

# Stimuli Sensitive Copolymer Poly(*N*-tert-butylacrylamide-*ran*-acrylamide): Synthesis and Characterization

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**ABSTRACT:** Temperature sensitive random linear and crosslinked copolymers of *N*-tert-butylacrylamide (NTBA) and acrylamide (Am) were synthesized by the solution polymerization method, using regulated dosing of comonomer Am having a higher reactivity ratio ( $r_{Am} = 1.5$ ) than NTBA ( $r_{NTBA} = 0.5$ ). Copolymers with varying feed ratios of NTBA and Am (80 : 20 to 20 : 80 mol %) were synthesized and characterized. For the synthesis of copolymer hydrogels, *N*', *N*-methylene bisacrylamide (MBA) (1.13 mol %) was used along with monomers. The effect of composition on transition properties was evaluated for the linear copolymers and their hydrogels. A definite trend was observed. The incorporation of a higher percentage of the hydrophilic comonomer Am in the structure resulted in the shifting of the transition temperature towards a higher value. The transition temperatures of the copolymers synthesized with feed compositions of 80 : 20, 70 : 30, 60 : 40, 50 : 50, 40 : 60, 30 : 70, and 20 : 80 mol % were found to be 2, 10, 19, 27, 37, 45, and

58°C, respectively. Differential scanning calorimetry (DSC) studies confirmed the formation of random copolymers. The copolymers synthesized with a monomer feed ratio of 50 : 50 with regulated dosing showed a single glass transition temperature ( $T_g$ ) at 168°C, while the copolymer synthesized with full dosing of Am at the beginning of the reaction showed two  $T_g$ s, at 134 and 189°C. The copolymer samples were analyzed by Fourier transform infrared spectroscopy (FTIR) for ascertaining the composition. The composition of the copolymers followed the trend of the feed ratio, but the incorporation of NTBA in the copolymers was found to be lower than the feed ratio because of lower than quantitative yields of the reactions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 672–680, 2005

**Key words:** stimuli-sensitive polymers; hydrogels; synthesis; *N*-substituted acrylamide; temperature sensitive

## INTRODUCTION

Ever since the observation of the lower critical solution temperature (LCST) phenomenon<sup>1</sup> for poly(*N*-isopropylacrylamide) (PNIPAA), a lot of effort has been expended that has resulted in commercialization of the stimuli-sensitive polymers, particularly in the medical field.<sup>2</sup> These polymers also find potential applications in the separation and recovery of chemicals.<sup>3–5</sup> An innovative application has been the development of clear/cloud glazing application, where the solar energy transmission in the room is regulated by the transparency of the solubilized polymer, below the transition temperature, and opacity of the precipitated polymer, above the transition temperature.<sup>6</sup> Transition temperatures of the polymer may be varied by changing the molecular structure.<sup>7</sup> For example poly(*N*-acryloylpiperidine) shows transition at 4–6°C, poly(*N*-*n*-butylacrylamide) at 25°C, poly(*N*-piperidylmethacrylamide) at 42°C, and poly(*N*-isopropylacrylamide) at 32°C. However, chemical modification by copolymerization is a simpler route for tuning the transition temperature to a desired value. Incorporation of hydrophilic comonomer leads to an increase

in the transition temperature, whereas incorporation of hydrophobic comonomer leads to a decrease. For example copolymerization of *N*-isopropylacrylamide, with butylmethacrylate, which is a hydrophobic monomer in a feed ratio of 96 : 4 mol %, gives a transition temperature of 29°C, while copolymerization with acrylamide, which is a hydrophilic comonomer in a similar feed ratio, gives a transition temperature of 35°C.<sup>8</sup> However, only a few polymer systems have been studied using this approach and most of them are based on *N*-isopropylacrylamide (NIPA).<sup>9–14</sup> NIPA has a drawback, that it is commercially unviable because it is synthesized in low yields. Therefore, more polymer systems need to be developed keeping the commercial applications in mind. Another major challenge in using stimuli-sensitive materials is their processability into desirable forms such as coatings, films, and fibers. Because stimuli-sensitive polymers are water soluble below the transition temperature, they are required to be polymerized in gel form. Often gels are thick due to poor mechanical strength and show slow diffusion of water in and out of gel at the transition temperature. This also leads to poor utilization of functional sites present in the gel in applications such as drug delivery, bioseparation, and purification, etc.

