

Influence of the Copolymer Architecture and Composition on the Response and Mechanical Properties of pH-Sensitive Fibers

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ABSTRACT: A series of copolymers based on acrylonitrile (AN) and acrylic acid (AA) with varying architecture and composition were synthesized using free radical polymerization. The distribution of monomers in the copolymer chains could be successfully controlled by regulating the addition of more reactive monomer (AA). Copolymers having nearly random distribution of comonomer moieties to block type distribution with different composition (10–50 mol % AA) were synthesized to investigate the effect of polymer architecture and composition on pH response and mechanical properties of resultant structures. These copolymers were solution spun from dimethylformamide-water system, drawn in coagulation bath, and annealed at 120°C for 2 h to make pH-sensitive fibers which were structurally stable without the need of chemical crosslinking. The fibers from block copolymers showed significantly better tensile strength (34.3 MPa), higher retractive forces (0.26 MPa), and enhanced pH

response (swelling 3890%) in comparison with fibers from random copolymer (13.55 MPa, 0.058 MPa, and 1723%, respectively). The tensile strength and retractive forces could be further improved to a value of 72 MPa and 0.36 MPa, respectively, by changing the composition of the block copolymer while retaining the swelling percentage similar to the random copolymer mentioned above. It is proposed that on processing to fibers, the block copolymers could form a segregated domain structure with separate domains of AA and AN, where AN domains were responsible for high structural integrity by providing connectivity among polymer chains, while AA domains showed improved response to changing pH of the environment. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3171–3182, 2007

Key words: pH-sensitive fiber; copolymerization; acrylic acid; acrylonitrile; architecture

INTRODUCTION

Recently, considerable research attention has been focused on responsive polymers because of their ability to respond, judge, and change their physical state drastically (undergo reversible change from a hydrophilic state to hydrophobic state) under small changes of external environment: temperature,¹ pH,² ionic strength, light, and electric field.^{3,4} These polymers are prime candidates for application in biomedical and engineering fields such as controlled drug delivery,^{5,6} artificial muscles, actuators,^{7–10} chemical separation, and biosensors.¹¹ So far they have been utilized in the gel form for diverse technological applications. While the basic concepts for design and synthesis of these environment sensitive hydrogels have been extensively studied, the potential applications of these hydrogels have not been

fully exploited because of their slow response, low efficiency, and poor mechanical properties. There have been several attempts to improve the response time by making porous gel structure; however, the mechanical properties could not be improved. The hydrogel response time strongly depends upon the diffusion rate of water which in turn depends on square of the gel dimensions.^{12,13} These limitations were expected to be overcome if the stimuli sensitive polymers could be processed into structurally strong unidimensional structures such as fibers. If such shape changing fiber could be produced they will make ideal candidates for artificial muscles and other robotic applications.

Recently, our group reported¹⁴ the development of temperature sensitive shape changing fibers. These fibers were solution spun from a specially designed series of linear temperature sensitive copolymers and were processed into fibers with oriented polymer chains to impart strength. However, these fibers were required to be chemically crosslinked to convert them into insoluble state. Though these fibers showed extremely fast response but they were found to be fragile when in swollen state.

In another approach,^{15–19} the existing poly(acrylonitrile) were modified to produce pH-sensitive fibers.

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In this approach, special acrylic fibers were thermally oxidized, where some of the CN groups underwent intra and interchain cyclization to provide the connected structure. The remaining CN groups were hydrolyzed or saponified to convert them into carboxylic acid groups. The cyclized acrylonitrile (AN) moieties remained unaltered even during hydrolysis and acted as a backbone rendering strength to the fiber while the hydrolyzed groups imparted pH sensitivity. Although this process appears to be suitable for the production of artificial muscles, it has some drawbacks. pH-sensitive fibers produced using this method are black in color, production rate is considerably slow, the parameters available for controlling the amount of cyclization and crosslinking in the fiber are limited, and producing fibers of varying chemical and physical architecture for tunable response is difficult.

Therefore, in this work, an alternate approach has been adopted to address some of the above drawbacks. In this approach, a series of pH-sensitive copolymers of controlled architecture and composition based on acrylic acid (AA) and AN were synthesized which when solution spun into fibers, showed good mechanical properties as well as enhanced pH response without the need of chemical crosslinking. It is suggested that fibers from such copolymers may have formed domains of AN and AA, where AN domains act as physical crosslinks and connect chains to allow transfer of the stresses along the fiber axis, while AA domains swell and deswell to give the desirable pH response. The size and distribution of domains of the two moieties were varied by altering the chemical architecture and composition of the copolymers and their effect on response and mechanical properties of fibers was investigated.

EXPERIMENTAL

Materials

AA and toluene were obtained from Merck India, Mumbai. AN was purchased from Central Drug House (p), New Delhi, and initiator α,α' -azobisiso-

butyronitrile (AIBN) from G.S.Chemical Testing Lab and Allied Industries, New Delhi. Solvents diethyl ether and dimethylformamide (DMF) from Qualigens Fine Chemicals, Mumbai, with the minimum assay of 99%. All chemicals were used without further purification.

Copolymer synthesis

Copolymer with enriched segments (blocks) (AA43B-AA10B)

Free radical copolymerization was carried out in a four-neck reactor in toluene at $65 \pm 1^\circ\text{C}$ under nitrogen atmosphere to produce a series of copolymers. The total monomer concentration was fixed at 20 wt %. The final AA content in the feed was varied from 10 to 42.7 mol %. Toluene (200 g) was taken in the reaction flask and degassed for 30 min. The initiator α,α' -azobisisobutyronitrile (0.057 mol %) was dissolved in AN and degassed for 30 min. It was then added to the reaction flask and the reaction was carried out for 30 min, before starting the addition of AA. The more reactive comonomer (AA) was degassed, and added intermittently in small doses (each dose of 0.9 g added in every 10 min) to the reaction mixture with constant stirring. The reaction was allowed to continue for an additional 30 min. The reaction mixture was cooled and then precipitated in excess diethyl ether to get white copolymer. The copolymers were washed three times with excess diethyl ether to remove traces of unreacted monomers and toluene, followed by repeated washing with excess acetone to remove any homopolymer of AA. The purified copolymers were dried in a vacuum oven at 60°C for 1 h. Gravimetric yield of the copolymers were about 35%. The various compositions along with copolymer codes are given in Table I.

