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Stimuli sensitive copolymer poly(*N*-*tert*-butylacrylamide-*ran*-acrylamide): processing into thin films and their transitional behaviour

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Abstract

Temperature sensitive polymer hydrogels are being extensively studied because of their potential applications in biomedical, robotics, and chemical industry. However, major hurdles in their development have been their slow response, low efficiency, and poor mechanical properties. One of the main reasons for these shortcomings is the difficulty of processing them into mechanically fine structures in polymer gel form. In this work, a novel approach has been developed to process temperature sensitive copolymers based on acrylamide into mechanically stable thin films. A series of temperature sensitive random linear copolymers of *N*-*tert*-butylacrylamide (NTBA) and acrylamide (Am) were synthesized by solution polymerization method, using regulated dosing of comonomer Am having a higher reactivity ratio ($r_{\mathrm{Am}} = 1.5$) than NTBA ($r_{\mathrm{NTBA}} = 0.5$). Copolymers with varying feed ratios of NTBA and Am (80:20 to 20:80 mol%) were synthesized and characterized. The actual incorporation of less reactive comonomer NTBA was found to be lower than the feed and was found to vary between 75 mol% with feed of 80 and 11 mol% for a feed of 20%. 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 microns could be 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 acrylamide 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 490 to 2980% and faster response time from 1280 min (in the first cycle) to 5 min compared to polymerized-gel samples (2 mm disc) of the same composition.

Keywords: Temperature sensitive; Processing; Poly(*N*-*tert*-butylacrylamide-*ran*-acrylamide)

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1. Introduction

In recent years, smart polymer/gels that experience reversible phase transition to external stimuli have attracted special attention. These polymers/gels undergo reversible volume change in response to a small variation in solution conditions (external stimuli), such as temperature [1–6], pH [1,7,8], and solvent composition [9,10]. Many temperature-sensitive polymers [1–6,11–16] such as poly(N-substituted acrylamide), poly(*N*-vinyl alkylamide), poly(vinyl methyl ether), and poly(ethylene glycol-*co*-propylene glycol) have been reported so far and they have been utilized in the gel form for diverse technological applications such as in controlled drug delivery, chemical separation and sensors. 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. This is primarily due to the drawbacks of such materials in the polymerized-gel form. The major drawback of these stimuli-sensitive polymers in gel form is their slow response. A disc shaped gel of poly(*N*-isopropyl acrylamide)-*co*-poly(ethylene oxide) of 0.7 cm diameter in dry state requires 75 h to attain equilibrium [17]. In another study, pH and temperature sensitive hydrogels based on *N*-acryloyl-*N*′-methylpiperazine and methyl methacrylate ions have been reported to show a reversible

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response to pH with a response time of 150 min [18]. In our study, poly(*N*-*tert*-butylacrylamide-*ran*-acrylamide) in the gel disc (2 mm) required 1280 min to attain equilibrium swelling in the first cycle [19]. Thus, the hydrogel response time or sensitivity is strongly influenced by diffusion rate, which in turn is dependent upon the gel thickness [15,20]. The response rate of a hydrogel is inversely proportional to the square of gel's dimensions. Therefore, the simplest way to improve the response time is to make hydrogels thinner and smaller. This usually makes the hydrogel systems too fragile and mechanically weak for applications.

Stimuli sensitive polymers (SSP) are expected to overcome above limitations and find numerous novel applications if

(a) These materials could be processed into thin films with thickness in the range of few microns
(b) These materials could be integrated as coatings to other non active substrates, and
(c) The resultant film or SSP-substrate composite could retain the thermo-sensitive property.

Thin films of SSP in this form are expected to show fast response to stimuli and better utilization of functional sites, while the integration to substrate can result in durable SSP's with improved mechanical properties.

In the present study, a series of linear copolymers of NTBA and Am (Fig. 1) were synthesized. The transition temperature in the polymers was designed by altering the ratio of NTBA and Am monomers. Polymers with transition temperature in the range of 17–38 °C were obtained. Acrylamide was selected as hydrophilic monomer with a functionality that can potentially be utilized for crosslinking or integration to substrate. Our aim was to convert linear stimuli sensitive copolymer into processable thin films. This novel approach comprised of two major steps

(i) Preparation of thin films from high molecular weight linear SSP copolymer containing reactive side groups.
(ii) Crosslinking of polymer chains at the reactive side groups using a suitable crosslinker in order to obtain stabilized insoluble thin films or coatings. The reactive side groups may also be used for integrating the film to any desirable substrate such as mechanically strong, flexible textile fabrics.

It is hoped that the above SSP-textile composites may open up additional applications in the areas of smart textiles.

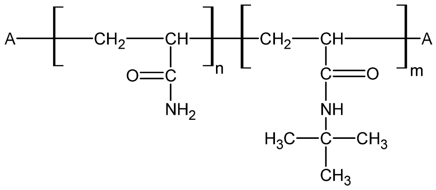

Fig. 1. Copolymer structure.

2. Experimental section

2.1. 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 of or exceeding 99% and were used without further purification.

