

# pH-Responsive Fibers Based on Acrylonitrile Acrylic Acid Block Copolymers: Effect of Spinning Conditions and Postspinning Operations on Response and Mechanical Properties

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**ABSTRACT:** pH sensitive poly(acrylonitrile-co-acrylic acid) having ~ 50 mol % acrylic acid with block type structure (AA50B) was synthesized by controlled dosing method of free radical polymerization. The polymer was converted into fibers by wet solution spinning technique in DMF-water system. The resulting block type copolymer could generate a domain type morphology with segregated domains of acrylonitrile and acrylic acid on heat-setting. The drawing ratio and heat-setting temperature had a significant effect on the formation of these domains and their stability. The domain formation was more pronounced when the fibers could be drawn to higher draw ratios during coagulation or heat-set at higher temperature. The stability of the fibers, which is influenced by domain formation, was lowest (at few cycles of transitions) when the fibers were heat-set at 100°C, while it is improved significantly to more than 50 cycles as the

heat-setting temperature was increased to 150°C. The coagulation conditions, drawing and the heat-setting also greatly influenced the mechanical properties, transition behavior, and retractive stresses of the responsive fibers. The tenacity improved by 6.6 times in swollen state and 1.4 times in deswollen state, while the retractive stresses during deswelling were significantly increased to about 4.7 times. However, the increased heat-setting temperature was also found to have a negative effect on the equilibrium swelling values as well as the response rate. The effect of heat-setting on chemical structure of the copolymer was also investigated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3792–3803, 2008

**Key words:** coagulation; drawing; heat setting; pH sensitive fibers; mechanical property

## INTRODUCTION

There is a growing interest in developing engineered actuation systems that have properties more in common with soft biological materials, such as muscles and tendons, than with traditional engineering materials. In an aqueous environment, hydrogels will undergo a reversible phase transformation that results in dramatic volumetric swelling and shrinking upon exposure and removal of a stimulus. Thus, these materials can be used as artificial muscle-like actuators,<sup>1,2</sup> valves,<sup>3</sup> and drug delivery systems.<sup>4</sup> Interest in hydrogels has gained momentum because these materials can be actuated by a variety of stimuli such as pH,<sup>5,6</sup> salinity,<sup>6</sup> electrical current,<sup>7</sup> temperature,<sup>8–12</sup> and antigens.<sup>13</sup>

So far, the stimuli sensitive polymers (SSP) are used in the hydrogel form for diverse applications; however, the potential application of these SSP polymers have not been fully exploited because of their slow response as well as low magnitude of swelling. Therefore, an alternate approach was recently proposed by our group to address some of the above-mentioned drawbacks.<sup>14,15</sup> In that approach, a series of pH sensitive copolymers of controlled architecture based on acrylic acid and acrylonitrile were synthesized, in which the solution spun into fine fibers, showed good mechanical properties as well as enhanced pH response without the need of chemical crosslinking. It was suggested that fibers from such copolymers might be forming domains of acrylonitrile and acrylic acid, where acrylonitrile domains acted as physical crosslinks and connected chains to allow transfer of the stresses along the fiber axis, while acrylic acid domains swelled and deswelled to give the desirable pH response.

The development of the domain morphology took place under heat-setting conditions, and therefore, it was expected that the response and mechanical properties might be an important function of the

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heat-setting conditions in these polymers. Also, the swelling is a diffusion controlled phenomenon. The response time, which is a function of the rate of diffusion of water in and out of the fiber, is dependent on both the diffusivity coefficient of the fiber matrix and square of the gel dimensions.<sup>16,17</sup> The modification of spinning conditions during wet spinning of pH responsive fibers may lead to finer and stronger fibers, which may help in achieving better response. Because of these reasons, in this article, an attempt has been made to investigate the effect of spinning conditions and postspinning operations on the response behavior and mechanical properties of the above fibers.

## EXPERIMENTAL

### Materials

Acrylic acid (AA) and toluene were obtained from Merck India, Mumbai. Acrylonitrile (AN) was purchased from Central Drug House (p), New Delhi and initiator  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN) from G. S. Chemical Testing Lab and Allied Industries, New Delhi. Solvents diethyl ether and *N,N*-dimethylformamide (DMF) were purchased from Qualigens Fine Chemicals, Mumbai. All chemicals were of minimum assay of 99% and were used without further purification.

### Copolymer synthesis and characterization

Controlled free radical copolymerization of AN and AA with 50 mol % feed of acrylic acid (AA50B) was carried out in a four-necked reactor in toluene at  $65^\circ\text{C} \pm 1^\circ\text{C}$  under nitrogen atmosphere as reported earlier.<sup>14</sup> The final acrylic acid content in the feed was kept at 50 wt % (42.7 mol %). The initiator AIBN was dissolved in acrylonitrile and degassed. It was then added to the reaction flask and the reaction was carried out for 30 min before starting the addition of acrylic acid. The more reactive comonomer was added after degassing in small regulated doses to the reaction mixture over a period of 3 h with constant stirring. The reaction was allowed to continue for an additional 30 min. The reaction mixture was cooled, precipitated, and washed in excess

diethyl ether. Homopolymer of acrylic acid was removed by thoroughly washing the product with excess acetone. The purified copolymer was dried in a vacuum oven at  $60^\circ\text{C}$  for 1 h. Gravimetric yield of the copolymer was  $\sim 37\%$ .

The intrinsic viscosity of the copolymers was calculated in DMF using Ubbelohde viscometer in a constant temperature bath at  $30^\circ\text{C} \pm 0.1^\circ\text{C}$ . Viscosity average molecular weight was determined by using Mark-Houwink relation as reported earlier.<sup>18</sup>

The composition of the copolymers was determined by using the peak areas corresponding to carbon atoms in the COOH of AA and CN groups of AN in quantitative  $^{13}\text{C}$  NMR spectrum.<sup>19</sup> Also the composition was confirmed using acid-base titration of COOH groups.<sup>20</sup>

### Solution spinning of pH sensitive fibers and optimization of coagulation bath condition

The dope solution of 33 wt % was prepared by stirring the purified and dried copolymer powder in DMF. The solution was kept in vacuum at the room temperature to allow deaeration before spinning. Fibers were extruded using a syringe type monofilament extruder into a coagulation bath (containing a mixture of water and DMF) at  $30^\circ\text{C}$ . The coagulation bath condition for fiber preparation was changed from pure water to DMF: water mixture. The DMF percentage was varied from 10 to 50%, and the spinning process was optimized to get finer dimension fibers. The extruded fibers were drawn to indicated values given in Table I. The coagulated fibers were dried under taut condition in air at  $30^\circ\text{C}$ .

