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Effect of copolymer architecture on the response of pH sensitive fibers based on acrylonitrile and acrylic acid

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Abstract

Copolymers of acrylonitrile and acrylic acid with high acrylic acid feed ratio of 43 mol% were synthesized using free radical polymerization. The architecture of copolymers was modified by regulating the dosing of more reactive comonomer-acrylic acid. ^{13}C NMR analysis confirmed that two copolymers – one (A) containing enriched blocks of individual monomer-residues (architecture close to a block copolymer) and the second (B) having nearly random distribution of the comonomers, could be successfully synthesized. The resultant acrylic acid content was determined to be nearly 50 mol% for both the copolymers. These copolymers were converted to fine fibers by solution spinning in DMF-water system, drawn in coagulation bath, and annealed at 120 °C for 2 h. The fibers were evaluated for pH response behavior, mechanical stability, and retracting stresses. The fiber A was found to have significantly higher swelling percentage (3300–3700%), faster response, and higher stability to repeated cycling compared to fiber B. Also, Fiber A showed lower thermal shrinkage, better mechanical properties during swelling and higher retracting forces during deswelling. These results indicate that the copolymer with enriched block architecture could possibly form segregated domain structure with acrylic acid domains facilitating enhanced pH response while acrylonitrile domains providing physical crosslinks for stronger mechanical strength. The study suggests that above approach may be more useful than chemically cross-linked gel rods in producing artificial muscles with faster response and good mechanical properties.

Keywords: pH Sensitive polymers; Poly(acrylonitrile-co-acrylic acid); Architecture; Artificial muscle; Smart fibers

1. Introduction

Stimuli sensitive polymers (SSP) are being extensively studied for the past decade due to their potential applications in areas ranging from controlled-delivery for functional substances (drugs, nutrients, herbicides, etc.) [1,2] to membranes for molecular separation [3–5], enzyme activity control [6,7], extraction [8], BioMEMS [9–11] such as hydrogel actuated microvalves and microfludic controllers in microchannels, and now recently for artificial muscles [12–14]. Stimuli sensitive polymers undergo reversible transitions under various stimuli such as pH [15], temperature [16], electric field [17],

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or electrolyte [18]. These environment sensitive polymers are also called ''Intelligent Polymers'' or ''Smart Polymers'' [19,20]. One of the important types of SSPs is pH sensitive polymers. These polymeric materials can sense the pH of their environment as a signal, judge the magnitude of the signal and change their properties accordingly.

The pH sensitive polymers undergo hydrophobic to hydrophilic state by the change in pH [21]. These polymers consist of ionizable pendant groups that can accept and donate protons in response to the environmental change in pH. As the environmental pH changes, the degree of ionization in pendant groups undergo dramatic change at a specific pH called pK_a. This rapid change in the net charge of pendant groups causes an alternation of the hydrodynamic volume of the polymer chains. This results in a transition from collapsed hydrophobic state to soluble hydrophilic state of the polymer [22]. In order to create structures that respond to pH change, these polymers are crosslinked to form hydrogels. Many systems based on copolymers of *N*-isopropyl acrylamide–acrylic acid [23], vinyl alcohol–acrylic acid [24], acrylonitrile–acrylic acid [25], poly(methacrylic acid) grafted with poly(ethylene glycol) [26] have been studied for various pH sensitive applications in the gel form.

The pH-sensitive hydrogel structures reported in the literature suffer from slow response 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 the slow response. Further hydrogels have poor mechanical properties and break down when subjected to repeated cycles. In order to improve response, porous gel rods have been investigated [27–29], however the porous structure gives much lower strength.

Recently, an approach was reported by our group [30] in which linear temperature sensitive copolymers were processed into fibers with oriented polymer chains to impart strength. However, these fibers were required to be chemically crosslinked to form insoluble state. Though these fibers showed extremely fast response but they were found to be fragile when in swollen state.

In another approach [21,31–34], the existing poly(acrylonitrile) are modified to produce pH sensitive fibers. Since PAN fibers are known to possess key engineering features such as excellent environmental stability and high tensile strength, they make a good starting material for producing strong pH sensitive fibers. In this approach, special acrylic fibers (SAF) are thermally oxidized, where some of the CN groups undergo cyclization to provide the connected structure. The remaining CN groups are hydrolyzed or saponified to convert them into carboxylic acid groups. The cyclized acrylonitrile moieties remain unaltered even during hydrolysis and act as a backbone rendering strength to the fiber while the hydrolyzed groups impart pH sensitivity. The modified PAN fibers, being of fine dimension (diameter in microns), exhibit good response to changing environment when activated electrically or chemically. This method has several advantages. First, it is a simple process that it involves only the modification of an existing precursor fiber and essentially, does not require any new polymer to be synthesized. Though this process appears to be suitable for the production of artificial muscles it too has some drawbacks.

pH Sensitive fibers produced using this method are black in colour that makes them inappropriate for textile applications. This colour is ascribed to the chemical conjugation of nitrile groups to form six-membered aromatic rings. The production rate of these fibers is considerably slow since it involves controlled oxidation of PAN at high temperature for long periods of time. Further, the parameters available for controlling the amount of cyclization and crosslinking in the fiber are limited since the precursor fiber used is of a specific microstructure and modifying the fiber to a great extent may result in deteriorating its mechanical properties. Due to this reason, 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 pH sensitive copolymers of controlled architecture based on acrylic acid and acrylonitrile have been synthesized which when solution spun into fine fibers, show good mechanical properties as well as enhanced pH response without the need of chemical crosslinking. It is suggested that fibers from such copolymers may form domains of acrylonitrile and acrylic acid, where acrylonitrile domains act as physical crosslinks and connect chains to allow transfer of the stresses along the fiber axis, while acrylic acid domains swell and deswell to give the desirable pH response.