2.2. Copolymer synthesis

2.2.1. Monomer synthesis

NTBA was synthesized by the Ritter's reaction, as reported previously [21]

2.2.2. Polymerization

Free radical polymerization reaction was carried out in methanol at 50 ± 1 °C in the presence of 0.1 mol% ammonium persulfate. The monomer concentration was fixed at 2 mol l^{-1}. The NTBA content of the monomer feed was varied from 100 to 20 mol% (Table 1). Gravimetric yields for these polymers were found to vary between 55 and 97%. To illustrate the polymerization procedure, the details for preparation of a linear copolymer (B80:A20) with 80 mol% of NTBA in the monomer feed is given below:

NTBA (3.048 g) and 25% of the calculated Am (total amount 0.426 g) were dissolved in methanol (15 ml). The monomer solution was degassed for 15 min, and then the initiator was introduced. The balance amount of acrylamide was introduced in three doses (0.1065 g each dose) after every 45 min interval. Each dosing was accompanied by degassing with nitrogen for 5 min. The polymerization was continued for about 12 h. Highly viscous reaction mixture was obtained.

After polymerization the reaction mixture was cooled and the copolymerized products were precipitated in acetone while stirring vigorously. The purified copolymers were dried in vacuum oven at 120 °C.

For comparison, 50:50 copolymer was also synthesized by adding full amount of acrylamide at the beginning of the reaction and this copolymer was coded as B50:A50F. PAm was synthesized by the procedure given in the literature [15, 20].

2.2.3. Scale-up polymerization of B40:A60

Based on the polymerization method reported above, larger batches of B40:A60 copolymer of NTBA and acrylamide were synthesized using conditions detailed in Table 2. Free radical polymerization reaction was carried

Table 1
Composition of copolymers obtained with varying feed ratios of NTBA with Am

Sample code	Composition feed ratio, NTBA:Am (mol%)	Final copolymer, NTBA:Am (mol%)
PNTBA	100:0	100:0
B80:A20	80:20	75:25
B70:A30	70:30	58:42
B60:A40	60:40	38:62
B50:A50	50:50	32:68
B50:A50F	50:50	30:70
B40:A60	40:60	27:73
B30:A70	30:70	26:74
B20:A80	20:80	11:89
Pam	100	0:100

out in a 2 l glass reactor. The evaporated methanol was allowed to reflux back into the reactor. The inert atmosphere was strictly maintained in order to obtain high molecular weight polymer.

2.3. Copolymer characterization

2.3.1. Determination of composition by FTIR [2]

The FTIR spectra were recorded on a Perkin Elmer BX II spectrophotometer. The intensity of the peak at 1225 cm^{-1} (due to $-C(CH_3)_3$ group) was normalized using C=O stretching peak of both NTBA and Am at 1665 cm^{-1}. The normalized height of the $-C(CH_3)_3$ peak at 1225 cm^{-1} was compared with that of the normalized PNTBA peak, to obtain the incorporation of NTBA in the copolymers. The compositions of the copolymer obtained by FTIR are given in Table 1.

2.3.2. Thermal studies

The Differential Scanning Calorimetry (DSC) studies were performed on Perkin Elmer DSC 7. The samples were heated from 50 to 300 °C, with a heating rate of 20 °C/min.

2.3.3. Determination of transition temperatures for the linear copolymer

Solutions of the linear copolymers were made in different concentrations varying between 4 and 0.1 wt%. These solutions were subjected to change in temperature in a thermo-regulated water bath. The transition temperature was recorded at the onset of turbidity. The transition temperatures were plotted against concentration to determine the LCST (Table 3).

Table 2
Polymerization conditions for NTBA/Am copolymer

Monomer 1	NTBA (g)	152.4
Monomer 2	Acrylamide (g)	127.8
Feed composition	NTBA:Am (mol%)	40:60
Initiator	Ammonium persulfate (g)	0.58
Solvent	Methanol (ml)	1500
Temperature	°C	50
Time	Hour	12
Atmosphere	Inert	Nitrogen

2.4. Processing into films

A 10% solution of linear copolymer (NTBA:Am :: 27:73) was prepared by stirring the purified and dried polymer powder in double distilled water. Predetermined quantity of selected crosslinker (CA or BTCA) 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 using it for coating. The glass slides were coated with the above solution and dried to obtain coating thickness of 0.2 ± 0.03 and 0.01 ± 0.002 mm. The coated slides were cured for carrying out crosslinking reaction. The coatings containing CA crosslinker were cured at 150 °C for 20 min, while the coatings containing BTCA were cured at 160 °C, for 25 min.

Coatings were obtained using varying crosslinker content as detailed in Table 4. The crosslinker content was calculated theoretically to correspond to certain mol% of available amide groups as per the monomer feed. The effective concentration of crosslinker with respect to acrylamide in the actual copolymer is also shown for comparison.

2.5. Determination of transition temperatures for the SSP films

Transition temperature for the films, was evaluated by the same method as for gels [19]. The glass slides coated with films were immersed in distilled water and the equilibrium swelling at each temperature was determined. The slides were kept for 15 min at each temperature for ensuring the attainment of equilibrium. This equilibrium time of 15 min was arrived at by experimentally determining time necessary for achieving the equilibrium. The transition temperature was determined by observing the change in swelling against temperature for the crosslinked films. The equilibrium swelling was determined as given below:

$$\mathrm{Swelling}(\%) = (W_t - W_\mathrm{d}) \times 100/W_\mathrm{d}$$

W_d and W_t represent the dry weight and the weight attained at time t, respectively. For equilibrium swelling values, time t refers to the equilibrium time. The coefficient of variation in swelling studies was found to be less than 2% of the measured values.