Random copolymer AA43R

The random copolymer of AA and AN was also prepared using the above method except that the solution of AA was added continuously (drop wise) to the reaction mixture over a period of 1 h 30 min

TABLE I
Viscosity Average Molecular Weight and Composition

Copolymer	Acrylic acid content in the monomer feed (mole %)	Molecular weight (M_v)	Composition (AA mol %)	
			By acidimetry	By ^{13}C -NMR
AA43R	42.7	3.5×10^5	48.07	50.07
AA43B	42.7	3.6×10^5	46.05	48.86
AA40B	40	3.4×10^5	42.14	—
AA30B	30	3.2×10^5	33.00	34.56
AA20B	20	3.4×10^5	24.64	—
AA10B	10	3.1×10^5	12.35	—

with constant stirring. The reaction was allowed to continue for an additional 30 min, precipitated and purified as mentioned above. The gravimetric yield was found to be 33%.

Copolymer characterization

Intrinsic viscosity

The intrinsic viscosity of the copolymers was determined in DMF using Ubbelohde viscometer in a constant temperature bath at $30 \pm 0.1^\circ\text{C}$. Molecular weight was determined using Mark-Houwink relation $[\eta] = KM^\alpha$, where $\alpha = 0.75$ and $K = 20.9 \times 10^{-5}$ dL/g were taken from the literature.²⁰

Determination of copolymer composition and sequence length by ^{13}C -NMR spectra

The ^{13}C -NMR spectra of the copolymers were recorded under the standard conditions at 80°C in DMSO-d_6 on a Bruker DPX-300-MHz Spectrophotometer. 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. The composition of the copolymer was calculated by the formula.

$$\text{Mole percent of acrylonitrile} = \frac{I_{\text{CN}}}{I_{\text{CN}} + I_{\text{CO}}}$$

where I_{CN} is the intensity of CN and I_{CO} is the intensity of CO as noted from the ^{13}C quantitative NMR. The sequence length of the two monomers in the copolymer was determined by evaluating the triads obtained for the above two carbons as per the reported approach in the literature.²¹ These triad fractions were obtained as normalized areas of the respective resonance signals.

Acidimetric titration

The 0.5 wt % solutions of copolymers in DMF were titrated against 0.05N aqueous NaOH (standardized) solution using phenolphthalein as an indicator as per the reported method for the copolymers of AN, AA, and methacrylic acid.²²

Solution spinning of pH-sensitive fibers

The dope solution was prepared by stirring the purified and dried copolymer powder in DMF. The solutions were 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 water. The extruded fibers were drawn to a draw ratio of 2.0

before the coagulation was complete. The coagulated fibers were dried under taut condition in air at 30°C .

Heat treatment of the as-spun fibers

All dried fibers were heat-treated in an air oven at a temperature 120°C for 2 h. The fibers were placed in taut condition on a wooden frame and fixed at both the ends to avoid shrinkage during annealing. All characterization and testing were carried out on heat-set fibers.

Thermal shrinkage

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

$$\text{Shrinkage \%} = \frac{\text{IL} - \text{FL}}{\text{IL}} \times 100$$

Wide angle X-ray diffraction

WAXD spectra of the heat-set fibers were recorded by X' Pert PRO machine of PANalytical between 2θ of 10 and 35° in the reflection mode. The fibers were cut into small pieces and placed in powder sample stage for the spectroscopy.

Mechanical properties

The tensile strength of the heat-set fibers 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

All 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 the 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 in a

Lieca microscope. The length of the fibers was also measured before and after the transition. The equilibrium volumetric swelling % was calculated from the changes in diameter and length of the fibers.

Hysteresis

The hysteresis during transition was studied by subjecting the heat-set fiber samples initially to swelling by increasing the pH of the bath, and subsequently, to the deswelling by decreasing the pH of the bath, thereby, reversing the cycle. At each pH the fiber was placed for 30 min before the measurement was taken.

Rate of transition

For determining the rate of transition, a single heat-set fiber was placed vertically in a measuring flask with a small weight of 63 mg tied at the lower end of the fiber. The % change in length with time 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 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. 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 heat-set 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.

RESULTS AND DISCUSSION

The copolymers of AN and AA were produced by free radical polymerization. AN was chosen to impart fiber-forming properties to the copolymer while AA was selected to provide pH response. The

approach was to control the distribution of both AN and AA moieties in the polymer chains in such a way that small block segments of each are possible. If this could be attained, then the segments of AN moieties from different chains may come together (phase separate), crystallize and form various tie-points to provide strength to the formed structure, whereas the block segments of AA may provide pH response through ionization under suitable environment. The proposed structure is shown schematically in Figure 1. In this model, the relative proportions of the two monomers as well as size of the segments in polymer chains is expected to decide the domain structure of the copolymer, and therefore, its ultimate properties in the fiber form.

Synthesis of pH-sensitive copolymers

Ideal structure for the above copolymer would be pure block copolymer; however, it is nearly impossible to achieve pure block structure in 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 AA is 2.502 and AN is 0.495),²³ suggesting that simple copolymerization would lead to formation of homopolymer of AA. Therefore, it was decided to synthesize copolymers with enriched segments (rather than pure block) of the two monomer-moieties using regulated dosing of the more reactive monomer-AA during polymerization. AA was added in small doses separated by predetermined time

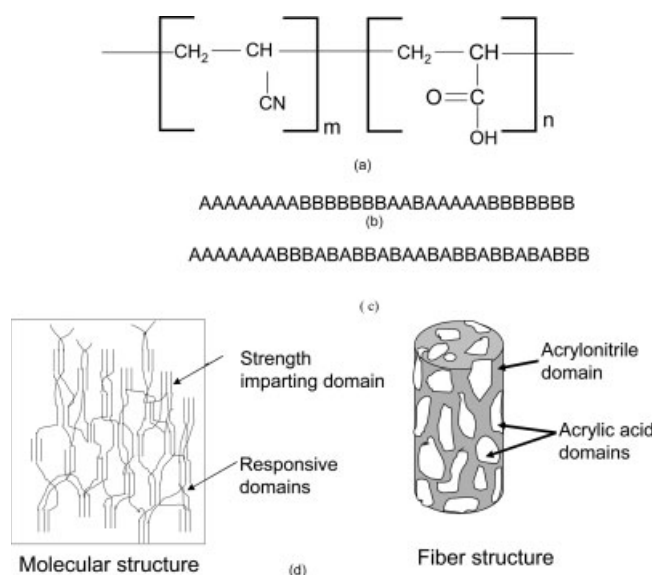


Figure 1 Proposed structure of the copolymers and fiber: (a) chemical structure, (b) architecture of AA43B, (c) architecture of AA43R, and (d) schematic of fiber structure depicting domain morphology.

intervals. It was hoped that whenever a dose of the AA was added it would get incorporated into the growing chains as a short blocks or enriched segments owing to its high reactivity ratio. During the interval between any two doses, scarcity of the AA monomer in the reaction medium would force the AN monomer to get incorporated as short blocks or enriched segments of AN moieties in the growing polymer chains.

