# SYNTHESIS AND PROCESSING OF TEMPERATURE-SENSITIVE COPOLYMERS OF *N-TERT*-BUTYLACRYLAMIDE AND ACRYLAMIDE

by

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## CERTIFICATE

This is to certify that the thesis titled, "SYNTHESIS AND PROCESSING OF TEMPERATURE-SENSITIVE COPOLYMERS OF *N-TERT*-BUTYLACRYLAMIDE AND ACRYLAMIDE", being submitted by Mr. Ninad S. Save, 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 him. Mr. Ninad S. Save has worked under our 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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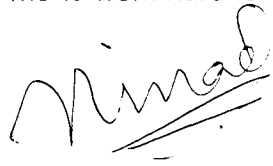

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## ABSTRACT

Temperature-sensitive polymers have a number of potential applications. In the hydrogel form they are not processable in fine shapes and have a slow response. Wide range of applications can be developed if the response time is improved. This dissertation deals with the synthesis, characterization and application of a new series of processable temperature-sensitive copolymers based on *N-tert*-butylacrylamide (NTBA) as a hydrophobic comonomer and acrylamide (Am) as a hydrophilic comonomer. Acrylamide has also been selected to provide a reactive site for the purpose of providing site for the formation of crosslinks.

In order to study the feasibility of the network formation and integrity to textile substrate through crosslink formation by anchoring the temperature-sensitive copolymer to the textile substrate poly(acrylamide) (PAm) has been used as a model polymer. From the different polycarboxylic acid crosslinkers evaluated, citric acid and 1,2,3,4-butanetetracarboxylic acid were found to be the most suitable crosslinkers. These reactions were evaluated with fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy and solubility studies. For studying the integrity with cellulose based textile substrates PAm coated cotton fabrics were made. The films and coatings were obtained by using PAm solution (4 wt. %) containing citric acid as a crosslinker (5–50 mol%), and sodium hypophosphite (0.3 wt. %) as a catalyst, followed by drying at 90 °C and curing at 150 °C. The water-vapor transmission rate (WVTR) values for these PAm coated fabrics were found to be excellent with only 5–23 % reduction compared to the values shown by control cotton fabric. It was found that a minimum of 20 mol % of crosslinker concentration based on amide groups is necessary for the integrity.

Temperature-sensitive random linear and crosslinked copolymers of NTBA and Am were synthesized by solution polymerization method, using regulated dosing of more reactive comonomer Am. Copolymers with varying feed ratios of NTBA and Am (80:20 to 20:80 mol %) were synthesized and characterized. For comparison copolymer hydrogels using MBA (1.13 mol %) were also synthesized. The composition of the copolymers determined by FTIR was found to lie between 75:25 and 11:89 mol %. DSC studies of copolymers synthesized by regulated dosing confirmed the formation of random copolymers. The transition temperature of the copolymers varied between 2 and 58 °C, while the swelling percentage varied between 42 ($\times \rho_{polymer}$) and 689 ($\times \rho_{polymer}$) % for the composition between 75:25 and 11:89 mol %. Reversible transition was observed over repeated cycling.

Linear copolymer with 40:60 feed ratio of NTBA and Am monomers, with actual incorporation of NTBA to the extent of 27 mol %, was selected for processing. The copolymer films of thickness in the range of 10-200 μm were obtained from aqueous solution in the presence of citric acid or 1,2,3,4-butane tetracarboxylic acid as crosslinkers and sodium hypophosphite as catalyst. Subsequently, the films were crosslinked at 150-160 °C to obtain mechanically strong insoluble films. The crosslinks were formed between reactive amide side groups of the Am moiety of the polymer and the carboxylic acid group of the crosslinker. The transition temperatures of the crosslinked films were found to shift towards the lower temperature from 37 °C (in linear copolymer) to 22-25 °C. High surface to volume ratio of the prepared films lead to significant increase in swelling percentage from 680 % in the polymerized-gel samples (2 mm disc) of the same composition to 4200 % and faster response time from 1280 minutes (in the first cycle) to 5 minutes compared to polymerized-gel samples (2 mm disc) of the same composition.

Smart breathable cotton fabrics and coated yarns were made by coating an aqueous solution (20 wt %) of the copolymer under optimized curing conditions. The integrity of the crosslinked coatings to the fabric and yarn was observed to be excellent. The temperature-sensitive copolymer after integration on the fabric and yarn through coating showed a transition in the temperature range of 15 to 40 °C. Below 15 °C, the coatings on fabric were found to swell by 1120 % while above 40 °C the coatings deswelled to swelling percentage of less than 70 % (on the basis of dry-weight). The transition to swelling was completed in about 20 minutes. The response was found to be reversible and stable to repeated cycles of transition. The coated-fabrics showed temperature-responsive water-vapor transmission rate (WVTR). The WVTR values of the responsive (40:60 copolymer coated) and non-responsive (PAm coated) breathable fabric were measured as a percentage (transmission percentage) of control uncoated substrate. The transmission percentage at 20 % relative humidity for copolymer coated fabrics was found to change across the transition temperature (15 to 45 °C) from 58 % to the 94 % compared to PAm coated fabric which changed only from 70 % to 94%, showing a clear response to changing environment temperature.

The coating on yarns was found to achieve equilibrium volumetric swelling of ~ 4500 % in about 5 minutes. A model-fabric made out of the coated yarns, showed a significant change in percentage-cover across the transition temperature. The model-fabric showed no open spaces (percentage-cover of 100 %) at 6 °C, open spaces increased to 57 % (percentage-cover of 43 %) above the transition temperature.

The temperature-sensitive copolymer when used in the conventional gel-disk form showed a swelling of 680 % in 1200 minutes. But on conversion into thin films into processable form the swelling percentage increased to ~ 4200 % and took just 5

minutes. Similar enhancement in the transition properties were observed with coated fabrics and yarns. The coatings on the fabrics showed a swelling percentage of 1120 % (in 20 minutes) while on the yarns a swelling percentage of 4500 % (in 5 minutes) was obtained.

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Textile Substrates: Fabric and Yarn