pH SENSITIVE FIBERS DERIVED FROM COPOLYMER OF ACRYLONITRILE AND ACRYLIC ACID DERIVATIVE

by

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to the

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Copolymer (2) Acrylic polymers

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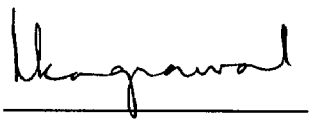
CERTIFICATE

This is to certify that the thesis titled, "**pH SENSITIVE FIBERS DERIVED FROM COPOLYMER OF ACRYLONITRILE AND ACRYLIC ACID DERIVATIVES**", being submitted by Ms. Anasuya Sahoo, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in the Department of Textile Technology is a record of bonafide research work carried out by her. Ms. Anasuya Sahoo has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.



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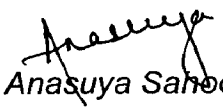

Anasuya Sahoo

ABSTRACT

The pH-sensitive hydrogel structures respond by swelling and deswelling (transition) to the changes in pH of the environment. They are excellent candidates for variety of applications such as drug delivery, sensors, chemical purifications, etc. The pH sensitive hydrogel systems reported in the literature suffer from slow response during transition in the range of several hours and poor magnitude of response (i.e. extent of swelling and deswelling). Since swelling and deswelling is a diffusion controlled phenomenon, thicker dimensions of hydrogels result in slower diffusion of water, which is subsequently responsible for their slow response. Further, hydrogels have poor mechanical properties and break down when subjected to repeated cycles.

In order to improve diffusion of water in and out of the structure during the transition, and hence, the response, the hydrogels are made into thin shapes (such as fibers) or porous structures. However, since the hydrogel structures are crosslinked to give stability during swelling, they are extremely weak, and thinning them down or making them porous further adds to their already fragile character. This places technological limits to their potential applications in areas such as artificial muscles, actuators, and smart textiles.

Therefore, alternate strategies must be investigated to simultaneously improve both the response and mechanical strength of the responsive structures. The main aim of the dissertation is to investigate the effect of polymer architecture and of the subsequent fiber morphology on the pH response and mechanical properties of the pH sensitive fibers with a view to address some of the drawbacks of the current systems.

For this, 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 mol% to 50 mol% AA) were synthesized. These copolymers were solution spun from DMF-water system, drawn in coagulation bath, and annealed to make pH sensitive fibers which were structurally stable without the need of chemical crosslinking. The properties of fibers from random and block copolymers with composition of `50 mol% AA were compared. Fibers from block copolymer (AA50B) showed significantly better tensile strength (34.3 MPa), higher retractive forces (0.26 MPa), and enhanced pH response (swelling 3890%) in comparison to fibers from random copolymer AA50R (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 from AA50B to AA30B while retaining the swelling percentage similar to the random copolymer AA50R mentioned above. It was proposed that on processing the block copolymers 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 allowed faster diffusion of water and ions to show enhanced response to changing pH of the environment compared to the fibers from random copolymer. TEM images of the films formed from these copolymers suggested that the size of the domains in films from block copolymer were in the range of about 5-10 nm compared to <2 nm in films from random copolymers.

It was hypothesized that since the formation of nanodomains of AN and AA had a great influence on the properties of the fiber, their domain size would have direct bearing on

the magnitude of the properties. Therefore, the block lengths of both AN (acrylonitrile) and AA (acrylic acid) moieties in the copolymers were varied by controlling the feeding pattern of the monomers during copolymerization. To test this hypothesis, four copolymers with acrylic acid content of ~30 mol% were synthesized in this series: random (AA30R) and three block copolymers with increasing block lengths (AA30B, AA30BI, AA30BII).

In accordance to our hypothesis, by changing the architecture of the copolymers (i.e. changing the distribution of comonomer moieties in copolymers with similar composition), the domain morphology, and hence, the properties of the fibers could be dramatically altered. The fiber's response at pH 10 in terms of change in length could be increased by 4 times while its response rate could be increased by 50 times from 0.25 %/min to 12 %/min with the increase in block length of AA moiety. At the same time, the tensile strength and retractive stress were increased by about 400% with the increase in the block length of AN moiety.