If the dosing pattern is able to regulate the distribution of two monomers in enriched segments, their relative amounts will be able to control the segment size and their relative proportion in a bulk polymer.

To ascertain the effect of this approach on the properties of the resultant polymer and its fiber, a copolymer (AA43R) with a near random architecture was also polymerized. In this, AA was added continuously at a very slow rate into the polymerization medium to compensate for the high reactivity of the AA monomer with its lower concentration compared with AN at any given time inside the reactor. The proposed structure of the copolymers is also shown in Figure 1.

Architecture of the copolymers

The first objective of this study was to investigate whether the approach of regulated dosing is capable of providing block segments of the comonomer. For this ^{13}C -NMR spectra of AA43B (block copolymer) and AA43R (random copolymer) in DMSO-d_6 were analyzed. These are shown in Figures 2 and 3, respectively. In the copolymers, the carbonyl and

nitrile carbon resonances are around $\delta 174$ – $\delta 177$ and $\delta 119$ – $\delta 123$ ppm, respectively. These NMR spectra were analyzed to find the composition and the sequence length distribution of the monomer units. The spectral region around $\delta 40$ – $\delta 20$ ppm was assigned to aliphatic carbon resonance. The methine ($-\text{CH}$) signals of AA (B) unit appeared around $\delta 40$ ppm in both the cases and the methine ($-\text{CH}$) signals of AN (A) unit appeared around $\delta 30$ – $\delta 20$ in both the copolymers.

The overall comonomer compositions of the two copolymers, AA43B and AA43R, were found to be very similar and were calculated to be 51.14 mol % and 49.93 mol % of AN (A) moieties. The composition was also confirmed by acidimetric titration and the results are summarized in Table I.

The expanded ^{13}C -NMR spectra of the nitrile ($-\text{CN}$) and carbonyl ($-\text{CO}$) carbon resonances of the poly(acrylonitrile (A)-*b*-acrylic acid(B)) are shown as insets in Figures 2 and 3. To understand the distribution of A and B units in the copolymers, the triads of the two regions were analyzed quantitatively. The analysis was based on the splitting resulting from the monomer distribution effects only. In the nitrile (A) region, only two peaks were visible in AA43B. The signals around $\delta 119$ – $\delta 120$ and $\delta 120$ – $\delta 121$ ppm were assigned to AAA and BAA triads, respectively.

The addition of the AA (B) to the triad causes a downfield shift in the position of AN carbonyl (A) in AAB. In the carbonyl carbon region, the resonance of the signals was around $\delta 174.0$ – $\delta 174.7$, $\delta 174.8$ – $\delta 175.6$, $\delta 175.7$ – $\delta 176.4$ ppm. These change with the

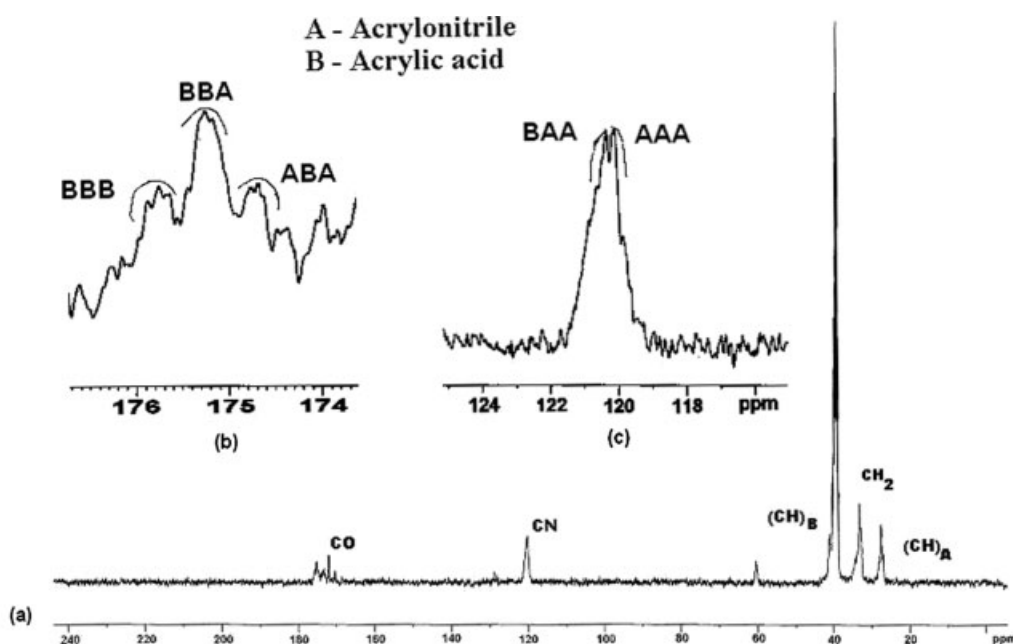


Figure 2 (a) ^{13}C -NMR spectrum of block copolymer AA43B in DMSO-d_6 , (b) the expanded carbonyl carbon region, and (c) nitrile carbon region.