Many authors use 'swelling ratio (%)' as the units for expressing swelling. However, this is erroneous. It should be either expressed as swelling ratio or swelling percentage (%). Swelling ratio should be calculated as the ratio of final weight (volume) to the initial weight (volume), while swelling percentage should be the change in weight over the initial weight expressed in percentage.

2.6. Swelling–deswelling kinetics of crosslinked SSP films

The rate of swelling of the crosslinked films on glass slides was investigated by immersing the coated, dried, and cured slides in distilled water at low temperature, significantly below the transition temperature (≤6 °C). The increase in water content was followed by measuring the change in weight of the film against time. The swelling percentage, at time t for the crosslinked films was determined as per the above equation.

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

2.7. Thermoreversibilty of crosslinked SSP films

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

3. Result and discussion

3.1. Copolymer synthesis and characterization

The reactivity ratios for copolymerization of NTBA and Am have been recently reported as 0.5 and 1.5, respectively, [23]. Therefore, during polymerization the dosing of more reactive monomer Am was regulated to obtain random copolymers of controlled composition. The monomer Am was introduced in four equal doses. Preparation of PNTBA and PAm was carried out for comparison with copolymers.

Table 1 shows the composition of copolymers as a function of acrylamide in the feed. The copolymer composition determined by FTIR was found to be different than the co-monomer feed composition. However, under the experimental conditions copolymers with a wide range of compositions were obtained. The NTBA incorporation in the copolymer was found to be lower than that fed in the comonomer feed. For the variation in comonomer feed ratios of NTBA:Am from B80:A20 to B20:A80, the composition of the copolymer varied between 75:25 and 11:89 (NTBA:Am). This is due to the lower propagation rate constant of growing radicals with vinyl groups of NTBA compared to Am monomer and different solubilities of monomers [24,25]. The copolymerization conditions were optimized to obtain high molecular weight copolymers.

The glass transition temperatures obtained from DSC studies are given in Table 3. PAm and PNTBA exhibited a T_g of 194 and 108 °C, respectively. The higher glass transition temperature value of PAm can be explained by presence of two hydrogen atoms in the amide group. These amide groups result in strong hydrogen bonding and hence reduced mobility of polymer chain. In all the samples except B50:A50F, a single glass transition temperature (T_g) was observed. The T_g varied with the composition of copolymers. With increase in Am content, the transition was found to shift to higher values indicating a nearly random distribution of NTBA and Am in copolymer segments. Interestingly, in the B50:A50F, two clear transitions at 134 and 189 °C were observed (Fig. 2). These two distinct glass transitions temperatures may correspond to the polymer segments rich in NTBA and Am, respectively. The heterogeneous distribution of Am in the polymer chains may cause heterogeneity at the molecular level composition.

3.2. Transition studies of linear copolymers

The phase transition behavior of linear copolymers was found to be quite sensitive, reversible, and reproducible to thermal stimuli. The transition temperature for linear copolymers are given in Table 3. The copolymers

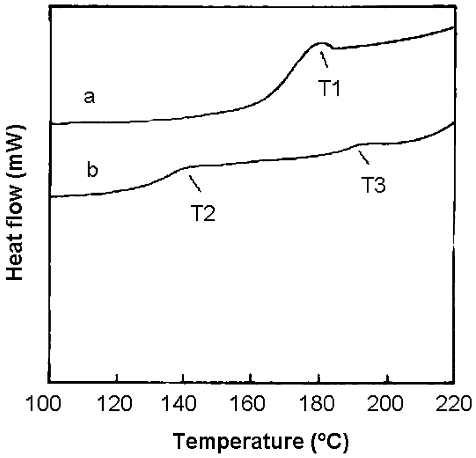

Fig. 2. Thermal transitions (glass transitions) of copolymers (a) B50:A50 ($T_1 = 168$ °C) and (b) B50:A50F ($T_2 = 134$ °C; $T_3 = 189$ °C) as obtained by differential scanning calorimetry (DSC).

Table 3
Compositional ratios of the copolymers and their properties

Comonomer feed ratio, NTBA:Am (mol%)	Copolymer composition by FTIR (NTBA) (mol%)	T_g (°C)	LCST (°C) for copolymer solutions, (conc. at LCST, wt%)
PNTBA	100	108	Insoluble
B80:20	75	146	Insoluble
B70:A30	58	146	Insoluble
B60:A40	38	158	17 (0.375%)
B50:A50	32	168	27 (0.15%)
B50:A50F	30	134, 189	34 (broad range)
B40:A60	27	160	37 (1.25%)
B30:A70	26	169	No LCST
B20:A80	11	174	No LCST
PAm	0	194	No LCST

B80:A20 and B70:A30 were insoluble in water, while in the copolymers B30:A70 and B20:A80 the LCST could not be observed may be due to extremely high hydrophilicity of the copolymer. The LCST varied between 17 and 38 °C, for the intermediate compositions, i.e. B60:A40, B50:A50, B50:A50F and B40:A60 copolymers. These copolymers exhibit a change in their LCST with change in composition. With increasing content of NTBA from 27 to 38 mol%, the LCST of the copolymers decreased from 38 to 17 °C. The LCST curves for these copolymers are shown in Fig. 3(a)–(d).