To obtain fast transitions, high functional efficiency, and good durability, it is, therefore, extremely impor-

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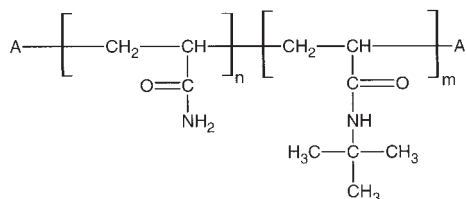


Figure 1 Copolymer structure.

tant that such stimuli sensitive polymer systems be developed that are processable into structurally strong, thin, desirable shapes. These polymers should also contain chemical sites that may be used for subsequent crosslinking.

This is a challenging task, because one is required to incorporate functionality while maintaining the transition behavior of the final system. This article is an attempt to develop such a copolymer system based on NTBA and Am (Fig. 1). NTBA is a highly hydrophobic monomer that on polymerization gives a theoretical LCST of about  $-5^{\circ}\text{C}$ , while acrylamide is a highly hydrophilic monomer that on polymerization does not show transition until the boiling point of water. This gives a possibility of achieving a wide range of transition temperatures on copolymerization. In addition, acrylamide has an amide side group, which may be utilized for crosslinking reaction subsequent to processing. The feasibility of carrying out crosslinking reactions in poly(acrylamide) has been recently published by our group.<sup>15</sup>

Though some copolymers of *N*-alkyl acrylamide and acrylamide have been reported recently in the literature,<sup>16,17</sup> study with respect to transitional behavior and reversibility in copolymers based on *N*-tert-butyl acrylamide (NTBA) and acrylamide (Am) requires further investigation before the above objectives may be realized.

The current study is an attempt to synthesize linear and crosslinked copolymers of NTBA and Am of high molecular weight, with varying compositions so that

tunable and reversible transitions may be obtained. The linear copolymers could be readily processed into thin films using available amide side groups. The approach for processing of these copolymers has been separately studied.<sup>18</sup>

## EXPERIMENTAL

### Materials

*Tert*-butanol, glacial acetic acid, methanol, sulfuric acid, acetone, and *N*, *N*-methylenebisacrylamide (MBA) were obtained from Qualigens Fine Chemicals, Mumbai. Acrylamide and ammonium persulfate were obtained from Merck (India), Mumbai. Acrylonitrile was purchased from GS Chemical Testing Lab and Allied Industries, Mumbai. All the chemicals were with minimum assay of or exceeding 99% and were used without further purification.

### Copolymer synthesis

#### Monomer synthesis

NTBA was synthesized by the Ritter's reaction, as reported previously.<sup>19</sup>

#### 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 2M. The NTBA content of the monomer feed was varied from 100 to 20 mol % (Table I). Both linear as well as crosslinked copolymers were prepared. For the crosslinked copolymers, MBA (1.13 mol %) was used along with monomers. 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.

TABLE I  
Compositional Ratios of the Copolymers and Their Transition Properties

Sample code	Feed ratio NTBA: Am (mol %)	NTBA content in copolymer by FTIR (mol %)	LCST for copolymer solutions ( $^{\circ}\text{C}$ ) (conc. at LCST, wt %)	Transition temperature for crosslinked copolymers ( $^{\circ}\text{C}$ )	Change in swelling % $6^{\circ}\text{C}$ to $80^{\circ}\text{C}$ (%)
PNTBA	100 : 0	100	Insoluble	No transition	-
B80 : A20	80 : 20	75	Insoluble	Begins at 2	42 to 19
B70 : A30	70 : 30	58	Insoluble	10	280 to 22
B60 : A40	60 : 40	38	17 (0.375%)	19	327 to 46
B50 : A50	50 : 50	32	27 (0.15%)	27	424 to 149
B50 : A50F	50 : 50	30	34 (over a broad range)	26, 37	458 to 182
B40 : A60	40 : 60	27	38 (1.25%)	37	480 to 182
B30 : A70	30 : 70	26	No LCST	45	483 to 311
B20 : A80	20 : 80	11	No LCST	58	689 to 506
PAm	0 : 100	0	No LCST	No transition	-

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 a vacuum oven at 120°C.

