

Temperature Responsive Fibers with Anisotropic Transitional Behavior

Ashwini K. Agrawal, Manjeet Jassal, Amrish Vishnoi, Ninad S. Save

Department of Textile Technology, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

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ABSTRACT: Temperature sensitive polymer hydrogels are being extensively studied because of their potential applications in the biomedical, robotics, and chemical industries. However, major hurdles in their development have been their slow response, low efficiency (swelling/deswelling ratios), and poor mechanical properties due to difficulty in processing them into mechanically strong and fine structures. Fibers made from such polymers would be highly desirable. A temperature sensitive random linear copolymer of *N*-*tert*-butylacrylamide (NTBA) and acrylamide (Am) was synthesized by the solution polymerization method, using regulated dosing of comonomers. Using a novel approach, a high molecular weight poly(*N*-*tert*-butylacrylamide-*ran*-acrylamide::27 : 73) has been converted to insoluble strong fibers with fineness of 30–50 microns by solution spinning, drawing, and subsequent crosslinking. Fibers were solution spun in acetone using a 14%

copolymer solution in acetic acid with polycarboxylic acid as a crosslinker and sodium hypophosphite as a catalyst. The crosslinks were formed, subsequent to drawing, between reactive amide side groups of the acrylamide moiety of the polymer and the carboxylic acid group of the crosslinker by thermal treatment at 160°C. The transition temperatures of the crosslinked fibers were found to shift towards the lower temperature from 37°C (in linear copolymer) to 22–25°C. These engineered fibers display sharp temperature sensitivity, extremely high reversible change in dimensions (1000% in diameter and ~70% in length), and extremely fast response time (< 20 s for expansion and < 2 s for contraction). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 681–688, 2005

Key words: stimuli sensitive polymers; fiber; processing; *N*-substituted acrylamide; hydrogels

INTRODUCTION

Smart or intelligent polymers that respond to their environment by changing their shape or properties are becoming an area of critical research worldwide. These polymers are prime candidates for a variety of applications^{1–16} in biomedical and engineering fields, such as controlled drug delivery, chemical separation, and tissue culture.

Stimuli sensitive polymers (SSP) hold great promise in the above-mentioned applications because of their capability of changing their physical properties when a small change (stimulus) in temperature, pH, stress, or electrical field occurs. In temperature sensitive polymers, transition occurs at a particular temperature known as the Lower Critical Solution Temperature (LCST). These polymers have both hydrophilic and hydrophobic structural moieties. Below LCST, the hydrophilic interaction dominates and the polymer becomes soluble in water, while above this temperature hydrophobic interactions predominate and the polymer becomes insoluble in water.¹⁷ These polymers find applications when polymerized in gel form. The

gels change shape by swelling in water below the transition temperature and deswell above the transition temperature.

Although many temperature sensitive polymer-hydrogels have been studied as of this date,^{1–22} they have yet to be utilized for any of the potential applications. In polymerized hydrogel form, their major drawback has been slow response, poor efficiency, and weak mechanical properties.^{23–27} These limitations were expected to be overcome if SSP materials could be processed into structurally strong thin films or preferably fine fibers (i.e., uni-dimensional structures). Fibers are flexible as they have high aspect ratio (i.e., length to diameter ratio) and have better functionality as they have large surface to volume ratio. They are mechanically strong and can be converted into a variety of two and three dimensional flexible structures such as ligaments (artificial muscles), woven fabrics, non-woven webs, and membranes. A smart fiber that changes shape with temperature stimulus would not only enable development of the above applications in a desirable manner, but also open up a wide window of new applications in areas such as intelligent textiles (both apparel and technical applications), robotics, and aerospace, etc.

Unlike gel-rods or films, SSP fiber is expected to have a large gel surface to volume ratio that would allow easy diffusion of water. Therefore, SSP fiber is likely to show fast transition and better utilization of functional

Correspondence to: A. K. Agrawal (ashwini_agrawal@hotmail.com) and M. Jassal (manjeetjassal@hotmail.com).

sites available inside the structure. SSP fibers would also have an advantage over grafted SSP membranes²⁸ in that they would not require support of inactive (passive) substrate, and therefore, would be able to show much higher functionality per unit weight of the material used. However, the technology of fiber spinning is complex and confined to only a few known non responsive polymers. Therefore, it would be highly desirable to find methods to produce fibers from temperature sensitive polymers.

