shrinking response time. Thus, it is possible that we can further improve the responsive rate of the PAN porous hollow gel fibers by further reducing protofilament size (external diameter and wall thickness) and further increasing porosity.

Reversibility to pH response

Figure 10 indicates that the PAN porous hollow gel fibers show a good reversibility in response to pH change. Under the alternative stimulus of $1M$ NaOH and $1M$ HCl, the gel fibers could elongate and contract repeatedly, and even after multiple repetitions, both the elongation/contraction ratio and the responsive rate were well reproductive.

CONCLUSIONS

In our present work, the preparation and pH responsive behavior of the PAN porous hollow gel fibers were discussed systematically. Several conclusions were obtained as follows:

1. The PAN hollow fibers after oxidation treatment were easy to be treated with alkaline solution, since the micropores on the fiber walls caused large contact surface with alkaline solution. Thus, the lower alkaline concentration and less alkaline treatment time were recommended. The adequate technologic parameters for the preparation of PAN porous hollow gel fibers (set oxidation temperature = 220°C, oxidation time = 30 min) were of NaOH concentration $0.5M$ and treatment time 20 min.
2. With FTIR, WAXD, and SEM analyses, it was found that the crystal structure of the PAN porous hollow oxidation fiber was damaged during alkaline treatment; a planar network structure was formed, and exhibited a characteristic of amphoteric gel fibers; the gelated fiber still conserved a hollow channel and finger-like pores on the fiber walls; and the degree of swelling was dependent on cyclization and alkaline treatment time: the higher cyclization, the lower swelling degree; the more alkaline treatment time, the higher swelling degree. Thus through the control of gel network structure and gel fiber morphology microscopically, we can realize to adjust swelling property of gel fibers macroscopically.

3. The PAN porous hollow gel fibers was swelling in a base solution and contracting in an acidic solution. The change in elongation was up to 90%, elongation/contraction responsive time was less than 20 s, and the maximum contraction force was up to 20 N/cm^{-2}.
4. The elongation/contraction behavior of the PAN porous hollow gel fibers could be divided into three pH regions: no hysteresis was found in region 1 (pH < 2) and region 3 (pH > 12), and a large hysteresis appeared in region 2 (pH = 2.0 to 12.0). And the PAN porous hollow gel fibers showed a good reversibility to pH response.

In conclusion, compared with solid gel fibers referred to Umemoto's work,[6] the responsive rate of hollow gel fibers was slower due to their diameter larger than that of solid gel fibers in that it was very difficult to spin a hollow fiber whose size was as small as a solid fiber. However, owing to the existence of innumerous micropores on the fiber walls, the responsive rate still amounted to 20 s (Umemoto's solid gel fiber was 2 s). Furthermore, solid gel fibers must be fully immersed in a stimulus medium to respond an external stimulus, while, the utility of a hollow-typed gel fiber was more convenient and practical because the stimulus medium could be directed through the hollow channel of fibers and was much easier to control.

References

1. Valentina Dinu, M.; Murat Ozmen, M.; Stela Dragan, E.; Okay, O. Polymer 2007, 48, 195.
2. Choe, K.; Kim, K. J.; Kim, D. J Intelligent Mater Syst Struct 2006, 17, 563.
3. Sahoo, A.; Ramasubramani K. R. T.; Jassal, M.; Agrawal, A. K. Eur Polym J 2007, 43, 1065.
4. Kuhn, W.; Hargitay, B.; Katchalsky, A.; Eisenberg, H. Nature 1950, 165, 514.
5. Tanaka, T.; Fillmore, D. J.; Sun, S. T. Phys Rev Lett 1980, 45, 1636.
6. Umemoto, S.; Okui, N.; Sakai, T. In Polymer Gels: Fundamentals and Biomedical Applications, DeRossi, D.; Kajiwara, K.; Osada, Y.; Yamauchi, A., Eds.; Plenum Press: New York, 1991; p 257–270.
7. Suzuki, M. In the Proceedings of the JUPAC CHEMRAWN VI; May 17–22, Tokyo, 1987, p IB11.
8. Shen, X. Y.; Wang, Q. R. Acta Polym Sin 2005, 1, 29.
9. Fanta, G. F.; Burr, R. C.; Doane, W. M. J Appl Polym Sci 1979, 24, 2015.