As can be observed from Fig. 3, the curve obtained for B50:A50F becomes nearly flat at concentrations above 0.5 wt%, which is characteristically different from the other curves. In all other three copolymers, a distinct LCST was observed which may be attributed to better homogeneity of the copolymer structure compared to B50:A50F.

3.3. Processing into films

As mentioned earlier, in order to obtain fast transitions, high functional efficiency and exploit new potential applications, it is extremely important that such stimuli sensitive polymer systems should be developed which can be processed into structurally strong, thin desirable shapes. This can be achieved by converting the linear copolymers (containing reactive groups) into desirable shapes and subsequently crosslinking (using suitable crosslinkers) them without adversely affecting the stimuli sensitive response of the material. The presence of reactive side

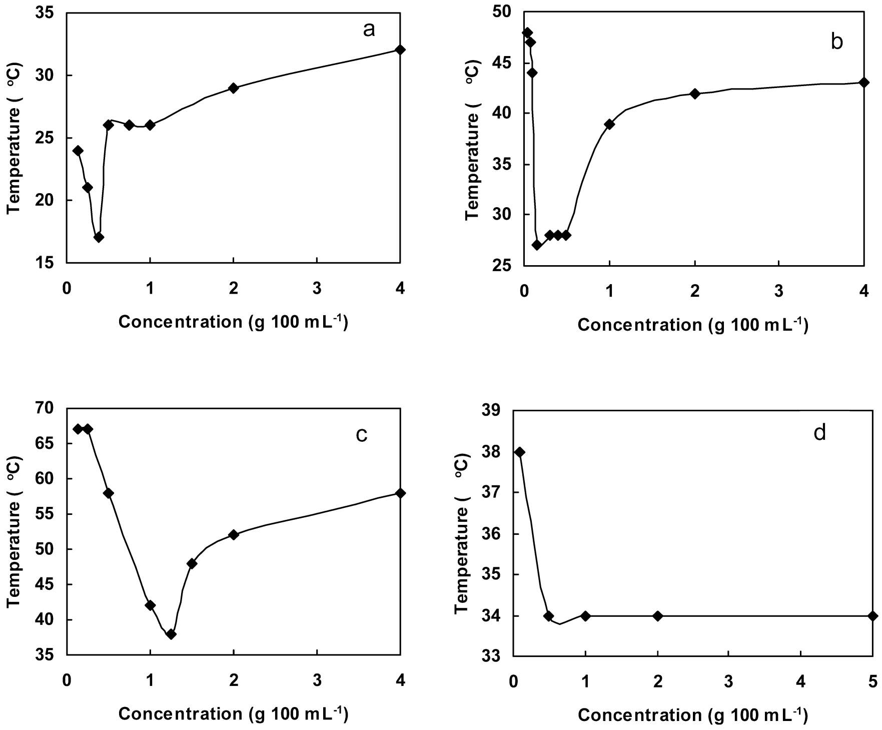

Fig. 3. Lower Critical Solution Temperature curves: (a) B60:A40, (b)B50:A50, (c)B40:A60, and (d)B50:A50F.

groups in the monomer can be utilized to introduce crosslinks with the help of polyfunctional crosslinkers. The crosslinker can bridge the inter polymer chains or integrate the chains to the substrate. This approach of incorporation of responsive polymers in the form of thin film/coating on reactive flexible substrate would provide active polymer layer on top of substrates. Such a structure would give mechanically strong SSP composites with large surface area.

In order to prepare thin film structures having transition near room temperature, copolymers with transition just above room temperature were thought to be suitable. Among them linear copolymer B40:A60 with 27 mol% NTBA was found to show a sharp reversible transition at 37 °C. Also this copolymer had a large fraction of acrylamide side groups desirable for crosslinking, therefore this copolymer was selected for converting into SSP films. The high molecular weight copolymer was prepared in large batches and was found to readily dissolve in water at temperatures lower than 37 °C (its LCST). The viscous solutions could be converted into thin uniform films on glass slides. Polycarboxylic acid based crosslinker in predetermined quantities along with catalyst were incorporated in copolymer solution for introducing crosslinking subsequent to processing.

Based on our previous study [26] on polyacrylamide, citric acid and BTCA were found to be appropriate crosslinking agents for carrying out reactions with amide side groups of the acrylamide moiety. Carboxylic acid was found to condense with amide side groups to form imide linkages. The feasibility of crosslinking polymer chains using amide side groups and polycarboxylic acid crosslinking agents in the presence of catalyst sodium hypo phosphite has been established using FTIR and NMR, and reported recently by our research group [26]. Therefore, the same crosslinkers were selected for obtaining crosslinks in SSP films of the copolymer.

The concentration of crosslinker was varied to obtain structures with different degrees of crosslink density. The concentration of crosslinker was calculated theoretically based on the mole percentage of amide groups to be crosslinked. The concentrations of crosslinkers used are shown in Table 4 for carrying out crosslinking to the extent of 36.9, 49.3 and 61 mol% of amide groups in the copolymer. Since citric acid has three carboxylic functional groups and BTCA has four, the concentration of citric acid used was higher for the same extent of crosslinking. These values are theoretically calculated, and due to incomplete utilization of all functional groups, the degree of crosslinking is expected to be lower. However, the three concentrations of crosslinker are likely to provide three different levels of crosslink density.