In this study, we have shown a commercially feasible approach of processing temperature sensitive polymers into mechanically strong smart fibers showing extremely fast and greatly enhanced transition properties.

EXPERIMENTAL

Materials

Tert-butanol, glacial acetic acid, methanol, sulfuric acid, acetone, and citric acid (CA) were obtained from Qualigens Fine Chemicals, Mumbai, India. Acrylamide and ammonium persulfate were obtained from Merck (India), Mumbai, India. Acrylonitrile and sodium hypophosphite were purchased from GS Chemical Testing Lab and Allied Industries, Mumbai, India. 1,2,3,4-Butane tetracarboxylic acid (BTCA) was procured from Lancaster Synthesis, England. All the chemicals were with minimum assay or exceeding 99% and were used without further purification.

Copolymer synthesis

Monomer synthesis

NTBA was synthesized by the Ritter's reaction, as reported previously.²⁹

Polymerization

Free radical polymerization reaction was carried out in methanol at $50 \pm 1^\circ\text{C}$ in the presence of 0.1 mol % ammonium persulfate. The monomer concentration was fixed at 2 mol L⁻¹. NTBA (152.4 g) and 25% of the calculated Am (total amount 127.8 g) were dissolved in methanol (1500 mL). The monomer solution was degassed for 45 min, and then the initiator was introduced. The balance amount of acrylamide was introduced in three doses (31.95 g each dose) after every 45 min interval. Each dosing was accompanied by degassing with nitrogen. The evaporated methanol was allowed to reflux back into the reactor. The polymerization was continued for about 12 h. A highly viscous reaction mixture was obtained. After polymerization the reaction mixture was cooled and the copolymerized product was precipitated in acetone while stirring vigorously. The purified copolymer was dried in

a vacuum oven at 120°C. Gravimetric yield for the polymer was found to be ~ 60%.

For comparison, crosslinked copolymer gel of the above composition was prepared using MBA (1.13 mol %) along with monomers. After polymerization, the gel was removed, precipitated, washed, dried, and cut into discs of about 2 mm thickness.

Copolymer characterization

Determination of composition by FTIR²¹

The FTIR spectra were recorded on a Perkin-Elmer BX II spectrophotometer. The intensity of the peak at 1225 cm⁻¹ (due to the -C(CH₃)₃ group) was normalized using the C=O stretching peak of both NTBA and Am at 1665 cm⁻¹. The normalized height of the -C(CH₃)₃ peak of the copolymer at 1225 cm⁻¹ was compared with that of the normalized peak of PNTBA, to obtain the incorporation of NTBA in the copolymers.

Solution spinning of SSP fibers

A 14% solution of linear copolymer (NTBA : Am::27 : 73) was prepared by stirring the purified and dried polymer powder in glacial acetic acid. A predetermined quantity of selected crosslinker such as butyl tetracarboxylic acid (BTCA) or citric acid (CA) and catalyst (sodium hypophosphite, 0.3 wt %) were added to the above solution. The solutions were kept for a day at the room temperature to allow deaeration before spinning. Fibers were extruded using a syringe type monofilament extruder into a coagulation bath containing acetone at room temperature.

The fibers after complete coagulation were taken out and mechanically drawn at draw ratios up to 6. The drawn fibers were dried under taut condition in air, and subsequently cured at 160°C for 25 min to obtain insoluble fibers.

Fibers were obtained using varying crosslinker content as detailed in Table I. The crosslinker content was calculated theoretically (given as wt % in solution) to correspond to certain mole % of available amide groups as per the monomer feed. The effective concentration of the crosslinker with respect to acrylamide in the actual copolymer is also shown.

Determination of transition temperatures for the SSP fibers

Transition temperature for the fibers was evaluated by immersing the samples in double distilled water maintained at a particular temperature. The temperature was varied over a range from 6 to 80°C, and equilibrium swelling in terms of diameter and length at each temperature was determined. The samples were kept for 15 min at each temperature to ensure the attain-

TABLE I
Crosslinker Concentrations Used for Preparing Spinning Dope

SSP fiber crosslinker concentration	BTCA concentration (wt % in solution)	BTCA (mol % of carboxylic groups based on available amide groups)
Low	2.631	37.9
Moderate	4.385	63.2
High	6.139	88.4

ment of equilibrium. This equilibrium time of 15 min was arrived at by performing preliminary experiments. The transition temperature was determined by observing the change in dimensions (length) against temperature for the crosslinked fibers.