### Heat treatment of the as-spun fibers

The dried fibers were heat-treated in an air oven at a temperature of  $100\text{--}150^\circ\text{C}$  for 2 h. The fibers were placed in taut condition in a wooden frame and fixed at both the ends to avoid shrinkage during annealing.

### X-ray diffraction

WAXD spectra of the fibers were recorded by X'Pert PRO machine of PANalytical between  $2\Theta$  of  $10^\circ\text{--}35^\circ$  in the reflection mode. The fibers heat-set

TABLE I  
Coagulation Conditions and the Maximum Stretch Imparted to the Fibers

Coagulation bath (water : DMF)	Stretching in coagulation bath (% extruded length)	Stretching in air (% of extruded length)	Total extension (% of extruded length)
100 : 0	100	Could not be stretched	100
90 : 10	100	200	300
70 : 30		Not suitable for spinning	
50 : 50		Not suitable for spinning	

at different temperatures were cut into small pieces and placed in powder sample stage for the spectroscopy.

### Thermal shrinkage

The shrinkage percentage of heat-set fibers was determined by taking a known length (IL) of the fiber, allowing it to shrink by immersing it in silicone oil bath at 100°C and 130°C. The final length (FL) of the fiber was determined after 10 min. The shrinkage percentage was calculated using the following relation.

$$\text{Shrinkage \%} = \frac{\text{IL} - \text{FL}}{\text{IL}} \times 100 \quad (1)$$

### FTIR analysis

The FTIR spectra of fibers heat-set at different temperatures were recorded on a Perkin-Elmer 883 spectrophotometer to study the effect of heat-setting temperature.

### Mechanical properties

The tensile strength of the fibers heat-set at different temperatures was recorded on Instron tensile testing instrument (Model no. 4202) at the crosshead speed of 10 mm/min. The fibers were conditioned by repeated swelling and deswelling for three cycles and then tested in both swollen and deswollen conditions. The diameter of the fiber was measured using Lieca optical microscope at 15 places along the length of the fiber samples used for the above measurements.

### Swelling behavior

The drawn and heat-set fibers were conditioned for three cycles of swelling and deswelling before carrying out the following measurements (except for cyclability test).

#### Equilibrium swelling

The equilibrium swelling behavior of heat set fibers was studied by immersing them in a slack condition in a pH 10 solution for a period of 180 min. The diameters of the fibers were measured under a Lieca microscope, while the lengths were measured using a linear scale in millimeters. The length and diameter of the fibers was measured before and after the transition. The volumetric swelling % was calculated

from the changes in diameter and length of the fibers.

$$\text{Swelling \%} = \frac{(\text{Volume of fiber at equilibrium} - \text{Initial volume})(100)}{(\text{Initial volume})} \quad (2)$$

#### Rate of transition

For determining the rate of transition, a single fiber was placed vertically in a measuring flask with a small weight tied at the lower end of the fiber to give a stress value of 0.05 MPa (at original diameter). The % change in length with time ( $t$ ) during swelling cycle was measured for both fibers at a pH of 10, while the rate of deswelling was evaluated at a pH of 2.

#### Cyclability

The drawn-heat-set fibers (without conditioning) were placed on a glass slide in slack condition and the glass slide along with fiber was immersed in a pH 10 solution for determining the change in dimensions. Similarly, the above slides were placed in a pH 2 solution for deswelling. At each stage samples were kept till equilibrium was reached. The reversibility of the transition was evaluated for several swelling–deswelling cycles.

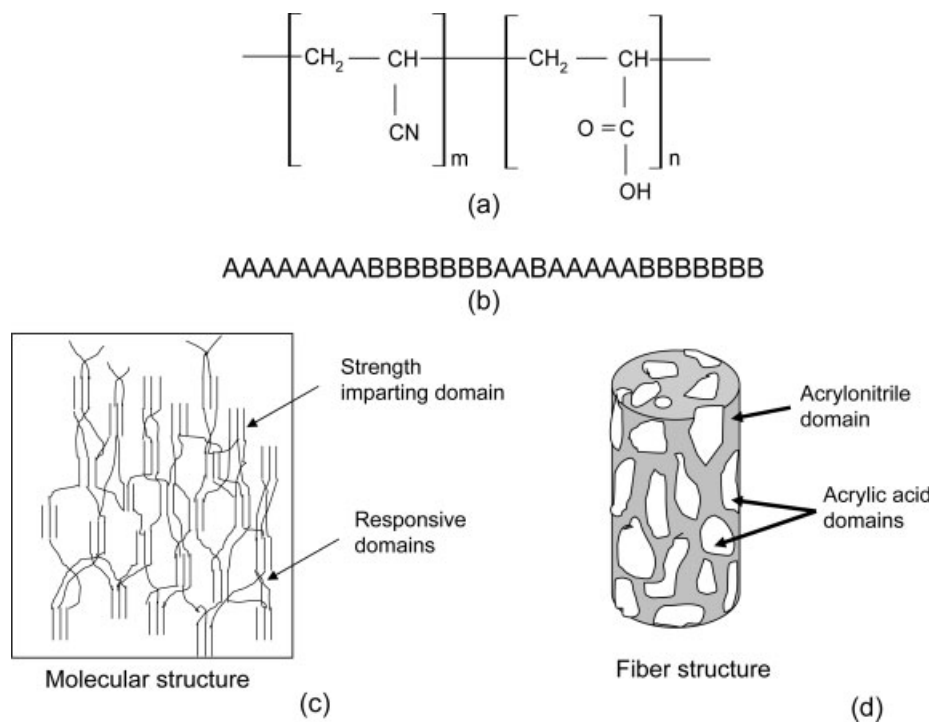
#### Retractive stress during deswelling

For determining the retractive stresses during deswelling, a single fiber was hung vertically in a measuring flask with a small weight of 63 mg tied at the lower end of the fiber. It was allowed to swell to its maximum in pH 10. Then, an additional weight in form of several metal rings weighting 8 mg each was attached to the lower end of the fiber. This fiber was hung in pH 2 for deswelling along with the additional weight. Subsequently, the rings were removed one at a time to determine the maximum weight under which the fiber was able to come back to its original shape and size.