The cast films on curing gave mechanically strong, durable, and insoluble films. The films with higher crosslinker concentration were found to have superior mechanical integrity suggesting higher degree of crosslinking. Uniform films with thickness of 0.2 and 0.01 mm were successfully prepared. Films formed using BTCA crosslinker were superior probably due to the availability of larger number of functional groups in each molecule compared to CA crosslinker. This will lead to higher probability of successful crosslinking between polymer chains. Therefore, thinner films were prepared using BTCA as crosslinker.

3.4. Transition studies of SSP films

The LCST of linear copolymer containing 27% NTBA has been given as 37 °C in Table 3. Since the crosslinking occurs at amide side groups, crosslinked SSP films were expected to show transition temperature dependent upon the crosslinker concentration. This is because crosslinking would affect the hydrophilicity of the copolymer. This strategy is rather interesting as it offers an alternate approach to control transition temperature and at the same time provides a method for obtaining thin processable films or coatings with fast transition. This approach may also be utilized for designing transition temperature near room temperature for this copolymer.

Figs. 4 and 5 show clear thermo responsive behaviour of the crosslinked processed SSP films (with 0.2 mm thickness) with CA and BTCA as crosslinkers, respectively. Similarly, Fig. 6 shows the behaviour of thin (0.01 mm) films obtained using BTCA. As expected, the incorporation of crosslinker caused a significant reduction in the transition temperature from 37 to about 20 °C. On introduction of crosslinker, the transition temperature of the SSP structure reduced from 37 to 25 °C and to 23 °C with CA and BTCA, respectively. As expected the thickness of the film had no influence on the transition temperature.

Table 4
Crosslinker concentration in the processed films

Crosslinker	Sample code	Concentration (wt%)	Carboxylic groups based on available amide groups (mol%)
BTCA	BT1 and BT11	1.826	36.9
	BT2 and BT21	2.447	49.3
	BT3 and BT31	3.021	61.0
CA	CT1	2.188	36.9
	CT2	2.925	49.3
	CT3	3.619	61.0

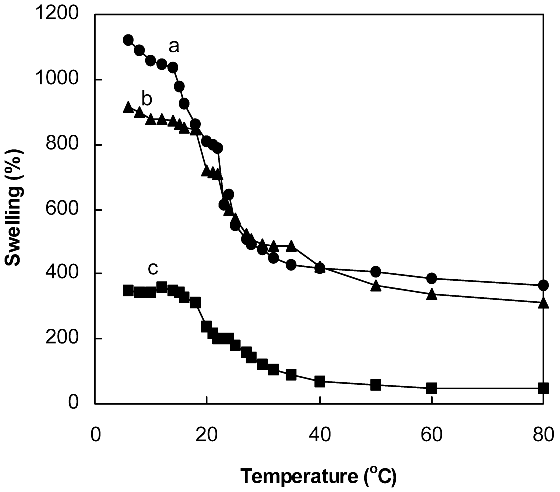

Fig. 4. Temperature dependence of equilibrium swelling of poly(NTBA-ran-Am :: 27:73) processed films of (0.2 mm) with CA content: (a) 36.9 mol% (b) 49.3 mol% (c) 61 mol%.

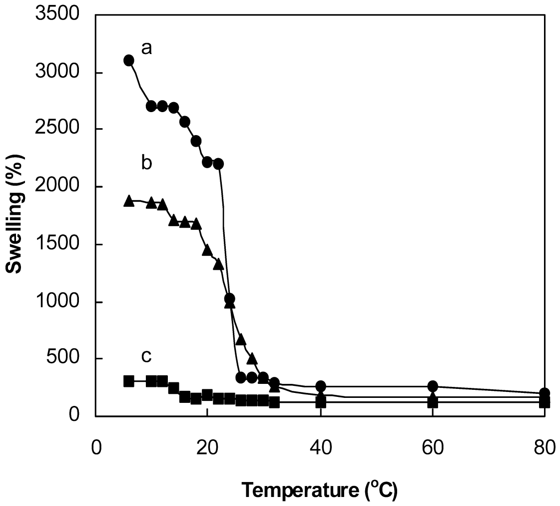

Fig. 6. Temperature dependence of equilibrium swelling of poly(NTBA-ran-Am :: 27:73) processed films of (0.01 mm) with BTCA content: (a) 36.9 mol%, (b) 49.3 mol%, (c) 61 mol%.

The crosslinking reaction of amide side groups of the linear copolymer with carboxylic acid functional groups reduces the availability of free amide groups and hence the hydrophilicity of SSP films. Such a reduction in hydrophilicity may be responsible for the lowering of transition temperature. The transition in the copolymers crosslinked using citric acid was found to occur at slightly higher temperature. Citric acid contains an alpha hydroxyl group; therefore for the equivalent concentration of carboxylic acid groups in the two crosslinkers, citric acid has higher hydrophilicity. This difference in hydrophilicity may alter the transition temperature to slightly higher values. The degree of crosslinking was initially thought to be a good means to control or tune the transition temperature by varying the crosslinker concentration, however, it appeared that for the given crosslinkers and in the concentration range studied, the effect was not pronounced. This may be due to either the saturation values achieved in lowering of the transition or heterogeneous structure resulting in relatively broad transitions. The studies could not be conducted at lower crosslinker concentration because the mechanical integrity of the films was found to be poor.

However, the effect of crosslinker concentration on swelling percentage was found to be significant as discussed later.