Transition kinetics of crosslinked SSP fibers

The rate of transition of the crosslinked fibers was investigated by immersing the samples in distilled water at low temperature, significantly below the transition temperature ($\leq 6^\circ\text{C}$). The increase in length of the sample was measured against time.

After ensuring the attainment of equilibrium, the kinetics of deswelling was studied (as mentioned above) by immersing the swollen fibers in a water bath maintained above the transition temperatures (80°C). The measurements were continued until equilibrium length was achieved in the collapsed state of the fibers.

Thermoreversibility of crosslinked SSP fibers

The reversibility of the transition with temperature was studied for the SSP fibers, by placing them in water alternately at temperatures of 6°C and 80°C , for four cycles.

RESULTS AND DISCUSSION

Methodology of fiber formation

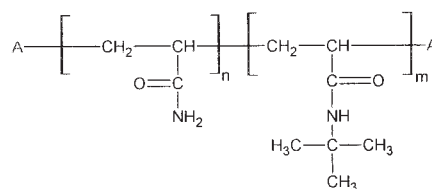
As discussed above, it was desirable to convert SSP into thin fibers. However, SSP synthesized as gels are not processable into fibers due to their crosslinked structure. Therefore, an alternate approach was necessary for producing SSP fibers that are stable during use. In this approach, a high molecular weight, linear SSP was synthesized, processed into fibers, and subsequently, crosslinked to make insoluble (stable) fibers. Though the approach appeared to be simple at the onset, it was a challenging proposition because it required investigations on different aspects of SSP as mentioned below:

- i. Synthesis of a suitable SSP system that had transitional response tunable in a wide range of temperature.

- ii. Production of SSP in high molecular weight, suitable for its conversion into oriented high strength fibers.
- iii. Development of a compatible solvent-nonsolvent system that could be used in solution spinning of SSP.
- iv. Development of a method of stabilizing (making insoluble) fibers, for example, the possibility of carrying out chemical crosslinks among polymer chains after spinning that would not compromise responsive behavior of the resultant fibers.

Synthesis of suitable SSP copolymers

The approach adopted to obtain processable stimuli sensitive polymer (SSP) was to first synthesize a suitable copolymer with at least one monomer having a free reactive site. This site could be later used for crosslinking, once the copolymer had been converted into a desirable form of fiber. However, the main challenge in doing so was the selection of an appropriate pair of comonomers that would give not only a reactive group but also a wide range of tunable transition temperatures. It is known in the literature^{30–36} that the transition temperature of a polymer may be increased by increasing the hydrophilic content of the polymer; alternately, it may be decreased by increasing the hydrophobic character. Therefore, by using two monomers, one hydrophilic and the other hydrophobic, polymer systems with tunable transitions can be obtained. Therefore, two monomers, *N-tert*-butyl acrylamide (NTBA) and acrylamide (Am), were selected for synthesizing the SSP copolymer (Structure 1).



Structure 1

NTBA was selected because it is a highly hydrophobic monomer that on homopolymerization gives a theoretical LCST of about 5°C , while acrylamide was se-

lected because it is a highly hydrophilic monomer with theoretical LCST of its homopolymer at above the boiling point of water. Varying molar composition of the two monomers was expected to produce copolymers with different transition temperatures, as may be desired in a particular application.

Several copolymers of the NTBA and acrylamide were prepared by varying the feed ratio of the monomers.^{35,36} Free radical polymerization was carried out in methanol using regulated dosing of the more reactive monomer, acrylamide. This ensured random copolymerization of the two monomers to give a single sharp transition. Copolymers with high molecular weight suitable for fiber formation could be synthesized by optimizing the initiator concentration, polymerization temperature, and time. The actual composition of the copolymer was evaluated using FTIR and was found to be different from the feed ratio used. The transition temperature of the copolymers (linear and gel) was found to vary in a range from 2 to 58°C by varying the composition of acrylamide from 25 mol % to 89 mol %.^{35,36} One of the copolymers obtained using a feed ratio of 40 : 60 (NTBA : Am) was found to have 27 mol % NTBA and a transition temperature of 37°C. This polymer was selected for conversion into the fibers because it had a low transition temperature and yet an adequate amount of acrylamide moieties for crosslinking at a later stage.