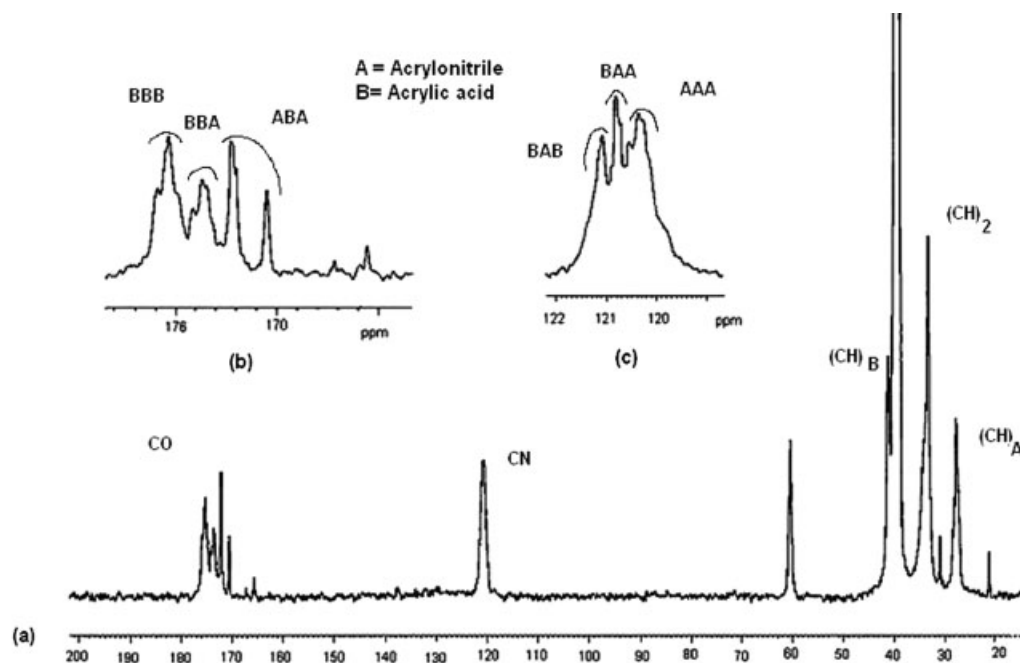


Figure 3 (a) ^{13}C -NMR spectrum of random copolymer AA43R in DMSO-d_6 , (b) the expanded carbonyl carbon region, and (c) nitrile carbon region.

copolymer composition and can be assigned to ABA, BBA, and BBB triad sequence, respectively. The relative fractions of various A and B centered triads were obtained for AA43B copolymer by integrating the area from the resonance signals.

Similarly, the triad composition of AA43R was analyzed and their relative fractions were evaluated by integration of the area under the signal peaks. The composition of the triads for the two copolymers is given in Table II. The table also shows the expected triad composition of a perfectly random copolymer of A and B with nearly 50 : 50 mol % comonomer compositions.

From the values of AA43B, one may infer that though the copolymer does not have large blocks of comonomers, it has short segments or enriched segments of A and B, and therefore, its structure may be considered near to the block type. This is also evident from the fact that there is no BAB component in the nitrile region and the composition of ABA is much less compared with that of BBB and BBA, in the carbonyl region. This implies that the approach of controlled dosing used in the experiment was effective in producing copolymers with separate enriched segments of AN and AA moieties. On the other hand, spectrum of AA43R (Fig. 3) shows the presence of all six types of triads in considerable amount. The fraction of AAA and BBB triads were very close to that of the theoretically expected fractions for a purely random copolymer. Only for BBA and ABA the compositions were a little different. Fraction of BBA was higher at the expense of fraction of ABA due to high reactivity of AA. On the ba-

sis of these results, AA43R could be safely considered to be a copolymer with high degree of randomness compared with the AA43B.

The copolymers AA43R and AA43B had nearly 50 mol % composition; therefore, the relative segment size of both the moieties is likely to be small, this is likely to form very small domains of nearly same size when the polymer is converted to a fiber

TABLE II
Composition of Triads in the Carbonyl and Nitrile Carbon Regions of ^{13}C -NMR Spectra of pH-Sensitive Copolymers

Copolymer	Sequence of triad	Triad composition (in fraction)	
		Experimental	Theoretical
AA43R	AAA	0.225	0.250
	BAA	0.466	0.500
	BAB	0.307	0.250
	BBB	0.242	0.250
	BBA	0.634	0.500
	ABA	0.137	0.250
AA43B	AAA	0.380	
	BAA	0.619	
	BAB	0.000	
	BBB	0.337	
	BBA	0.470	
	ABA	0.191	
AA30B	AAA	0.391	
	BAA	0.606	
	BAB	0.000	
	BBB	0.218	
	BBA	0.436	
	ABA	0.337	

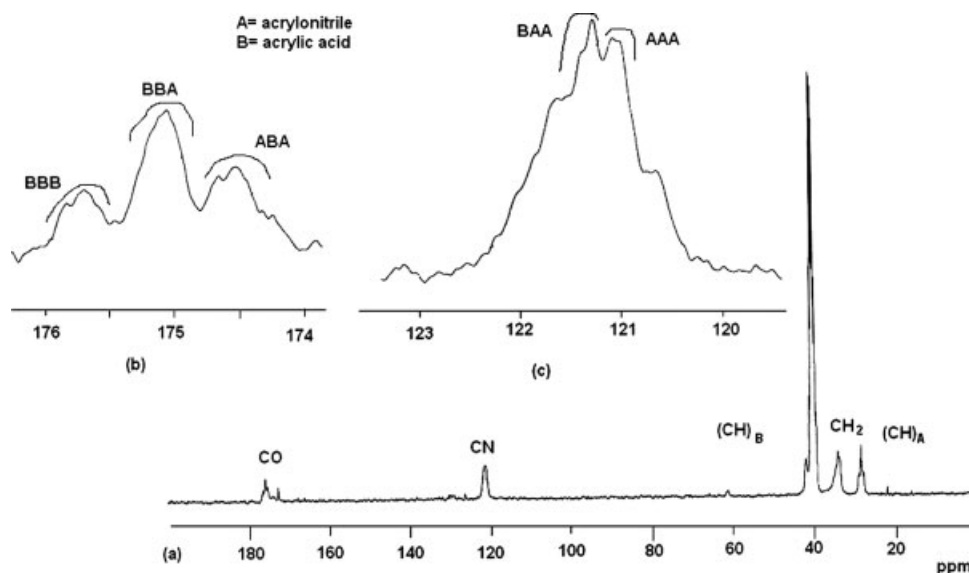


Figure 4 (a) ^{13}C -NMR spectrum of block copolymer AA30B in DMSO-d_6 , (b) the expanded carbonyl carbon region, and (c) nitrile carbon region.

form. To vary the relative sizes of the two types of domains, composition of the copolymer was varied by increasing the molar concentration of AN moieties from 50 to 90 mol %. Same procedure, which was used for the synthesis of AA43B, was used for all the copolymers AA40B-AA10B, i.e., regulated addition of the more reactive monomer AA in pre-specified doses separated by interval of time. If the adopted method of polymerization is able to incorporate higher mole % of AN, then it is expected that these copolymers will not only have small blocks of AA as before, but also very large blocks of AN. The composition of the copolymer was calculated by acidimetric titration and the mole percentage of AA in different copolymer is given in Table I. The compositions of the copolymers were found to be very close to the feed ratio of the two monomers.