In the case of both linear and crosslinked copolymerization, the reaction mixture becomes viscous/viscous-gel only after about 3 h at the above conditions. The reaction mixture remains highly fluid until this time. The dosing rate was decided based on a preliminary series of experiments so that more reactive monomer is available at lower concentrations to allow even distribution during these initial few hours of polymerization. Thereafter, the higher availability of the second comonomer (NTBA) is likely to ensure random distribution to a great extent. No monomer was added after the reaction mixture started to become viscous or viscous-gel.

For comparison, 50 : 50 copolymer was also synthesized by adding the 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.<sup>15,20</sup>

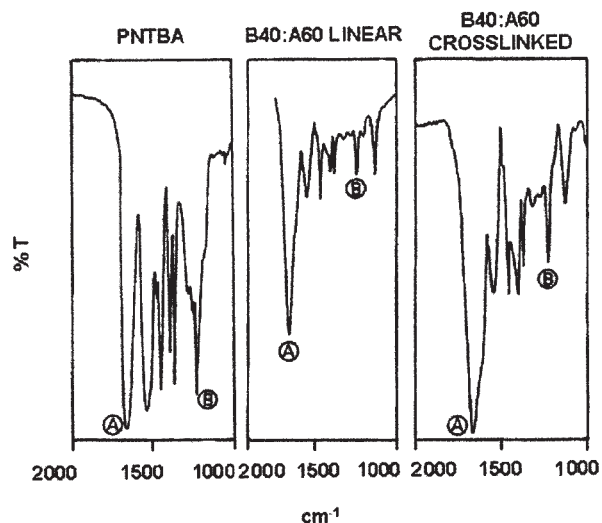
### Copolymer characterization

Determination of composition by FTIR<sup>17</sup>

The FTIR spectra were recorded on a Perkin-Elmer BX II spectrophotometer. The intensity of the peak at 1225 cm<sup>-1</sup> (due to -C(CH<sub>3</sub>)<sub>3</sub> group) was normalized using the C=O stretching peak of both NTBA and Am units at 1665 cm<sup>-1</sup>. The normalized height of the -C(CH<sub>3</sub>)<sub>3</sub> peak at 1225 cm<sup>-1</sup> was compared with that of the normalized PNTBA peak, to obtain the incorporation of NTBA in both the linear and crosslinked copolymers. The FTIR spectra of linear and crosslinked B40 : A60 copolymer is given in Figure 2 as an illustration. The compositions of the copolymer obtained by FTIR are given in Table I.

### Thermal studies

Thermogravimetric analysis was carried out on a Perkin-Elmer TGA 6. The samples were heated from 50 to 600°C, at the rate of 20°C min<sup>-1</sup>. The Differential Scanning Calorimetry (DSC) studies were performed on a Perkin-Elmer DSC 7. The samples were heated from 50 to 300°C, with a heating rate of 20°C min<sup>-1</sup>.



**Figure 2** The FTIR spectra (in selected range of 1000 cm<sup>-1</sup> to 2000 cm<sup>-1</sup>) of poly(*N-tert*-butylacrylamide), B40 : A60 linear, and B40 : A60 crosslinked polymers showing the amide peak marked as A and the *tert*-butyl peak marked as B.

### X-ray studies

The X-ray diffractograms of powdered samples were recorded on a Philips X-Ray Generator 1730/10 to assess the degree of order in these polymers. The diffractograms for samples PAm, PNTBA, and copolymers 40 : 60, 50 : 50, and 50 : 50F were recorded after drying.

### Determination of transition temperatures for the linear and crosslinked copolymers

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

For gels, the transition was determined by measuring the swelling % (gravimetrically) at different temperatures. The gel discs were left at each temperature in the thermostatic bath until they reached equilibrium. Equilibrium swelling (%), for the crosslinked copolymers, was determined as:

$$\text{Equilibrium swelling (\%)} = (W_e - W_d) \times 100 / W_d \quad (1)$$

$W_d$  and  $W_e$  represent the dry weight and the weight attained after equilibrium, respectively.