As mentioned earlier, to achieve stabilization after fiber spinning, it was desired to have a reactive site with which crosslinks could be formed among the polymer chains. Towards this, the amide side group in the acrylamide moiety was considered. To the best of our knowledge, this amide group had never been used earlier for carrying out crosslinking reactions because of its low reactivity. However, the crosslinking reaction between the amide side group of the copolymer and polycarboxylic acid compounds as crosslinkers was found to be feasible in the presence of sodium hypophosphite as a catalyst. The mechanism of crosslinking using NMR and FTIR techniques has been separately investigated and recently published by our group.³⁷

Solution spinning of fibers

Solution wet spinning was selected as the method of choice for forming fibers because *N*-substituted polyacrylamides do not show melting. Copolymer poly(NTBA : Am::27 : 73) was soluble in water at temperatures lower than 37°C. However, water was not found to be an appropriate solvent for spinning mainly because of two reasons. First, because of the high viscosity of the polymer solution in water, higher solid content could not be added in the spinning dope. Secondly, the highly viscous dope was difficult to deaerate, which eventually lead to fiber breakages during spinning.

Several known miscible chemicals were scanned for forming a solvent and nonsolvent pair for the above polymer. Glacial acetic acid and acetone were found to be the appropriate solvent and nonsolvent, respectively, for carrying out solution spinning. The above copolymer (27 : 73) could be readily dissolved in high concentrations (10–20 wt %) in glacial acetic acid. It was easier to deaerate and spin into a coagulation bath containing acetone. The only problem faced with using acetone was its high volatility. If the freshly spun fiber was taken out of the coagulation bath before complete removal of the acetic acid, evaporation of acetone (nonsolvent) lead to re-dissolution of the fiber in trapped traces of acetic acid (which is the solvent).

Freshly coagulated fiber could be subjected to mechanical drawing in the coagulation bath. Significant draw ratios of up to six (mechanical extension up to 500%) could be imparted, allowing orientation of the polymer chains in the resultant fibers. Drying of drawn fiber in taut condition was found to be necessary to dimensionally stabilize the spun fiber structure. The fibers could be spun in fine diameters in the range of 30–50 microns. The dried fibers could be readily cured at high temperature (~ 160°C) to obtain insoluble fiber. Curing could be accelerated at higher temperatures, for example, at 200°C, the curing time reduced from 25 min to 3–5 min. The amount of catalyst was found to influence the curing time. However, no attempt was made to optimize the catalyst concentration or curing conditions.

Availability of polycarboxylic acid (BTCA or CA) as a crosslinker and sodium hypophosphite as a catalyst inside the spun fiber resulted in formation of crosslinks among the polymer chains. BTCA with four carboxylic acid groups was found to yield better stabilization of the spun fiber compared to citric acid, which has three carboxylic acid groups. Fibers with different crosslinker concentrations were prepared to study the effect of crosslink density on their transition behavior. Three concentrations of crosslinkers were used, which were calculated based on moles of available amide side groups in the copolymer: low (37.9 mol %), moderate (63.2 mol %), and high (88.4 mol %). A typical optical micrograph of the cured SSP fiber with 37.9 mol % crosslinker is shown in Figure 1(a).

Shape changing behavior of SSP fibers

The SSP fibers were found to change shape (with respect to both diameter and length) when immersed in a water bath maintained at different temperatures. The cured fiber was placed at 6°C for 15 min and then transferred to 80°C for 15 min. This was repeated several times. This wide temperature range was taken just to ensure experimental inclusion of all transition states. However, as discussed in the later section, the transition was sharp and occurred reversibly in a very narrow range of temperature (3–4 degrees). The fibers