3.5. Swelling/deswelling kinetics of crosslinked films

The swelling–deswelling kinetics of crosslinked SSP films were studied in third cycle to determine the effect of film thickness on diffusion of water in and out of the processed samples. Figs. 7 and 8 depict the change in swelling percentage with time (rate of swelling) for CA and

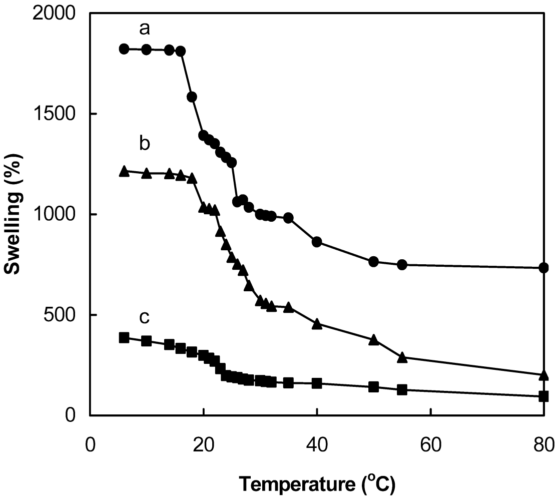

Fig. 5. Temperature dependence of equilibrium swelling of poly(NTBA-ran-Am :: 27:73) processed films of (0.2 mm) with BTCA content: (a) 36.9 mol% (b) 49.3 mol% (c) 61 mol%.

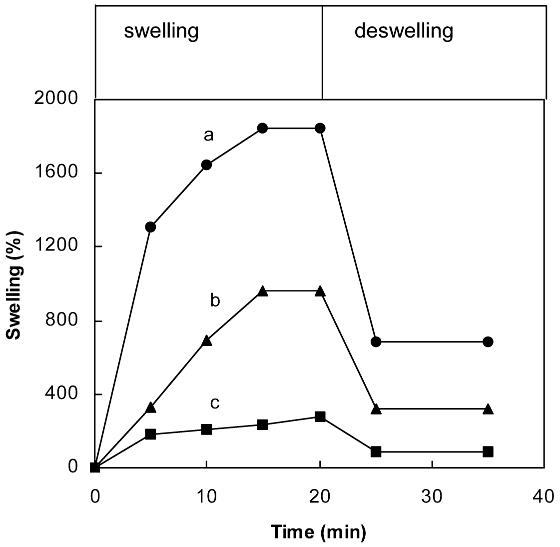

Fig. 7. Rate of transition of poly(NTBA-ran-Am :: 27:73) processed films (0.2 mm) with CA content: (a) 36.9 mol%, (b) 49.3 mol%, (c) 61 mol%.

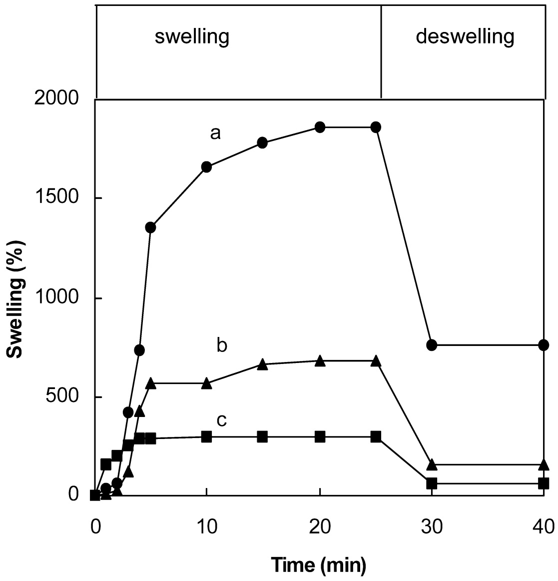

Fig. 8. Rate of transition of poly(NTBA-ran-Am :: 27:73) processed films (0.2 mm) with BTCA content: (a) 36.9 mol%, (b) 49.3 mol%, and (c) 61 mol%.

BTCA crosslinked films when subjected to temperatures below transition, at 6 °C.

The swelling–deswelling of the both SSP films (thickness 0.2 mm) on the glass slides exhibited a very sharp response compared to polymer–gel discs (2 mm) [19]. As seen from the figure, when the temperature of the swollen SSP film is modulated from 6 to 80 °C, it takes only 5 min to expel the water to attain equilibrium collapsed-state. On the other hand, swelling appeared to be a little slower and took almost 15–20 min to attain equilibrium swollen state. In comparison, the polymer-hydrogel discs (with thickness of 2 mm) required nearly 1280 min (time taken in the first cycle) or > 120 min (time taken in subsequent cycles) to attain the equilibrium swelling [19].

Rate of deswelling was found to be faster than the rate of swelling in SSP films. The faster rate of deswelling may be attributed to faster diffusion at higher temperature and to ease of collapse of the polymer structure during deswelling due to internal stresses. The increasing stresses inside the structure during swelling provide resistance to diffusion of water from outside to inside, whereas during deswelling the internal stresses help in pushing the water out.