The equilibrium swelling % was calculated using eq. (1) for the deswollen gels as well. The transition temperatures were determined by first determining the start and end point of the inflection in the curves obtained between swelling % and temperature. Subsequently, tangents were drawn at these points, and the middle point of the straight line joining the start

TABLE II  
Thermal Properties of SSP Copolymers

Polymer sample	$T_g$ (°C)	Degradation temperature (°C) and % weight loss					
		1 <sup>st</sup> step			2 <sup>nd</sup> step		
		Temp range (°C)	$T_{pk1}$	% wt loss	Temp range (°C)	$T_{pk2}$	% wt loss
PNTBA	108	330–386	369	48	386–463	406	28
B80 : A20	146	244–359	331	33	359–507	433	45
B70 : A30	146	251–334	305	27	334–484	431	51
B60 : A40	158	235–330	295	20	329–479	419	62
B50 : A50	168	255–347	317	17	347–467	431	53
B50 : A50F	134, 189	266–337	310	20	266–495	426	57
B40 : A60	160	265–351	326	21	351–487	419	59
B30 : A70	169	266–349	316	18	349–502	424	55
B20 : A80	174	261–365	331	18	365–500	426	59
PAm	194	259–356	331	15	356–494	412	62

and end points was taken as the transition temperature. This procedure is very similar to that carried out in determining thermal transition  $T_g$  in any polymer. The swelling % was found to vary among various samples of the same composition within  $\pm 5\%$  of the values reported.

#### Swelling studies of crosslinked copolymers

The swelling kinetics of crosslinked copolymers was investigated by immersing 2 mm discs of copolymer gels in distilled water at a temperature of 6°C, which is lower than the transition temperature of all polymers except B80:A20. The increase in water content was followed by the determination of gel weight against time. The swelling percentage, at time  $t$  for the crosslinked copolymers, was determined as

$$\text{Swelling (\%)} = (W_t - W_d) \times 100 / W_d \quad (2)$$

$W_d$  and  $W_t$  represent the dry weight and the weight attained after time  $t$ , respectively.

After ensuring the attainment of equilibrium, the deswelling kinetics of the copolymer gels was followed by applying a temperature change to 80°C (at 1200 min of the experiment time).

#### Thermoreversibility of crosslinked copolymers

The dried gel disk samples were conditioned by swelling and deswelling them twice. The reversibility of conditioned copolymer gel discs was studied by placing them alternately at temperatures of 6°C and 80°C for three additional cycles. The gel discs were kept immersed (at the above temperature) for 3 h to attain equilibrium.

## RESULTS AND DISCUSSION

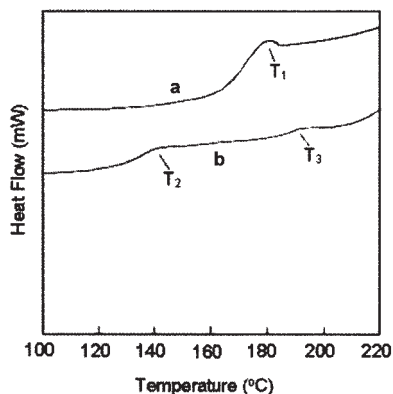
### Copolymer synthesis and characterization

The reactivity ratios for copolymerization of NTBA and Am have been recently reported as 0.5 and 1.5, respec-

tively,<sup>21</sup> for polymerization at 50°C. Therefore, during polymerization the dosing of the more reactive monomer Am was regulated to obtain random copolymers of controlled composition. The monomer Am was introduced in four equal doses over a time period of 2 h and 15 min at the beginning of the reaction. Addition of monomers after this period was not found to be suitable because the viscosity of the reaction medium was found to rise significantly at around 3 h. The interval of 45 min for each dosing gave random copolymers, and it was arrived at after carrying out preliminary experiments. Preparation of poly(*N*-tert-butylacrylamide) (PNTBA) and poly(acrylamide) (PAm) was carried out for comparison with copolymers.