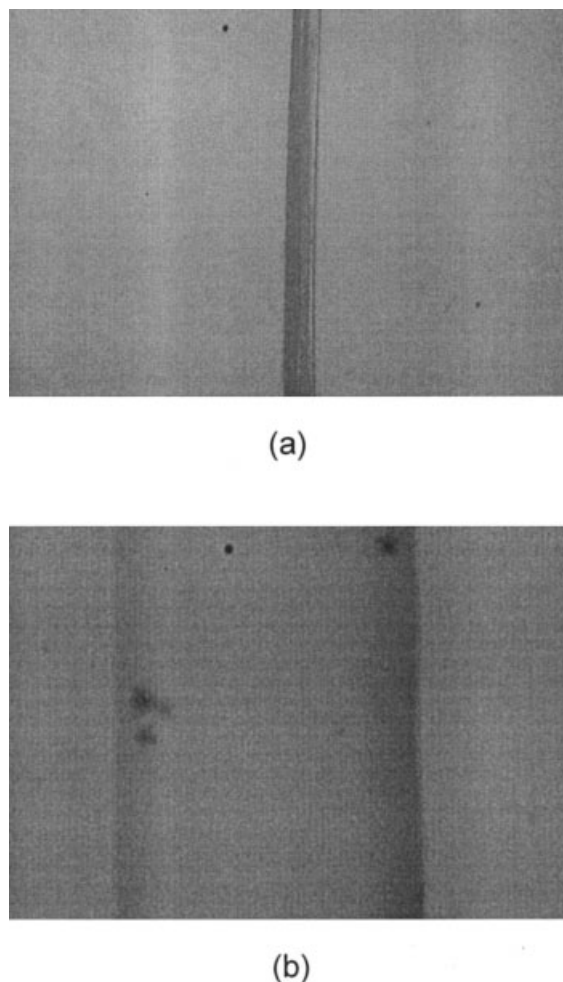


Figure 1 The optical microscopic view at $100\times$ of SSP fiber produced from poly(NTBA : Am::27 : 73) copolymer with 37.9 mol % crosslinker concentration: (a) as-spun and cured fiber; (b) fiber at equilibrium swelling in water at 6°C .

swelled at low temperature and collapsed at high temperature, showing clear transition in shape and size between the two temperatures. Figures 2(i), (ii), and (iii) depict the change in diameter, length, and volume of the fiber, respectively, in each cycle of swelling and deswelling. The increase in diameter was found to be about 550% in the first cycle and 950% from the second cycle onwards for fiber with low (37.9 mol %) crosslinker concentration. Figures 1(a) and 1(b) show the change in diameter of this fiber as seen under an optical microscope at a magnification of $100\times$.

Similarly, the fibers showed a dramatic increase in their length by about 60–70%. The volumetric change in shape amounted to 178 times (17,800%) from the dried state. The change in volume between every swelling and deswelling was about 18 times (from 1000% to 17,800%) for the fiber with low crosslinker concentration. The fibers did not expel water completely at the collapsed state. This may be due to trapped water inside the phase separated structure.

The diameter increase was about 550% for the SSP fiber with high (88.4 mol %) crosslinker concentration. Even for this SSP fiber, the volumetric change was 3500 to 7500% between the collapsed and swollen state. These values clearly indicated very high functionality of the SSP in fiber form. Lower swelling ratio obtained in this fiber was because of compact structure with a high degree of crosslinking.^{19,22} The deswelling was also to a lower extent probably again due to a higher degree of crosslinking, which led to a higher amount of trapped water inside the structure.³⁸

The anisotropic change in dimensions of the fiber (higher change in diameter than length) on swelling clearly indicated anisotropic structure of the fiber, where chains are preferentially oriented in the direction of the fiber axis. This is depicted in Figures 2(iv) and (v), where two fibers having moderate concentration of crosslinker (63.2 mol %) prepared using different draw ratios are subjected to swelling-deswelling cycles. As can be seen from the figures, the fiber with higher drawing leads to a larger change in diametric swelling. This is because during swelling, the water is accommodated between the parallel polymer chains giving rise to higher diametric swelling in fiber with higher orientation. An opposite effect was seen in the longitudinal swelling for the same reason.

The swelling percentage of SSP fibers were compared to those of the copolymer hydrogel disc (2 mm thickness) produced using the same composition of the copolymer. Table II lists the values of both the SSP fiber, films,³⁵ and the SSP-hydrogel disc. Clearly, it can be seen that the swelling value obtained in the fiber was orders of magnitude higher than that obtained in the films and hydrogel disc. The swelling ratio of 178 obtained for SSP fiber, to our knowledge, is possibly the highest reported among all studies. This opens up vast applications of these fibers in drug delivery where high loading is of great significance.