## RESULT AND DISCUSSION

### Synthesis of pH sensitive copolymers

Ideal structure for a block copolymer is defined segments of one monomer followed by another and so on; however, it is nearly impossible to achieve pure block structure in free radical polymerization. Rather the distribution of monomers in such system depends on the reactivity ratios of the two monomers. In our case, the reactivity ratios of the two monomers are widely different (reactivity ratio of acrylic acid is 2.502 and acrylonitrile is 0.495)<sup>21</sup> sug-



**Figure 1** Proposed structure of the copolymers and fiber (a) chemical structure (b) schematic of AA50B (c) schematic of fibers consisting of domain morphology.

gesting that simple copolymerization would lead to the formation of either homopolymer of acrylic acid or acrylic acid rich copolymer. Therefore, it was decided to synthesize the copolymer with enriched segments (rather than pure block) of the two monomer-moieties using regulated dosing of the more reactive monomer, acrylic acid during polymerization. Acrylic acid was added in small doses separated by predetermined time intervals. It was hoped that whenever a dose of the acrylic acid was added it would get incorporated into the growing chains as a short block or enriched segment owing to its high reactivity ratio. During the interval between any two doses, scarcity of the acrylic acid monomer in the reaction medium would force the acrylonitrile monomer to get incorporated as short block or enriched segment of acrylonitrile moieties in the growing polymer chains. The proposed structure of the copolymers is also shown in Figure 1.

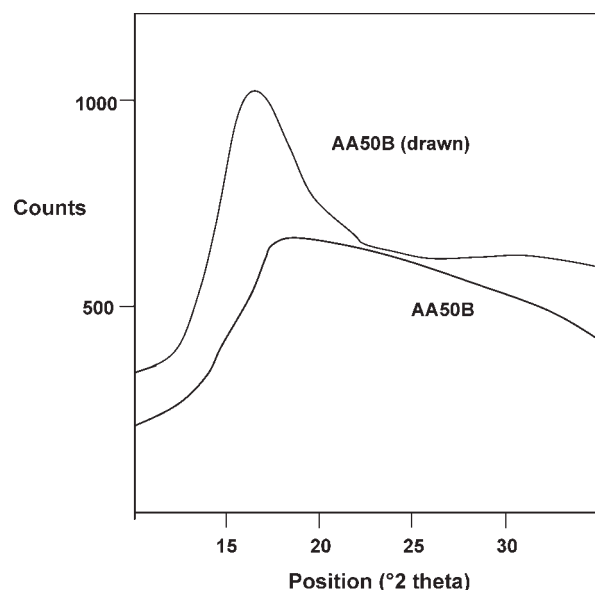
The above approach could produce copolymers where the distribution of the comonomer moieties could be controlled to a great extent giving rise to a block type copolymer. The structure and properties of these block type copolymers in comparison to their random counterparts have been reported earlier.<sup>14,15</sup> The quantitative analysis of <sup>13</sup>C NMR proved that there was significant increase in the concentration of segmented acrylonitrile and acrylic acid moieties compared to the random structure using the modified polymerization approach. The copoly-

mer synthesized for this study had a molecular weight of  $3.6 \times 10^5$  g/mol. The overall comonomer composition of the copolymer AA50B was calculated to be 48.86 mol % of acrylic acid moieties by quantitative <sup>13</sup>C NMR. The composition was also confirmed by acidimetric titration.

#### Solution spinning and optimization of coagulation bath condition

Like polyacrylonitrile, the synthesized copolymers were soluble in DMF; therefore, they could be readily solution wet spun using DMF as a solvent and water as a coagulant. In wet spinning process, morphological structures as well as mechanical properties are strongly influenced by the mass transfer between the spinning line and the surrounding medium, i.e., the coagulation bath. The coagulation bath condition was changed from pure water to DMF:water mixture. The DMF percentage was varied from 10 to 50% and the spinning process was optimized. The stretching process is very important in altering the fiber structure and enhancing the fiber properties. The various coagulation bath conditions and the maximum stretching that could be imparted in those coagulation baths are given in Table I. The spun fibers were drawn first in coagulation bath followed by stretching in air before the coagulation was complete, and subsequently washed with water. In 70 : 30 and 50 : 50 (water : DMF) bath, the fibers





**Figure 2** Effect of drawing on X-ray diffraction of pH sensitive fibers heat set at 120°C (AA50B, 120  $\mu\text{m}$  and AA50B, 38  $\mu\text{m}$ ; drawn).

could not be solution spun or stretched because the copolymer did not precipitate well because of the high-concentration of DMF in the coagulation bath. Hence, only 100 : 0 and 90 : 10 coagulation baths were used for the spinning process. The fibers could be stretched to only two times in the coagulation bath containing pure water, while they could be stretched two times in the coagulation bath and two times in the air when 90 : 10 bath was used. Also much finer fibers could be spun in coagulation bath containing 10% DMF. This gave two diameters of fibers, 120  $\mu\text{m}$  from pure water bath and 38  $\mu\text{m}$  from 90 : 10 bath. The coagulated fibers were dried under taut condition in air at 30°C.

### Heat treatment of the as-spun fibers

The approach used in polymerization was to control the distribution of both acrylonitrile and acrylic acid moieties in the polymer chains so that block type structure could be obtained. It was expected that that formation of blocks or enriched segments would

result in acrylonitrile moieties from different chains to come together (phase separate), crystallize and form various tie-points to provide strength to the formed structure, whereas, the block segments of acrylic acid may form responsive domains to provide pH response through ionization under suitable environment. Our recent experiments have shown that the formation of domain morphology was in fact possible and the resultant fiber is stronger than the fibers produced from random copolymers. Also, the acrylic acid domains could provide faster diffusion of water to give larger and rapid swelling and deswelling under suitable pH.<sup>14,15</sup>

The phase separation could be facilitated by providing heat during heat-setting of the fibers under taut conditions. However, acrylonitrile is sensitive to heat and undergoes cyclization and dehydrogenation on prolonged heating at high temperature. Therefore, the temperature of heat-setting is likely to play an important role in the formation of stabilized structure. Therefore, the freshly spun fibers were annealed in taut condition at 100, 120, or 150°C for a period of 2 h. This temperature range was chosen to avoid excessive anhydride formation in acrylic acid segments (which is known to start at  $\sim 170^\circ\text{C}$  and high degree of cyclization of the adjacent acrylonitrile groups, which usually occurs at  $> 220^\circ\text{C}$ .<sup>22,23</sup> The chemical changes that occurred at these temperatures are discussed later.