Understanding of spinning and coagulation phenomena in pH sensitive copolymers is important in obtaining defect free fibers through wet spinning. Towards this, the phase diagrams of copolymers of acrylonitrile (AN) and acrylic acid (AA) were constructed using linearised cloud point correlation to investigate the phase behaviour and mechanism of protofiber formation during solution spinning. The miscibility region in the phase diagram was found to increase with the increase in AA content of the copolymers. For various compositions, χ_{13} (polymer-water interaction parameter) values were estimated by sorption experiment. As the hydrophilic nature of the polymer increased with the increase in the content of acrylic acid, the χ_{13} interaction parameter was found to decrease from poly(acrylonitrile) homopolymer to its copolymer with 50 mol% acrylic acid (AA50B). The polymer-solvent interaction parameters (χ_{23}) and composition at the

critical points for all the polymers were determined by fitting the theoretical bimodal curves to the experimental cloud point curves using Kenji Kamide equations. The polymer composition at the critical point was found to increase by 400% with increasing AA content. The polymers were solution spun in DMF-water coagulation bath at 30 °C and their protofiber structures were investigated under Scanning Electron Microscopy. The observed morphological differences in protofibers were explained on the changes brought about in the phase separation behaviour of the polymer-solvent-nonsolvent systems. The copolymers with higher acrylic acid content could be solution spun into void free homogeneous fibers even at conditions that produced void filled inhomogeneous fibers in poly(acrylonitrile) and its copolymers with lower AA content. The experiments demonstrated the important role of thermodynamics in deciding the protofiber morphology during coagulation process.

The coagulation conditions, drawing and heat-setting parameters were found to have a significant impact on the mechanical properties, transition behavior and retractive stresses of responsive fibers. Using modified spinning conditions; fibers having fine diameters up to 38±2 μ could be readily produced.

The finer fibers from AA50B (38μ) showed a stable, reversible transition with an equilibrium volumetric swelling of 22200% at pH 10; whereas the thicker fibers from AA50B (120μ) showed volumetric swelling of only 3300-3600%. Also, the fibers from AA50B (38 μ) showed significantly higher strength (1.2-1.6 times), and retractive stress (1.2 times) during the transition compared to the fibers from AA50B (120 μ). The rate of transition was also found to be higher for the former fibers.

Annealing at a temperature of 120 ^{0}C for 2 h was found to be essential in obtaining a stable morphology in the fibers. At 100 °C, the fibers were not stable in pH solutions and

were quickly disintegrated. With increasing the heat-setting temperature from 120 °C to 150 °C, the fibers assumed better stability. The tenacity during swelling was significantly improved by 6.6 times, while the retractive stress was increased by 4.7 times. However, the increase in heat setting temperature had a negative effect on the pH response.

pH sensitive copolymer, poly(acrylonitrile-co-methacrylic acid) (MA30B), was synthesized to study the effect of bulky $-CH_3$ group of methacrylic acid on the properties of the pH responsive fibers. The fibers from MA30B, were compared to fibers from AA40B, which had similar acidic monomer content. MA30B showed higher volumetric swelling compared to AA40B possibly because of the bulky $-CH_3$ group in methacrylic acid, which tend to open up the responsive domains of the fibers. The volumetric swelling was 5010% in Ma40B compared to 3610% swelling in AA40B. Also the rate of change of length was faster compared to the fibers from AA40B.

However, the bulky group also affected the bonding in the acrylonitrile domains indicated by somewhat lower mechanical properties of the fibers. On the other hand, the inclusion of bulky monomer MA at ~7 mol% along with 27 mol% of AA could significantly improve the response properties of the resultant fiber while retaining the mechanical properties to a much higher extent.

Also, for the first time, temperature sensitivity was discovered in the copolymers based on acrylonitirle. The fibers showed dual sensitivity to both varying pH and temperature. The fibers when subjected to change in temperature at an alkaline aqueous medium, showed temperature dependent swelling behaviour. The behaviour was reversible and stable to repeated cycling. At lower temperature they exhibited more swelling compared to the temperature above the transition temperature. Transition point at pH 10 could be modulated from 40 °C to 62 °C by varying the composition of the copolymer from 10

mole % to 50 mole % of acrylic acid. The pH of the medium also had a significant effect on the transition temperature of the copolymers because it affected the ionization of the carboxylic groups in acrylic acid moieties. The dual response to pH and temperature stimuli in acrylic fibers is an important discovery and is expected to support the development of new application in smart textiles and related areas.

The above results suggest that the control of the chemical architecture of polymers and physical morphology of the pH responsive structure may be the key in producing pH responsive fibers with both better mechanical properties and higher pH response that is suitable for their applications in artificial muscles, actuators and smart textile.

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