The lower increase in size of the SSP fibers in the first swelling cycle after curing may be due to limited opening up of the structure. Thereafter, the fibers could be repeatedly swollen and collapsed to the same extent in all subsequent cycles. This indicated high stability of the fiber structure in repeated cycling of transitions.

Rate of transition in SSP fiber

As mentioned earlier, one of the major drawbacks of the SSP polymer-gels is their slow rate of transition. Normally in polymer-gels, this is of the order of several hundred minutes. Figure 3(i) shows the rate of change in shape for the SSP fiber. The transition rate for all the swelling cycles was extremely fast and was found to be complete in about 20 s. Equilibrium was achieved in about 20 s, while half of the change ($\sim 50\%$) was nearly immediate and occurred in the first 5 s. Compared to swelling, the deswelling was still faster and the entire

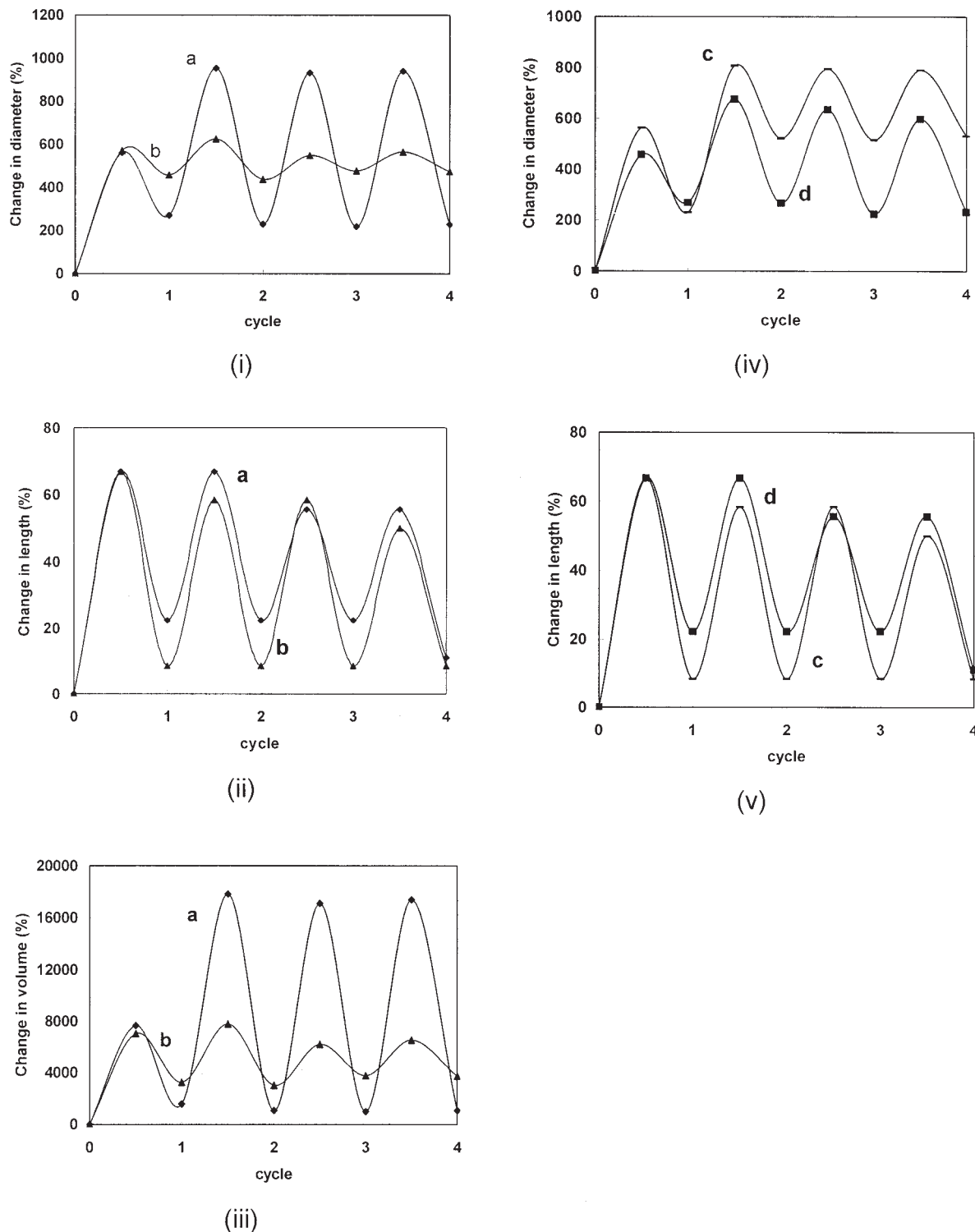


Figure 2 Change in shape of different SSP fibers when subjected to swelling-deswelling cycles between 6°C and 80°C, respectively: (a) fiber with 37.9 mol % crosslinker concentration; (b) fiber with 88.4 mol % crosslinker concentration; (c) fiber with 63.2 mol % crosslinker concentration with draw ratio of 6; (d) fiber with 63.2 mol % crosslinker concentration with draw ratio of 3.

change occurred spontaneously (<2 s). Diffusion of water out of the structure during collapsing appears to be a favorable process unlike swelling. This may be due to higher diffusion rates at higher temperature used for deswelling and also positive pressure provided by the swollen structure under stress.³⁸

The rates of transition for different SSP structures such as gel disc, films,³⁵ and fiber, obtained from the same copolymer are compared in Table II. The time for 50% transition was found to reduce dramatically from 75 min for the gel disc to under 5 s for the SSP fiber. Interestingly, thinner film (coated on a glass slide) of

TABLE II
Transition Properties of SSP Structures

NTBA : Am (27 : 73) copolymer with 37.9 mol % crosslinker conc.	Equilibrium swelling %	Response time (during swelling)	