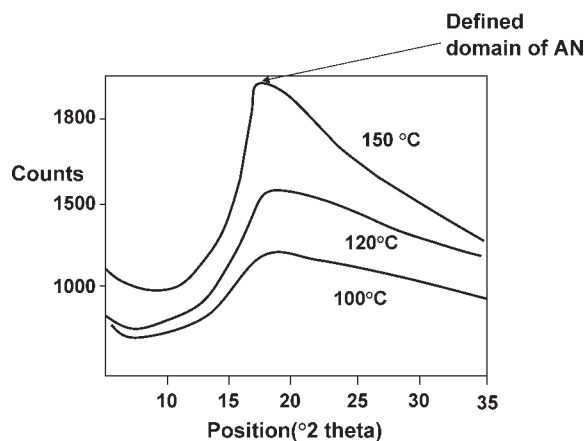
### Fiber morphology

#### Effect of drawing

X-ray diffraction study of both the homopolymers of PAN (polyacrylonitrile) and PAA (polycyclic acid) was carried out. The PAN homopolymer shows two distinct peaks at  $2\theta = 17^\circ$  and  $2\theta = 29^\circ$ . The homopolymer of PAA shows a peak at  $2\theta = 22^\circ$ . X-ray diffraction spectra of both fibers AA50B (120  $\mu\text{m}$ ) and AA50B (38  $\mu\text{m}$ ) after heat-setting at 120°C for 2 h are given in Figure 2. The spectrum of less drawn fiber from AA50B (i.e., 120  $\mu\text{m}$ ) shows a broad peak indicative of formation of poor order in the fiber even after heat setting. However, in the case of more drawn fibers from AA50B (i.e., 38  $\mu\text{m}$  diameter), a

**TABLE II**  
Thermal Shrinkage of pH-Sensitive Fibers

Diameter of fiber from copolymer AA50B ( $\mu\text{m}$ )	Heat setting temperature ( $^\circ\text{C}$ )	Thermal shrinkage % (temperature of silicone bath)	
		(100 $^\circ\text{C}$ )	(130 $^\circ\text{C}$ )
38	100	5.07	15.38
38	120	2.4	11.50
38	150	1.21	8.25
120	120	4.76	13.6



**Figure 3** Effect of heat-setting temperature on X-ray diffraction of the pH sensitive fibers (AA50B, 38  $\mu\text{m}$ ).

definite increase in the intensity at  $2\theta = 17^\circ$  was observed even though the chemical composition and the conditions of heat-setting of the fibers were same as the other fiber. This indicated the formation of better ordered domains of polyacrylonitrile in the finer diameter (38  $\mu\text{m}$ ) fiber. Thermal shrinkage of a fiber is also a good measure of stability of its structure. Fiber AA50B (38  $\mu\text{m}$ ) showed lower shrinkage at both 100 and 130°C in oil bath than AA50B (120  $\mu\text{m}$ ) further supporting the concept of formation of more stable domains of acrylonitrile (Table II). The results signify the importance of higher drawing of fibers in coagulation bath in obtaining better phase separation and domain formation.

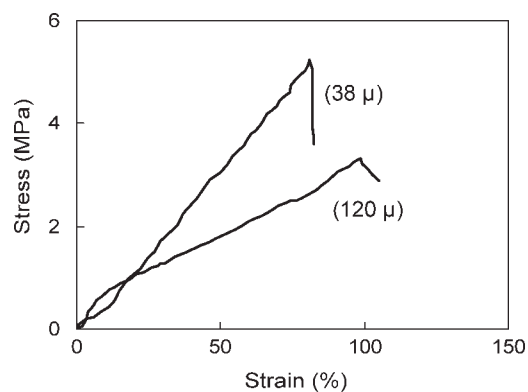
#### Effect of heat setting temperature

Also X-ray diffraction was studied for the fibers (AA50B) to investigate the effect of heat setting temperature. X-ray diffraction spectra of fibers AA50B (38  $\mu\text{m}$ ) heat set at 100, 120, and 150°C for 2 h are given in Figure 3. As the heat-setting temperature was increased from 100 to 150°C, a definite increase in the intensity (sharpness) of peak at  $2\theta = 17^\circ$  was observed which indicated the improvement in the ordered domains of polyacrylonitrile. Thermal shrinkage of the fibers also reduced significantly with higher heat-setting temperature as given in Table II. The higher temperature would help in mobilizing the polymer chains to allow better phase segregation and connectivity among the polyacrylonitrile segments. Also, imperfections in crystalline or ordered domains may be reduced with increased temperature of heat-setting under taut condition.

#### Mechanical properties

##### Effect of drawing

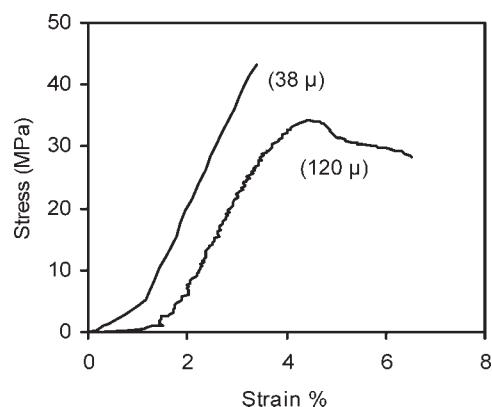
Figures 4 and 5 show stress–strain curves for the two fibers in swollen and deswollen conditions. As



**Figure 4** Stress–strain curves of the pH sensitive fibers in swollen state (AA50B, 120  $\mu\text{m}$ ; AA50B, 38  $\mu\text{m}$ ).

expected, the fibers showed higher extension and lower tenacity in the swollen state as compared to the deswollen state. However, the tenacity in swollen conditions shown by fiber from AA50B (38  $\mu\text{m}$  dia) were significantly higher (1.6 times) compared to that shown by the fibers from AA50B (120  $\mu\text{m}$  dia) (Table III). The higher tenacity (by 1.25 times) of fibers from AA50B (38  $\mu\text{m}$  dia) under deswollen state may be attributed to somewhat higher orientation due to drawing; however, higher tenacity under swollen state clearly indicates better connectivity among polymer chains due to well formed acrylonitrile domains. The drawing of fibers during coagulation is unlikely to increase the orientation of the fibers to a large extent due to high rate of relaxation of the polymer chains in swollen state.