The composition of AA30B was also calculated by ^{13}C -NMR, and the composition was found to be A (acrylonitrile) moieties 65.44 mol % and B (AA) moieties 34.56 mol %. The composition was very similar to the test results of acidimetric titration. The spectrum for AA30B is given in Figure 4. The compositions of the triads of the copolymer are given in Table II. It may be seen from the composition, that though the molar concentration of AA has reduced to just $\sim 35\%$, there is still a significant amount of AA moieties present as short blocks indicated by the presence of BBB and BBA signals.

Solution spinning of the stimuli sensitive fibers and heat treatment

Like polyacrylonitrile, the synthesized copolymers were soluble in DMF; therefore, they could be read-

ily solution wet spun using DMF as a solvent and water as a coagulant. The spun fibers were drawn by $2\times$ in coagulation bath and subsequently washed with water. To facilitate the formation of domains in the spun fibers, the drawn fibers were annealed in taut condition at 120°C for a period of 2 h. This temperature was chosen to avoid both the anhydride formation in AA segments (which starts at $\sim 170^\circ\text{C}$ and cyclization of the adjacent AN groups, which occurs at $> 220^\circ\text{C}$).^{23,24} Fine fibers with a diameter of $120 \pm 3 \mu\text{m}$ were obtained from all the copolymers.

Fiber morphology

Thermal shrinkage

Shrinkage in a fiber is indicative of the degree of stability of the morphological structure. The drawn and heat-set fibers produced from block copolymer AA43B had significantly lower shrinkage percentage compared with the fibers from random copolymer AA43R at the temperatures significantly above the glass transition temperature (Table III). The lower

TABLE III
Shrinkage Percentage of pH-Sensitive Fibers

Fiber	Temperature of silicone bath	
	100°C	130°C
AA43R	7.3%	20.0%
AA43B	4.76%	13.6%
AA40B	3.6%	13.2%
AA30B	2.7%	12.5%
AA20B	1.4%	10.41%
AA10B	0.0%	8.1%

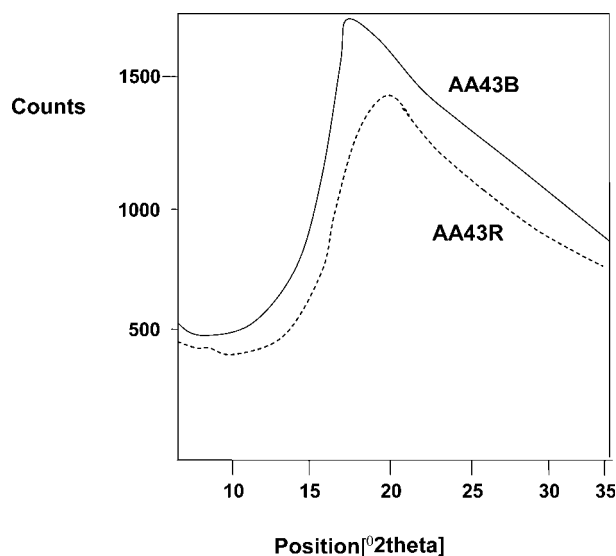


Figure 5 X-ray diffraction of the heat-set pH-sensitive fibers from AA43B and AA43R.

shrinkage in block copolymer fibers possibly indicates that on drawing and annealing, the AA and AN segments in the copolymer could phase separate and form domains resulting in a fiber structure which was more stable. Similarly the stability of all other fibers having different composition (AA10B-AA43B) was determined and is shown in Table III. In accordance to our model, increasing the molar concentration of AN in the copolymer had a positive effect in stabilizing the domain structure. This is evident from the decrease in thermal shrinkage of the fibers with increasing AN content.

X-ray diffraction

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, AA43B and AA43R, are given in Figure 5. The spectrum of fiber from AA43R shows a broad peak indicative of poor order in the fiber. However, in the case of fibers from block copolymer AA43B, a small but definite increase in the intensity at $2\theta = 17^\circ$ is observed which indicates the presence of ordered domains of polyacrylonitrile. The X-ray diffraction spectra of other fibers (AA10B-AA43B) are given in Figure 6. The copolymer AA10B, which has 90 mol % of AN, showed a very sharp reflection at $2\theta = 17^\circ$, although the increase in the concentration of AA resulted in broadening of the peak at $2\theta = 17^\circ$. Similarly, the peak at $2\theta = 29^\circ$ was comparatively sharper in case of AA10B, while with increase in AA content the peak became diffused. It was observed that as the

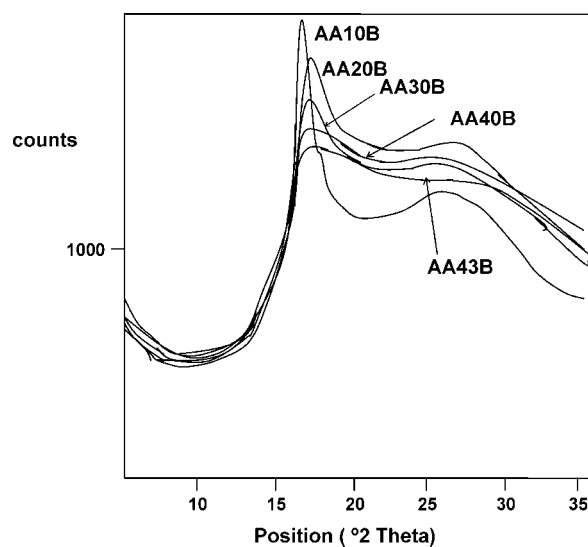


Figure 6 X-ray diffraction of the heat-set pH-sensitive fibers from AA43B-AA10B.

AN content in the copolymer was increased, the peaks at $2\theta = 17^\circ$ and 29° were better defined indicating the formation of large domains of AN in AN rich copolymers.