		For 50% change (sec)	For 100% change (sec)
Hydrogel* (2 mm thick)	490	4500	9000
Film on glass slide (0.2 mm thick)	1850	240	1200
Film on glass slide (10 μ thick)	3000	\approx 30	300
Fiber (30 μ diameter)	17800	< 5	20

*Crosslinker concentration of 1.13 mol% MBA w.r.t. total monomer in the feed.

10 microns exhibited considerably slower transition rate than the fiber of 30 microns. The fast transitions obtained in the SSP fiber was most likely due to the large surface to volume ratio provided by the fine fiber structure. This enabled faster diffusion of water in and out of the structure at the transition temperature. Also, faster diffusion in the SSP fiber compared to thicker

films may also be due to lower build-up of swelling stresses inside the finer fiber structure.

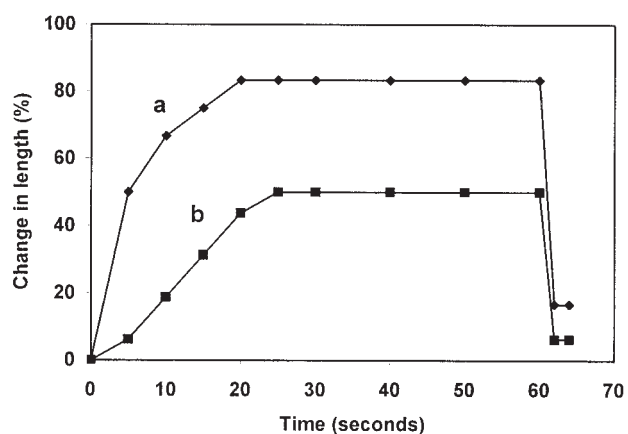
Temperature of transition of SSP fiber

The transition temperature of the fiber was determined by slowly scanning the change in length of the fiber with temperature. Figure 3(ii) depicts the transition curves of the SSP gel-disc and SSP fiber. The transition temperature of the SSP fiber was found to shift to a lower temperature of about 28°C for SSP fiber with low crosslinker (37.9 mol %) concentration compared to the transition temperature of the copolymer gel-disc (37°C). Unlike the gel-disc, where crosslinking had been carried out during polymerization using a divinyl crosslinker comonomer, the crosslinking reaction in the fiber was carried out using polycarboxylic acid compounds at the amide side groups. This may have lowered the hydrophilic character of the copolymer in the fiber compared to that of the gel disk, resulting in the above transitional shift. This argument is further supported by the fact that the transition temperature was found to shift to a still lower value of 26°C with increase in crosslinker concentration (88.4 mol %). Another important observation was that the transitions were sharp and the majority of change occurred within a temperature range of 3–4 degrees. No significant hysteresis was observed in swelling and deswelling cycles.