One of the most important mechanical aspects of the pH responsive structures is their ability to retract (deswell) under stress. For applications such as artificial muscles and actuators, the structure should be able to change shape under load. Table III compares the mechanical properties of the two fibers. Also, it shows the amount of applied stress that the fibers could resist during deswelling. Interestingly, the



**Figure 5** Stress–strain curves of the pH sensitive fibers (AA50B, 120  $\mu\text{m}$ ; AA50B, 38  $\mu\text{m}$ ) in deswollen state.

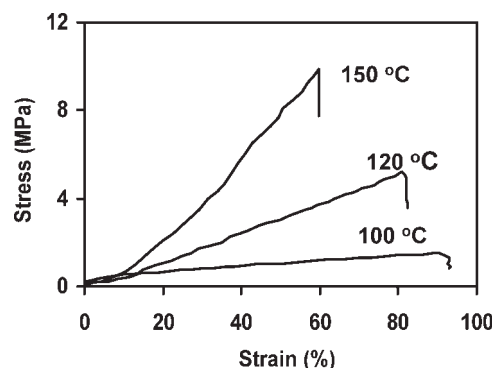
**TABLE III**  
Mechanical Properties of the Fibers

Diameter of fibers from copolymer AA50B ( $\mu\text{m}$ )	Temperature of heat setting ( $^{\circ}\text{C}$ )	Retractive stress during deswelling (MPa)	Breaking force in swollen condition (MPa)	Breaking force in deswollen condition (MPa)
120	120	0.26	3.31	34.29
38	120	0.31	5.24	43.06
38	100	0.09	1.48	36.87
38	150	0.42	9.84	52.56

fiber from AA50B (38  $\mu\text{m}$  dia) could retract under an opposing stress of about 1.2 times than fibers from AA50B (120  $\mu\text{m}$  dia). This clearly signifies the improvement obtained in the domain morphology of the finer fibers on drawing.

#### Effect of heat setting temperature

Figures 6 and 7 show the effect of heat-setting temperature on the stress-strain properties of the fibers in swollen and deswollen conditions. With the increase in heat-setting temperature from 100 to 150 $^{\circ}\text{C}$ , the mechanical properties were significantly improved. The tenacity improved to 6.6 times in swollen state and to 1.4 times in deswollen state (Table III). Although the retractive stresses were significantly increased to about 4.7 times, the increase in the mechanical properties indicated that the structure became more stable with heat-setting, possibly due to the formation of domain morphology as suggested earlier. During the heat-setting, the weak association of the AN domains may be replaced with structure having better packing characterized by the increase in crystallinity and crystalline perfection. Table III compares the mechanical properties of the two fibers at different heat setting temperatures.



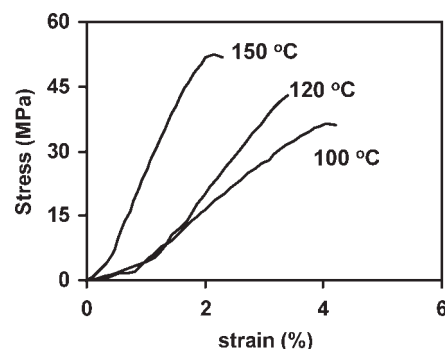
**Figure 6** Effect of heat setting temperature on the stress-strain curves of the pH sensitive fiber (AA50B, 38  $\mu\text{m}$ ) in swollen condition.

#### pH response properties

The pH sensitive fibers show swelling and deswelling in alkaline and acidic pH solutions, respectively. The  $\text{p}K_a$  value of polyacrylic acid is 4.28.<sup>24</sup> Therefore, below pH 4.28, the  $\text{H}^+$  ion concentration in the solution is very high. This effectively suppresses the ionization of carboxylic acid groups and the carboxylate groups change to COOH groups. The polymeric chains in the fiber remain in the coiled state resulting in deswelling. As the pH is increased above the  $\text{p}K_a$  value, the fiber swells because the concentration of negatively charged carboxylate ions increases. When the carboxylate groups in the polymer chain are fully ionized the effect of electrostatic repulsion is the highest and the gel fibers expand significantly at about a pH of 10.

#### Equilibrium swelling

*Effect of drawing.* The volumetric equilibrium values and time of change for swelling and deswelling in free condition for the fibers AA50B (120  $\mu\text{m}$ ) and AA50B (38  $\mu\text{m}$ ) are shown in Table IV. These values were obtained for the fibers when swollen in slack conditions. The fibers from AA50B (120  $\mu\text{m}$ ) achieved equilibrium swelling in 45 min with a volumetric change of about 3890%; whereas, the equilibrium swelling of the fibers from AA50B (38  $\mu\text{m}$ ) was significantly higher at about 22,166% and was



**Figure 7** Effect of heat-setting temperature on stress-strain curves of the pH sensitive fibers AA50B, 38  $\mu\text{m}$  in deswollen condition.