Table I shows the composition of copolymers as a function of acrylamide in the feed. The copolymer composition determined by FTIR was found to be different from the comonomer 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 (refer to the reactivity ratios described above) and different solubility of monomers.<sup>22,23</sup> The copolymerization conditions were optimized to obtain high molecular weight copolymers.

The glass transition temperatures obtained from DSC studies are given in Table II. PAm and PNTBA exhibited a  $T_g$  of 194°C and 108°C, respectively. The higher glass transition temperature value of PAm can be explained by the presence of two hydrogen atoms in the amide group. These amide groups result in strong hydrogen bonding and hence reduced mobility of the 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 the copolymers. With increase in Am content, the transi-



**Figure 3** Thermal transitions (glass transitions) of copolymers (a) B50 : A50 ( $T_1 = 168^\circ\text{C}$ ) and (b) B50 : A50F ( $T_2 = 134^\circ\text{C}$ ;  $T_3 = 189^\circ\text{C}$ ) as obtained by differential scanning calorimetry (DSC).

tion was found to shift to higher values, indicating a nearly random distribution of NTBA and Am in copolymer segments. Interestingly, unlike B50 : A50, in B50 : A50F, two glass transition temperatures at 134 and 189°C were observed (Fig. 3). These two distinct glass transition 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.

The X-ray diffractogram of homopolymers of Am and NTBA showed broad peaks at the  $2\theta$  angle of  $20.2^\circ$  and  $18^\circ$ , respectively (Fig. 4). The copolymers exhibited peaks between  $2\theta$  of  $18^\circ$  and  $20.2^\circ$ . PNTBA showed a more intense peak compared to PAm and copolymers. Annealing at  $180^\circ\text{C}$  caused a slight increase in the intensity of the peak in PNTBA and copolymers. Such an increase in intensity may be caused by some ordering of the polymeric chains due to higher mobility at annealing temperature.

The thermal degradation of homo and copolymers was observed to occur in two steps (Table II). In poly(acrylamide), the degradation occurred at peak temperatures of ( $T_{p1}$ )  $331^\circ\text{C}$  and ( $T_{p2}$ )  $412^\circ\text{C}$ , and weight losses of 15 and 62%, respectively. Poly(acrylamide) is known to decompose above  $290^\circ\text{C}$  with liberation of ammonia and formation of imide groups.<sup>24</sup> The presence of ammonia in the degradation products has also been verified by gas chromatography.<sup>25</sup>

In PNTBA, the degradation occurred at a higher temperature. The substitution of amide-H with the *tert*-butyl group increases the steric hindrance and hence makes it more difficult for the adjacent amino group to interact. As shown in Table II, the weight loss due to the first step was more prominent in PNTBA, and the weight loss due to the second step was more prominent in PAm. A gradual increase in the content of NTBA in the copolymer resulted in higher weight loss in the first step and reduced weight loss in the

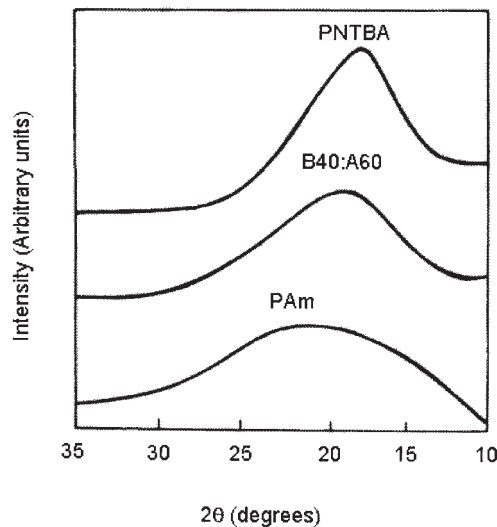
second step due to the random distribution of monomers in the copolymer. However, at  $500^\circ\text{C}$  the total weight loss in the two polymers was comparable, indicating no significant difference in their thermal stability. However, due to small differences, we would not like to make any conclusive inferences.