Mechanical properties

Figure 7 shows stress–strain curves for fibers AA43B and AA43R to compare the effect of comonomer distribution on mechanical property of the fibers in swollen and deswollen conditions. Figures 8 and 9 compare the stress strain curves of the fibers with different comonomer contents. As expected, all the fibers showed higher extension and lower tenacity in the swollen state compared to deswollen state. However, the tenacity shown by the fiber from AA43B was significantly higher (about 3–4 times) compared to that shown by the fibers from AA43R in both states (Table IV). This implies that the fibers

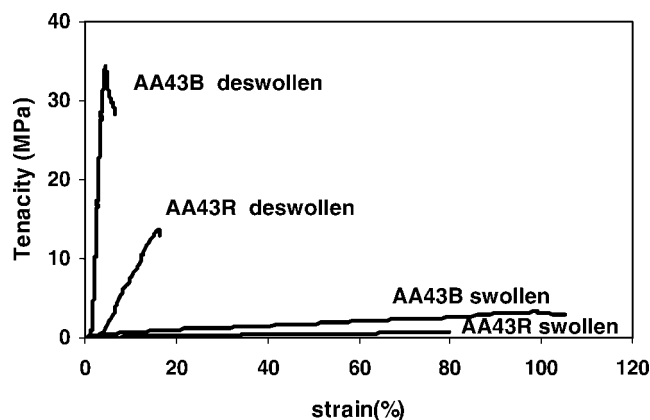


Figure 7 Stress–strain curves of the pH-sensitive fibers from AA43B and AA43R in swollen and deswollen states.

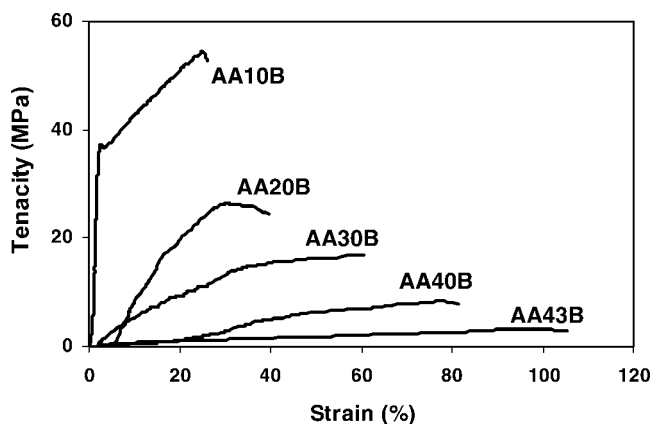


Figure 8 Stress-strain curves of the pH-sensitive fibers from AA43B-AA10B in swollen state.

from AA43B have a well connected polymer chain structure possibly due to the presence of polyacrylonitrile domains, and therefore, is able to bear higher stresses.

The mechanical properties can be further be improved by increasing the content of AN in block copolymer. As the concentration of AN was increased from 50% in AA43B to 90% in AA10B, the breaking stress was found to increase significantly by 1500% in swollen condition. Similarly, the breaking stress in deswollen condition also increased by ~ 1000%. This increase was likely to be due to the higher amount of AN, which is the strength imparting part in the fibers.

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 IV compares the maximum retractable stress along with the mechanical properties of all the fibers. Clearly, the fiber

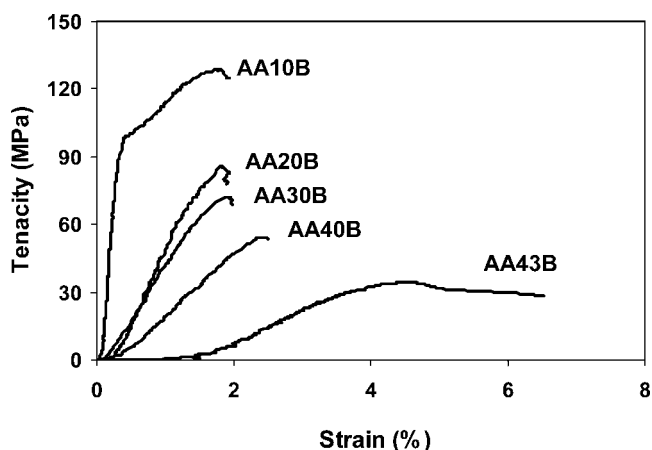


Figure 9 Stress-strain curves of the pH-sensitive fibers from AA43B-AA10B in deswollen states.

TABLE IV
Mechanical Properties of pH-Sensitive Fibers

Fiber	Retractive force during deswelling (MPa)	Breaking force in swollen condition (MPa)	Breaking force in deswollen condition (MPa)
AA43R	0.058	0.78	13.55
AA43B	0.26	3.31	34.29
AA40B	0.29	8.67	54.38
AA30B	0.36	16.84	72.04
AA20B	0.47	26.46	86.05
AA10B	0.59	54.44	128.52

from AA43B could retract under an opposing stress of about 500% higher than fibers from AA43R. This clearly signifies the improvement obtained by controlling the chemical architecture and physical morphology of the fibers. A further increase in the AN moieties in the fibers in the block copolymers AA10B-AA40B significantly improves the amount of applied stress that the fibers could resist during deswelling. As the concentration of AN moieties was increased from 50 to 90 mol %, the fibers showed an increase of about 200% in the retractive force. It is interesting to observe that the change in the morphology of the polymer from a random structure to block had a greater impact on the retractive forces than changing the amount of AN moieties (i.e., composition).

In general, a living skeletal muscle can contract and elongate about 30% in length and in the time scale of about 10^{-3} to 10^{-2} seconds. From the view point of application in artificial muscles, though the change in length of the fibers is sufficient for the practical application but the response time is still too slow to compare it with contraction speed of a living muscles. Again the maximum generating force in the living muscles is reported at 4–10 kg/cm² (0.4 MPa).

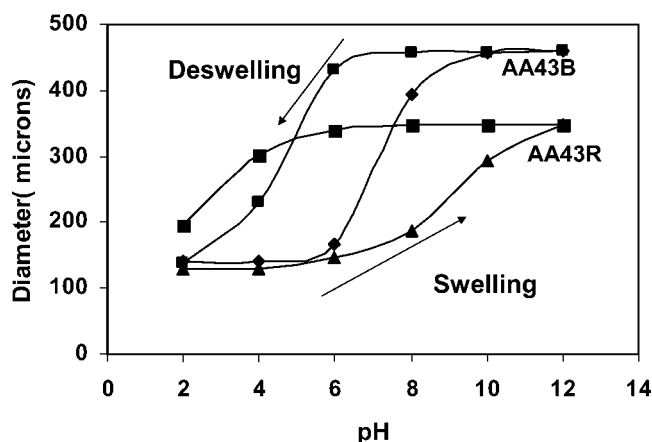


Figure 10 Diameter of pH-sensitive fibers as a function of pH of the external solution during swelling and deswelling cycles (a) AA43B, (b) AA43R.