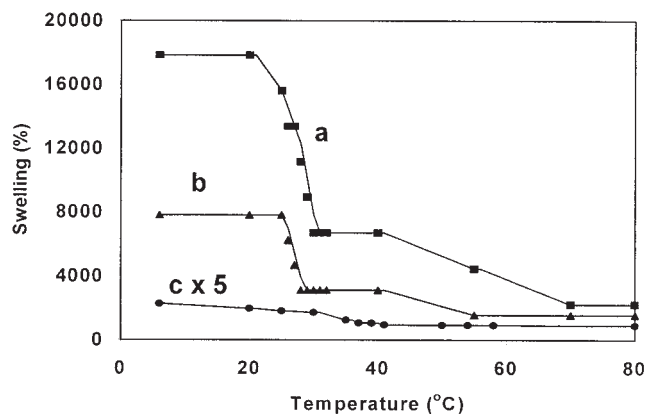
Mechanical properties of SSP fibers

The mechanical properties of the prototype fibers were evaluated by the constant rate of loading method. The results are shown in Table III. The values of strength obtained for SSP fiber were reasonably high. In comparison, gel disc structures were fragile. The SSP fiber prepared in this study could hold weights in excess of 1000 times their own weight (based on the weight of 1 m length).

As-spun fibers were found to be stronger (0.136 GPa for sample with 30% crosslinker concentration) than the cured fibers (0.102 GPa). However, on conditioning in a humid environment, the strength of the uncured fiber was found to fall to a much greater extent



(i)



(ii)

Figure 3 (i) Rate of transition and (ii) transition temperature of SSP fibers: (a) fiber with 37.9 mol % crosslinker concentration; (b) fiber with 88.4 mol % crosslinker concentration; (c) Copolymer gel of the same composition shown for comparison.

TABLE III
Mechanical Properties of SSP Fiber

Fiber sample	Tensile properties (GPa)	
	Low crosslinker conc.	High crosslinker conc.
As spun (dry)	0.136	0.022
As spun (conditioned*)	0.031	0.018
Cured (dry)	0.102	0.038
Cured (conditioned*)	0.084	0.021

* Conditioning was carried out at RH 95; 30°C temperature for 24 h.

(0.031 GPa) than that of the cured samples (0.084 GPa). The fall in strength is due to absorbed moisture that results in lowering of intermolecular forces between the chains. Among the cured fibers, the strength of the fiber was found to drop with the increase in crosslinker concentration.

CONCLUSION

Synthetic fibers and filaments find widespread use because they are mechanically strong and can be converted into a variety of two and three dimensional flexible structures. However, the existing fibers are passive. If a fiber could change shape with external stimulus such as temperature, it would enable development of intelligent structures for producing environment adaptable textile, artificial organs for biomedical, and robotic applications. In this study, a smart fiber/filament has been produced from temperature sensitive polymer that changes shape quickly and reversibly with small changes in the environment temperature. The temperature responsive fiber was developed from a specially engineered stimuli sensitive copolymer poly(*N*-tert-butylacrylamide-*ran*-acrylamide::27 : 73) containing amide as the reactive side group that enabled processing while maintaining its stimuli sensitive behavior. The SSP fiber showed a sharp reversible transition at 28°C for crosslinker concentration of 37.9 mol %. The transition behavior was found to be a function of crosslinker concentration. The transition response time was merely ~ 20 s to equilibrium swelling and spontaneous deswelling. During transition, the diameter and length of the SSP fiber could be reversibly changed by 1000 and 70%, respectively. Unlike hydrogel structures, which gave only isotropic transitions, the engineered fiber was found to possess strong anisotropic transitional behavior. The anisotropic response could be tuned by controlling morphology (i.e., orientation) of the fiber. The temperature sensitive fibers were able to overcome the major drawbacks, such as slow response, poor efficiency, and poor mechanical properties, exhibited by temperature sensitive hydrogels.

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