**TABLE IV**  
**Equilibrium Swelling/Deswelling of pH Sensitive Fibers Heat-Set at 120°C and Tested under Slack Condition**

Diameter of fibers from copolymer AA50B ( $\mu\text{m}$ )	pH 10				pH 2	
	Change in diameter (%)	Change in length (%)	Volumetric swelling (%)	Time of swelling (min)	Deswelling (%)	Time of deswelling (min)
120	414	227	3,890	45	100.15	5
38	1,098	184	22,166	18	100.1	0.33 (20 s)

achieved in much shorter time of 18 min. Similarly, the deswelling was faster in AA50B (38  $\mu\text{m}$ ) fiber, where the time of deswelling reduced to 20 s from 5 min in AA50B (120  $\mu\text{m}$ ) fiber. The rate of diffusion of water in and out of the fiber is dependent on diffusivity coefficient of the fiber matrix and the path of diffusion. This drastic reduction in the response time as well as the increase in the amount of swelling percentage may be due to two factors: (a) reduction of diameter to a smaller value, i.e., smaller paths of diffusion and lower levels of opposing internal stresses on swelling; (b) the formation of better domains of acrylic acid.<sup>14,15</sup> It appears that since drawing has facilitated the phase segregation and formation of well defined domains, it leads to better diffusivity coefficient of the water through the fiber. Also, well defined domains may swell to a larger extent under similar conditions.

Interestingly, both the fibers have taken significantly lower time but have swelled to significantly higher values compared to poly(acrylic acid) gel disks, particles or rods reported in the literature.<sup>25-27</sup> Also, the fibers have shown significantly higher mechanical properties and retractive stresses. This difference in their response and mechanical properties is attributed to the structure and morphology of these fibers.

*Effect of heat setting temperature.* The volumetric equilibrium values and time of change for swelling and deswelling in free condition for the fibers AA50B heat set at temperatures 100, 120, 150°C are shown in Table V. The fibers heat-set at 100°C showed a higher percentage of swelling compared to the fibers heat set at 120 and 150°C, however, were not stable in pH 10 solution and disintegrated before they achieved the equilibrium swelling. This indicated that a temperature of 100°C was not sufficient to bring about phase segregation to form the domain

morphology. The fibers heat set at 120 and 150°C were quite stable and achieved the equilibrium swelling. The amount of swelling in case of 150°C heat set fibers was significantly less compared to the fibers heat set at 120°C. Similarly, the rate of deswelling was faster for the fibers heat set at 120°C than the fibers heat set at 150°C. The fibers heat set at 120°C deswelled to original shape within 20 s while the fibers heat set at 150°C required 4 min for the same.

The possible reason is the extent of binding the structure is undergoing due to domain formation at high temperature (150°C) of heat-setting. Also, it is known that the PAN undergoes chemical reactions when exposed to long times at higher temperatures. The possible chemical changes that may occur in these fibers are described in a later section.

#### Kinetics of transition

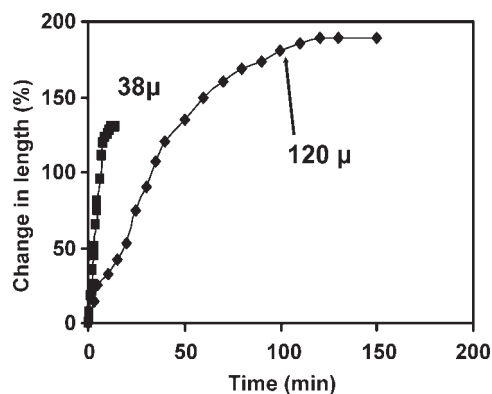
*Effect of drawing.* The change in length curves for swelling and deswelling for pH sensitive fibers under a small tensile stress of 0.05 MPa are given in Figures 8 and 9. From the figures, it can be seen that the fiber from AA50B (38  $\mu\text{m}$ ) has a significantly faster rate of change in length, but achieved a lower equilibrium length compared to the fiber from AA50B (120  $\mu\text{m}$ ). The above results clearly show the great influence of fiber dimension and domain morphology on the swelling/deswelling rate of pH sensitive fibers. The lower percentage change in length (though volumetric change was significantly higher) in case of AA50B (38  $\mu\text{m}$ ) is possibly due to the higher orientation of molecular chains in the fiber structure, which would allow more lateral swelling than axial swelling of the fiber.

*Effect of heat setting temperature.* The change in length curves for swelling and deswelling for pH sensitive fibers (heat set at three different temperatures) under

**TABLE V**  
**Effect of Heat Setting Temperature on Equilibrium Swelling/Deswelling of AA50B (38  $\mu\text{m}$ ) Fiber Tested Under Slack Condition**

Heat setting temperature (°C)	pH 10				pH 2	
	Change in diameter (%)	Change in length (%)	Volumetric swelling (%)	Time of swelling (min)	Deswelling (%)	Time of deswelling (s)
100	1,462	200	42,806	Stable up to 20 min	100	Instant
120	1,098	184	22,166	20	100.1	20
150	669	152	6,786	38	112.49	240



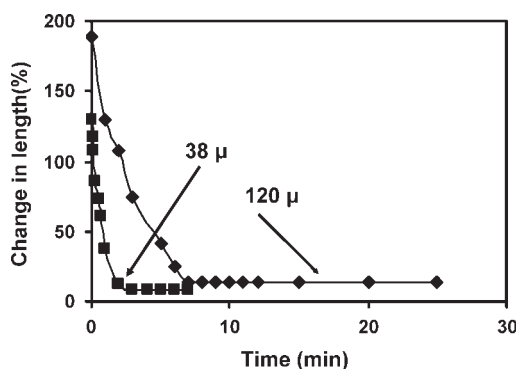


**Figure 8** Effect of drawing (AA50B, 120  $\mu\text{m}$  vs. 38  $\mu\text{m}$ ) on rate of swelling transition of pH sensitive fibers heat-set at 120°C under a stress of 0.05 MPa.

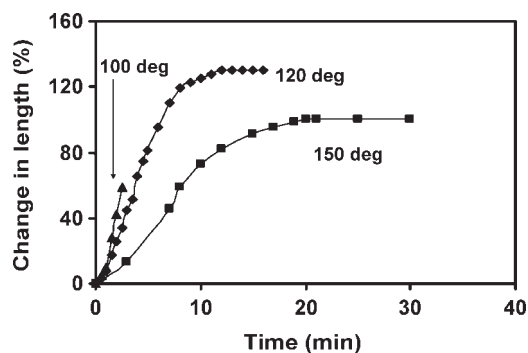
a small tensile force of 0.05 MPa are given in Figures 10 and 11. A small force of 0.05 MPa was applied to the lower end of the fiber to avoid curling of the fiber for precise length measurement. The rate of transition was found to depend on the strength of alkali solution and the weight applied during the transition. The fibers heat set at 100°C showed a higher rate of swelling compared to the fibers heat set at 120°C and 150°C; however, they were not stable in pH 10 solution and disintegrated before they achieved the equilibrium swelling. The fibers heat set at 120°C showed faster rate of change and achieved higher final length than the fibers heat-set at 150°C. The results were similar to those obtained for equilibrium swelling experiments.