TABLE V
Equilibrium Swelling/Deswelling Without Any Load

Fiber	pH 10			pH 2		
	Change in diameter %	Change in length %	Volumetric swelling %	Time of swelling (min)	Volumetric deswelling %	Time of deswelling (min)
AA43R	321	167	1723	50	150.28	15
AA43B	414	227	3890	45	100.15	5
AA40B	412	211	3601	45	100.35	5
AA30B	318	143.75	1508	50	101.59	7
AA20B	267.5	139	1012	50	101.23	8
AA10B	207.5	116	500	52	101.53	9

It could be considered that the contraction force of the fibers containing AA30B (30 mol % AA) is 0.36 MPa which is nearly equal to that of the strength of the living muscles.²⁵

Evaluation of transition properties

The pH-sensitive fibers showed swelling and deswelling in alkaline and acidic pH solutions, respectively. The pK_a value of polyacrylic acid is 4.28,²⁶ below pH 4.28 the 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 AA moieties in the polymeric chains in the fiber remain in the coiled state resulting in deswelling. As the pH is increased above the pK_a value, the fiber swells because the concentration of negatively charged carboxylate ions increases. When the carboxylate groups in the AA part of the polymer chain are fully ionized the effect of electrostatic repulsion is higher and the gel fibers expand significantly at about a pH of 10.

A hysteresis was observed in fiber from AA43B as shown in Figure 10 implying that the swelling did not start until the pH was increased above 6, and similarly in the reverse cycle, the deswelling did not begin until the pH was decreased below 5.5. How-

ever, the transition was sharp and was complete in a narrow pH range. On the other hand, in the case of fibers from AA43R, the hysteresis was significantly higher. The swelling started at a pH 8 and continued till a pH of 12 while the deswelling started at a pH 5 and the fiber did not achieve its original shape even at a pH of 2.

The volumetric equilibrium values and time of change for swelling and deswelling in free condition for all the copolymers (AA43B - AA10B and AA43R) are shown in Table V. These values were obtained for the fibers when swollen in slack conditions. The fibers from AA43B achieved equilibrium swelling in 45 min, with a volumetric change of about 3890%, whereas the equilibrium swelling of the fibers from AA43R was about 1730%. The change in length curves for swelling and deswelling for pH-sensitive fibers under a small tensile force of 0.05 MPa are given in Figures 11 and 12. From the figure, it can be seen that the fiber from AA43B has a significantly faster rate of change in length, and ultimately, a higher equilibrium value in swelling compared with the fiber from AA43R. The above results clearly show the great influence of polymer architecture on the swelling behavior of pH-sensitive fibers.

As expected, the equilibrium swelling must also depend on the AA content of the fibers. The equilibrium swelling was highest at 3890% for 50 mol %

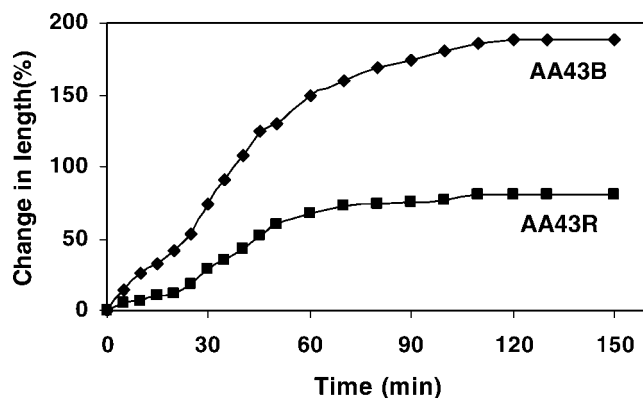


Figure 11 Rate of swelling of pH-sensitive fibers from AA43B and AA43R under a stress of 0.05 MPa.

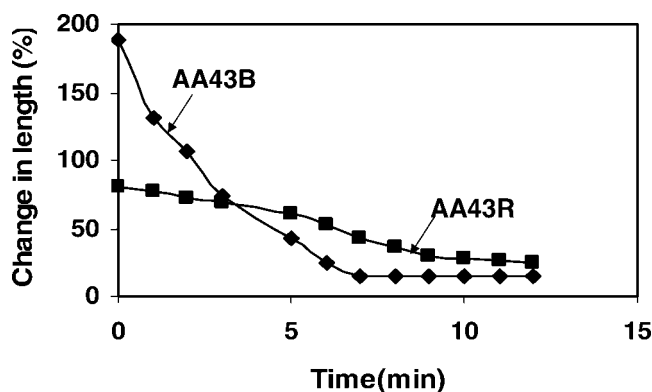


Figure 12 Rate of deswelling of the pH-sensitive fibers from AA43B and AA43R under a stress of 0.05 MPa.

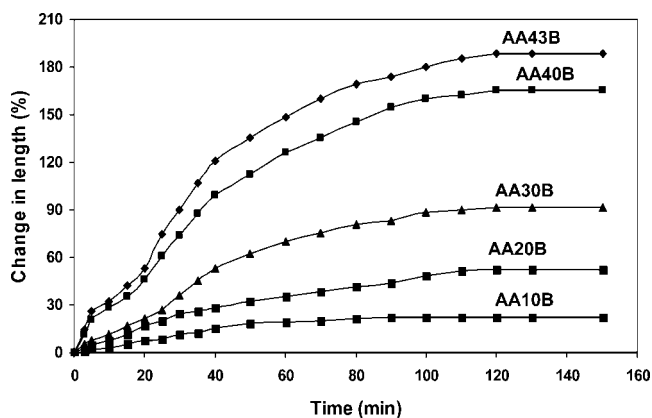


Figure 13 Rate of swelling of pH-sensitive fibers from AA43B-AA10B under a stress of 0.05 MPa.

fibers (AA43B) and was least for AA10B at 500%. Figures 13 and 14 show the rate of change of length of the fibers AA10B-AA43B with time under a small tensile force of 0.05 MPa for swelling and deswelling, respectively. Clearly, the rate at which fibers attained the equilibrium swelling/deswelling increased with the increase in the AA content of the copolymers.