The quicker response in the SSP films can be attributed to the faster diffusion of water in and out of the sample primarily due to lower thickness of the SSP films compared to the hydrogel discs. Since the hydrogel dimensions (thickness) control the speed of its response to external stimuli, the thinner films of 0.01 mm were expected to give still faster response. Fig. 9 gives response of thin SSP films obtained using equivalent concentration of BTCA crosslinker. Both the swelling and deswelling were found to be extremely fast. As seen in the figure, the response of these thin films was faster by about two orders of magnitude compared to gel disks. Importantly 70% of swelling occurred almost spontaneously (Table 5). This is attributed to larger surface to volume ratio.

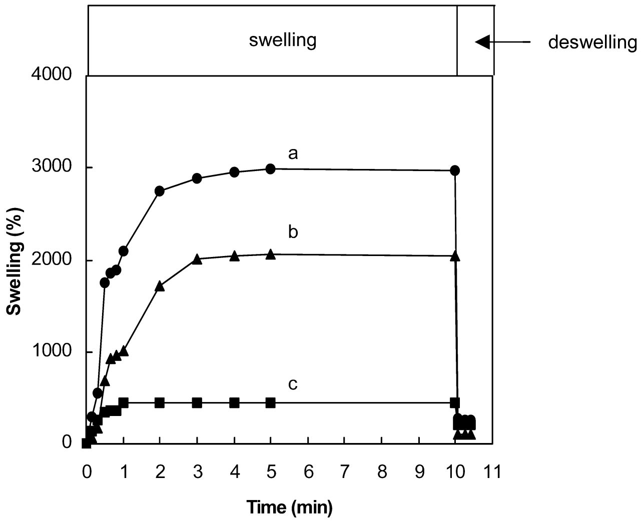

Fig. 9. Rate of transition of poly(NTBA-ran-Am :: 27:73) processed films (0.01 mm) with BTCA content: (a) 36.9 mol%, (b) 49.3 mol%, and (c) 61 mol%.

3.6. Extent of swelling and its reversibility

The swelling percentage of the different SSP structures was compared at equilibrium. These values are listed in Table 5 and the behavior is shown in Figs. 10–12. The extent of swelling was found to be 4 times higher in SSP films with thickness 0.2 mm than the gel discs (2 mm) [19]. This is in spite of the lower number of hydrophilic amide groups available in the crosslinked SSP films compared to gel discs. The swelling percentage was still more pronounced for SSP films of thickness 0.01 mm. In these films the maximum swelling of about 3000% was attained, which was 6 times that of gel discs. The higher swelling

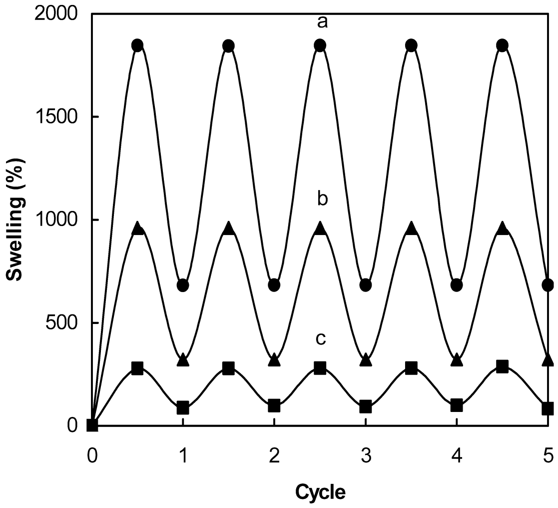

Fig. 10. Reversibility of transition in poly(NTBA-ran-Am :: 27:73) processed films (0.2 mm) with CA content: (a) 36.9 mol%, (b) 49.3 mol%, and (c) 61 mol%.

Table 5
Comparison of swelling behaviour and response time of different SSP structures

Sample B40:A60	Structure thickness (mm)	Equilibrium swelling (%)	Time for 70% of equilibrium swelling (min)
Gel disc B40:A60	2	490	~90
BT1	0.2	1860	5
BT2	0.2	1845	8
BT3	0.2	270	2
BT11	0.01	2980	~1
BT21	0.01	2050	~1
BT31	0.01	450	<1
CT1	0.2	1845	7
CT2	0.2	960	11
CT3	0.2	270	7

percentage may be attributed to ease in opening up of thin film structure due to lower development of internal stresses.

The swelling ratios of the processed films followed an inverse relationship with the polycarboxylic crosslinker concentration. The swelling% in the thicker SSP films decreased from 1860 (or 1845) to 270 with increase in crosslinker concentration from 36.9 to 61 mol%. A similar effect of increasing crosslinker concentration was also seen in thinner films (0.01 mm), where swelling decreased from 3000 to 450%. Higher crosslink density intensifies a resistance to chain extension, thereby reducing the equilibrium swelling. Higher crosslinking also reduces the availability of free amide side groups and hence alters the hydrophilic content in the SSP. Both these factors contribute towards lowering of equilibrium swelling in the SSP films with higher crosslink density.

Effect of the two crosslinkers, CA and BTCA, on the swelling behaviour was studied. Swelling percentage for BTCA based SSP films was found to be a little larger than the CA based SSP films obtained with equivalent concentration of crosslinker. This difference indicated that the structure developed due to BTCA was relatively more open.

The reversibility of transition in the SSP films was studied by repeatedly subjecting them to swelling and deswelling. This was achieved by placing them in water at 6 °C and at 80 °C, respectively, for five cycles. Figs. 10 and 11 show swelling and deswelling behaviour of thicker films (0.2 mm) obtained using CA and BTCA crosslinkers, respectively. Fig. 12 shows the reversible behaviour of the thin SSP films (0.01 mm) using BTCA crosslinker. As seen in the figures, the SSP films exhibited excellent reversibility indicating the stability of structure during repeated transitions.