### Cyclability

*Effect of drawing.* The cyclic swelling/deswelling behavior of the two fibers AA50B (38  $\mu\text{m}$ ) and AA50B (120  $\mu\text{m}$ ) for the first four cycles is shown in Figure 12. During the first two cycles in fibers from AA50B (120  $\mu\text{m}$ ), the swelling was in the range of



**Figure 9** Effect of drawing (AA50B, 120  $\mu\text{m}$  vs. 38  $\mu\text{m}$ ) on rate of deswelling of the pH sensitive fibers heat-set at 120°C under a stress of 0.05 MPa.

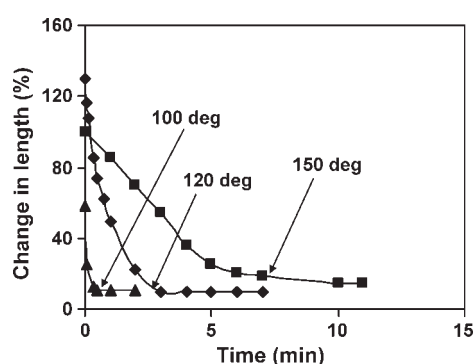


**Figure 10** Effect of heat setting temperature on rate of swelling transition of pH sensitive fibers (AA50B, 38  $\mu\text{m}$ ) under a stress of 0.05 MPa.

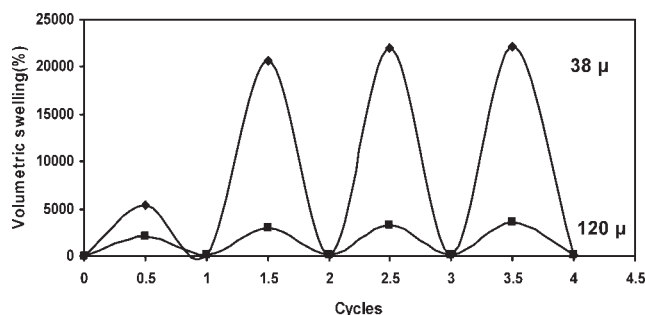
~ 1200–1300%. Subsequently, the swelling percentage increased to ~ 3300–3669%. This may be due to the fact that the fibers underwent conditioning (opening up of the structure) in the first two cycles and then in the subsequent cycles showed a stable response. In the case of fibers from AA50B (38  $\mu\text{m}$ ), 1st cycle showed swelling in the range of 5356%, which increased to ~ 22,165% in the subsequent cycles.

*Effect of heat setting temperature.* Heat-setting temperature has an impact on the stability of the fibers for repeated cycles of swelling and deswelling. The fibers heat-set at 100°C were not able to withstand repeated cycling and were disintegrated in a few cycles. As the heat setting temperature was increased from 100 to 150°C, the stability of the fibers for repeated cycling increased to more than 50 cycles without any visual deterioration. The cyclic swelling/deswelling behavior of fibers heat set at three different temperatures for the first four cycles is shown in Figure 13. However, with increase in the heat setting temperature, the final volumetric swelling value decreased from 42,806% to 6786%.

From the above mentioned results, it is inferred that heat-setting was extremely important in obtain-



**Figure 11** Effect of heat-setting temperature on rate of deswelling of the pH sensitive fibers (AA50B, 38  $\mu\text{m}$ ) under a stress of 0.05 MPa.



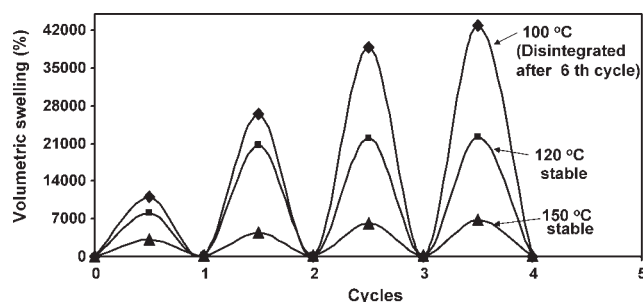
**Figure 12** Effect of drawing (AA50B, 120  $\mu\text{m}$  vs. 38  $\mu\text{m}$ ) on cyclic swelling and deswelling of the pH sensitive fibers heat-set at 120°C.

ing the stable morphology of the pH responsive fibers.

### Chemical changes during heat-setting

Presence of acrylic acid comonomer in copolymers of polyacrylonitrile may alter initiation of the cyclization reactions. To understand the chemical changes that the fibers may undergo along with the physical morphological changes described earlier, copolymers were analyzed using FTIR spectrometer. The FTIR spectra of the fibers heat set at three different temperatures are presented in Figure 14.

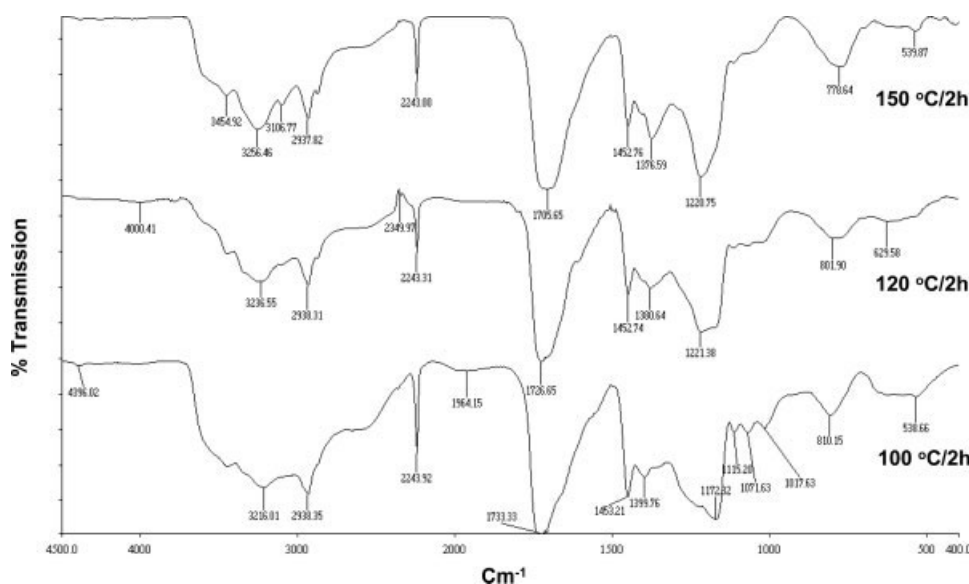
As reported in the literature,<sup>22,28</sup> the major absorption bands in acrylonitrile copolymers are: CN stretching at 2240  $\text{cm}^{-1}$ , C—H stretching at 2937  $\text{cm}^{-1}$ , C—H bending at 1450 and 1250  $\text{cm}^{-1}$ , and C—H in plane deformation at 1368  $\text{cm}^{-1}$ . Additional bands at 1730 and 3410  $\text{cm}^{-1}$  appear due to stretch-