Compared with gel-rods/discs, these fibers have shown significantly faster response and much higher swelling percentage because of the improved morphology and their much finer dimensions compared with gel rods or gel structures of polyacrylic acid in the literature.^{27–29}

Cyclability

The as-spun fibers from AA10B-AA43B and AA43R showed higher volumetric swelling in comparison with the drawn and annealed fibers. However, the as-spun fibers were not able to withstand repeated cycling and were disintegrated. The fibers on heat-setting at 120°C were stable to repeated cycling and did not show noticeable deterioration in strength even after ~ 15 cycles for AA43B. The cyclic swell-

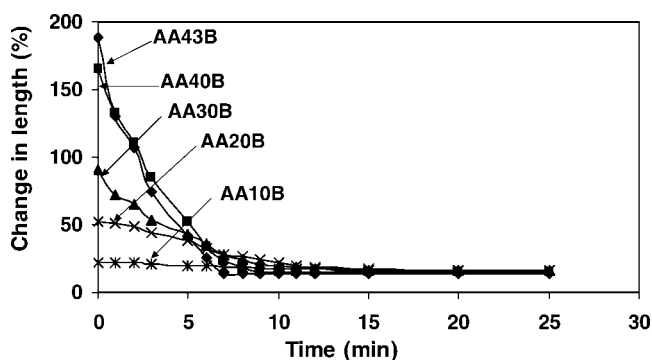


Figure 14 Rate of deswelling of the pH-sensitive fibers from AA43B-AA10B under a stress of 0.05 MPa.

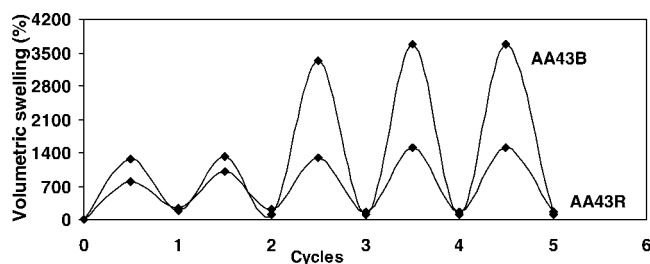


Figure 15 Cycles of swelling and deswelling of the pH-sensitive fibers from AA43B and AA43R.

ling/deswelling behavior of the two fibers (AA43B and AA43R) for the first four cycles is shown in Figure 15. The annealed fiber from AA43B exhibited excellent reversibility, however, the fibers from AA43R showed incomplete reversibility. During the first two cycles in fibers from AA43B, the swelling was in the range of ~ 1200 to 1300%. Subsequently, the swelling % 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 AA43R, initial two cycles showed swelling in the range of ~ 700 to 1000%, which increased only to ~ 1500% in the subsequent cycles. The swelling values obtained in cycling experiment were a little less than the equilibrium values shown in Table V because the fibers were kept at each cycle for only 30 min, which is less than the time required to reach the equilibrium values.

The cyclic swelling/deswelling behavior of the fibers (AA10B-AA43B) for the first four cycles is shown in Figure 16. The annealed fibers from all the copolymers exhibited excellent reversibility. During the first two cycles in fibers from AA40B, the swelling was in the range of ~ 1100 to 1280%. Subsequently, the swelling % increased to ~ 3100–3480%. Whereas, for AA10B the swelling was in the range ~ 227–242% in the first two cycles and was ~ 311–316% in the subsequent cycles. As mentioned above,

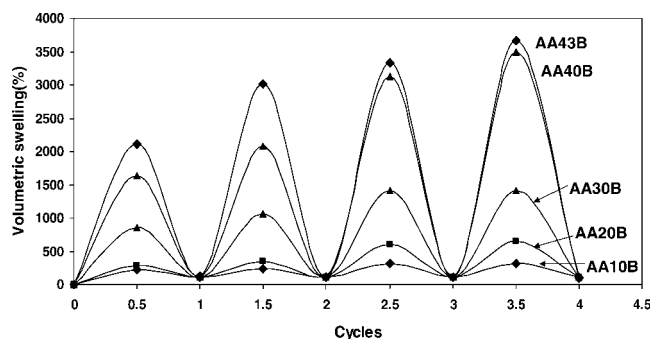


Figure 16 Cycles of swelling and deswelling of the pH-sensitive fibers from AA43B-AA10B.

the values indicated here are also not the equilibrium values.

CONCLUSIONS

pH-sensitive polymers, poly(acrylonitrile-co-acrylic acid), were synthesized using free radical polymerization by varying the AA content from 10 to 50 mol %. The architecture of the copolymers could be successfully controlled using the approach of regulated dosing of the more reactive comonomer, AA. Using quantitative ^{13}C -NMR, copolymer (AA43B) prepared with intermittent dosing of AA was found to have the block-type architecture, while the one (AA43R) prepared with continuous dosing of AA was found to have comparatively more random distribution of comonomer moieties.

The copolymers were converted to fibers by solution spinning and annealed at 120°C to get a stable morphology. The shrinkage and x-ray studies indicated that the block type copolymers, AA10B-AA43B, on conversion to fiber and annealing, could phase separate and form segregated domain morphology, while such a structure could not be formed in fibers with random distribution of comonomer moieties (AA43R).

The chemical architecture and physical morphology of the fibers as well as the comonomer content were found to have a significant impact on their mechanical properties, transition behavior and retractive forces during the transition. The fibers from block copolymer showed significantly higher strength, extensibility and retractive forces compared with fibers from random type copolymers. These properties could be further improved by increasing the AN content to up to 90 mol %. Swelling behavior was also superior for fibers from block type copolymers. The extent and rate of swelling was higher while the hysteresis was lower for fibers from block type structures. However, as expected, the extent and rate of swelling decreased with increasing AN content. As a result of these changes, the fibers from AA30B were able to show significantly better mechanical properties and retractive forces compared with fibers from AA43R while still maintaining the similar swelling ratio. The study suggests that the control of the chemical architecture and physical morphology of

the pH responsive structure may be the key in producing pH responsive fibers with both higher mechanical properties and pH response that is suitable for their applications in artificial muscles and actuators.

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