In the deswelled state, the SSP films were observed to retain some amount of water. The presence of hydrophilic acrylamide units and the crosslinked structure both may be responsible for entrapment of water. The thicker films (0.2 mm) retained 700–70% water in the collapsed state depending upon the extent of crosslinking. The amount of retained water decreased with increase in crosslinker concentration. At higher concentrations of crosslinker relatively less number of free amide groups were available to impart hydrophilicity to the polymer resulting in lower water retention. In thinner films of 0.01 mm the water was expelled (diffused out) to a greater extent compared to thick

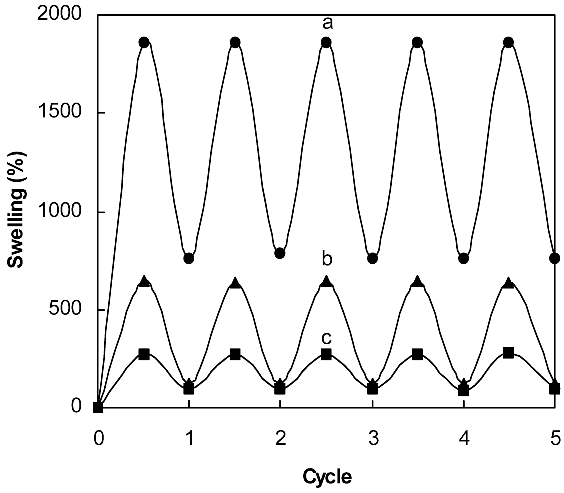

Fig. 11. Reversibility of transition in poly(NTBA-ran-Am :: 27:73) processed films (0.2 mm) with BTCA content: (a) 36.9 mol%, (b) 49.3 mol%, and (c) 61 mol%.

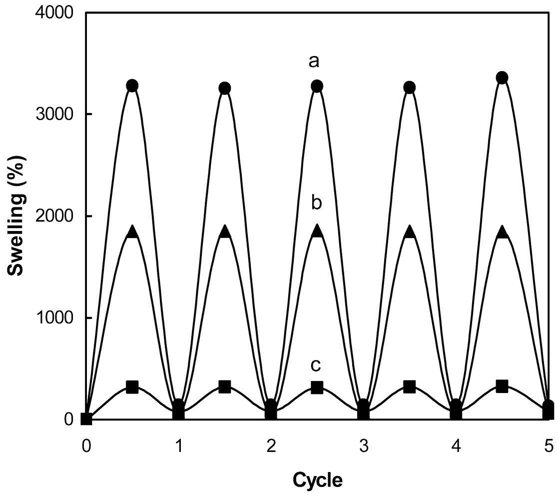

Fig. 12. Reversibility of transition in poly(NTBA-ran-Am :: 27:73) processed films (0.01 mm) with BTCA content: (a) 36.9 mol%, (b) 49.3 mol%, and (c) 61 mol%.

films, indicating better reversibility. In these films the effect of crosslinker concentration was not observed.

4. Conclusions

A series of temperature sensitive linear poly(*N-tert*-butylacrylamide-*ran*-acrylamide) were synthesized by free radical copolymerization in methanol at 50 °C. The copolymers with varying feed ratios of NTBA and Am (80:20 to 20:80 mol%) were synthesized and characterized. Regulated dosing of Am, having a higher reactivity ratio ($r_{\mathrm{Am}} = 1.5$) than NTBA ($r_{\mathrm{NTBA}} = 0.5$) was found to be necessary for obtaining random copolymers exhibiting single glass transition temperature and well defined LCST curve. The incorporation of the NTBA comonomer in the copolymers was found to be lower than the feed because of its lower reactivity.

A method of processing copolymers based on polyacrylamide, such as the above series, into thin films or coatings has been investigated. In these copolymers, the amide side groups of acrylamide moiety could be exploited to provide sites for crosslinking with polycarboxylic acid crosslinkers for creating mechanically strong thin hydrogel structures. Using this approach, the aqueous solution of high molecular weight copolymer of NTBA and acrylamide (27:73 mol%) was coated on substrate in presence of polycarboxylic crosslinkers and catalyst. The coated and dried films were crosslinked by curing at 150–160 °C for 15–20 min. The crosslinked thin films of thickness 0.01–0.2 mm were found to be insoluble and mechanically stable. The utilization of amide side groups for crosslinking was also evident from the fact that the transition temperature of the crosslinked films decreased to 22–25 °C from 37 °C of the linear copolymer. The processed film structures (thickness 0.01 mm) were found to have greatly enhanced 'rate of swelling' and 'swelling% at equilibrium' compared to gel discs of 2 mm thickness. The response time decreased by about two orders of magnitude from 1280 min to under 5 min, whereas the swelling% increased from 490 to 2980%. The swelling% was also found to be a function of crosslinker concentration.

This approach to process SSP can be adopted to integrate SSP on to variety of substrates such as textile yarns and fabrics, where polyfunctional compounds can crosslink polymer chains to free reactive sites available on the substrate. Such integrated structures would enable applications that require fast response time coupled with high functionality, efficiency, and mechanical properties.

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