**Figure 13** Effect of heat-setting temperature on cyclic behavior of swelling and deswelling of the pH sensitive fibers (AA50B, 38  $\mu\text{m}$ ).

ing of C=O and O—H stretching in COOH groups present in these copolymers i.e., acrylic acid.

As the heat set temperature increases from 100 to 150°C, the peaks corresponding to free OH groups in the range of 1115–1018  $\text{cm}^{-1}$  slowly begin to decrease in intensity. Also the peak corresponding to the CO group of COOH at 1730  $\text{cm}^{-1}$  broadens and gradually shifts towards the lower frequency with increase in the heat set temperature from 100 to 150°C. In the 2900–3500  $\text{cm}^{-1}$  region, small changes in the spectra are observed, which indicate the initiation of the oxidation reactions.<sup>22,28,29</sup> Simultaneously, a gradual decrease in the intensity of OH stretching of COOH groups (at 3450  $\text{cm}^{-1}$ ) is also observed. These changes in the FTIR suggest the participation of COOH groups in some reactions even at these low heat setting temperatures. However, no additional bands were observed in the 1610–1575  $\text{cm}^{-1}$  and the intensity of nitrile absorption remained nearly unaltered, ruling out the formation of conjugated C=C structures in any appreciable amount at



**Figure 14** FTIR spectra of the pH sensitive fibers (AA50B, 38  $\mu\text{m}$ ) heat set at 100, 120, and 150°C.

these temperatures. Though there was slight yellowing of the samples during heat-setting, which suggested the formation of some conjugated structures.

The above discussion indicates that with increase of heat-setting temperature, gradual removal or non-availability of free OH groups may be responsible for the lower amount of swelling as well as the slower response of the fibers. The decrease in free OH groups may be occurring due to their participation in the decarboxylation reactions. This is further supported by the appearance of very weak shoulder at about  $1800\text{ cm}^{-1}$ .

## CONCLUSIONS

pH sensitive polymer, poly(acrylonitrile-co-acrylic acid, 50 : 50), was synthesized using free radical polymerization, where more reactive monomer acrylic acid was added in regulated doses to produce block copolymer structure. The copolymer was converted into fibers by solution spinning in DMF-water system at  $30^\circ\text{C}$ . Coagulation bath concentration was modified from pure water to DMF:water of 10 : 90 mixture so that the coagulation rate could be controlled and the spinning fibers could be drawn to a greater extent to get the finer diameter. Using modified conditions fibers with  $38 \pm 2\ \mu\text{m}$  diameter could be produced.

The coagulation conditions, drawing, and the heat-setting temperature were found to have a significant impact on mechanical properties, transition behavior, and retractive stresses of the responsive fibers. The finer fibers from AA50B ( $38\ \mu\text{m}$ ) showed a stable, reversible transition with an equilibrium volumetric swelling of 22,200% at a pH of 10 as compared to their thicker version of  $120\ \mu\text{m}$ , which showed volumetric swelling of only 3300–3600%. Also, the finer fibers from AA50B ( $38\ \mu\text{m}$ ) showed significantly higher strength (1.6 times), and higher retractive stress (1.2 times) during the transition compared to the fibers with higher diameter ( $120\ \mu\text{m}$ ). The rate of transition was also found to be higher for the finer fibers, and their equilibrium deswelling time was also significantly lower at 20 s. These changes in properties of the two fibers is attributed to the formation of better domain structure because of higher drawing imparted to the coagulating fiber. Formation of domains was supported by lower thermal shrinkage values and marked increase in peak intensity and sharpness of X-ray diffraction peak at  $2\theta = 17^\circ$  of the finer fibers, which is also characteristic of polyacrylonitrile phase.

Heat-setting temperature had a great impact on the stability of the fibers for repeated cycles of swelling and deswelling. Although the fibers heat-set at  $100^\circ\text{C}$  were not able to withstand repeated cycling and were disintegrated in a few cycles, the fiber

heat-set at  $150^\circ\text{C}$  could withstand more than 50 cycles without any visual deterioration. However, the increased heat-setting temperature was found to have a negative effect on the equilibrium volumetric swelling as well as the response rate. As the heat-setting temperature was increased from 100 to  $150^\circ\text{C}$ , the equilibrium volumetric swelling value decreased from 42,800% to 6800% for AA50B ( $38\ \mu\text{m}$ ) and response time for deswelling increased is from instantaneous to 4 min. However, the mechanical properties were significantly improved. The tenacity improved to 6.6 times in swollen state and 1.4 times in deswollen state. The retractive stress was significantly increased to about 4.7 times. The increase in the mechanical properties indicated that the structure became more stable with heat-setting, possibly because of the formation of well connected domain morphology. The FTIR spectroscopy of the heat-set samples suggested that though samples had undergone some chemical changes in relation to disappearance of OH groups of COOH, there are no significant indications of formation of cyclised structure at these temperatures.

The study suggested that the control of physical morphology of the pH responsive structure may be the key in producing pH responsive fibers with desirable mechanical properties and pH response that may be suitable for their applications in smart textile, artificial muscles, and actuators.

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