### Transition studies of linear copolymers and crosslinked gels

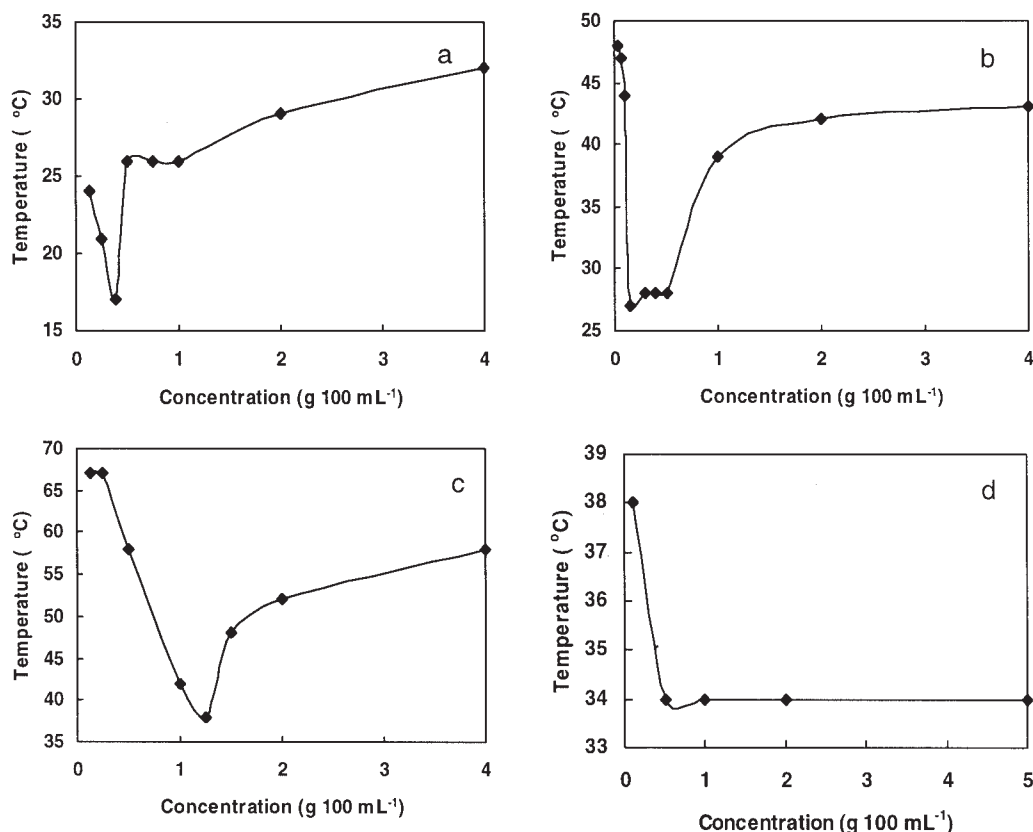
The phase transition behavior of linear copolymers was found to be quite sensitive, reversible, and reproducible to thermal stimuli. The transition temperatures for linear copolymers are given in Table I. The copolymers B80 : A20 and B70 : A30 were insoluble in water; while in the copolymers B30 : A70 and B20 : A80, the LCST could not be observed, maybe due to extremely high hydrophilicity of the copolymer. The LCST varied between  $17$  to  $38^\circ\text{C}$  for the intermediate compositions, that is, 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  $17^\circ\text{C}$ . The LCST curves for these copolymers are shown in Figures 5(a) to (d).

As can be observed from Figure 5(d), the curve obtained for B50 : A50F becomes nearly flat at concentrations above 0.5 wt %, which is characteristically different from the other curves. In the other three copolymers, a distinct LCST was observed, which may be attributed to better homogeneity of the copolymer structure compared to B50 : A50F.

Figures 6(i) and (ii) show swelling % versus temperature plots for copolymer gels on heating or cooling. The swelling % was found to vary among various samples of the same composition within  $\pm 5\%$  of the



**Figure 4** X-ray spectrograms of PNTBA, PAm, and copolymer B40 : A60.



**Figure 5** Lower critical solution temperature curves: (a) B60 : A40, (b) B50 : A50, (c) B40 : A60, and (d) B50 : A50F.

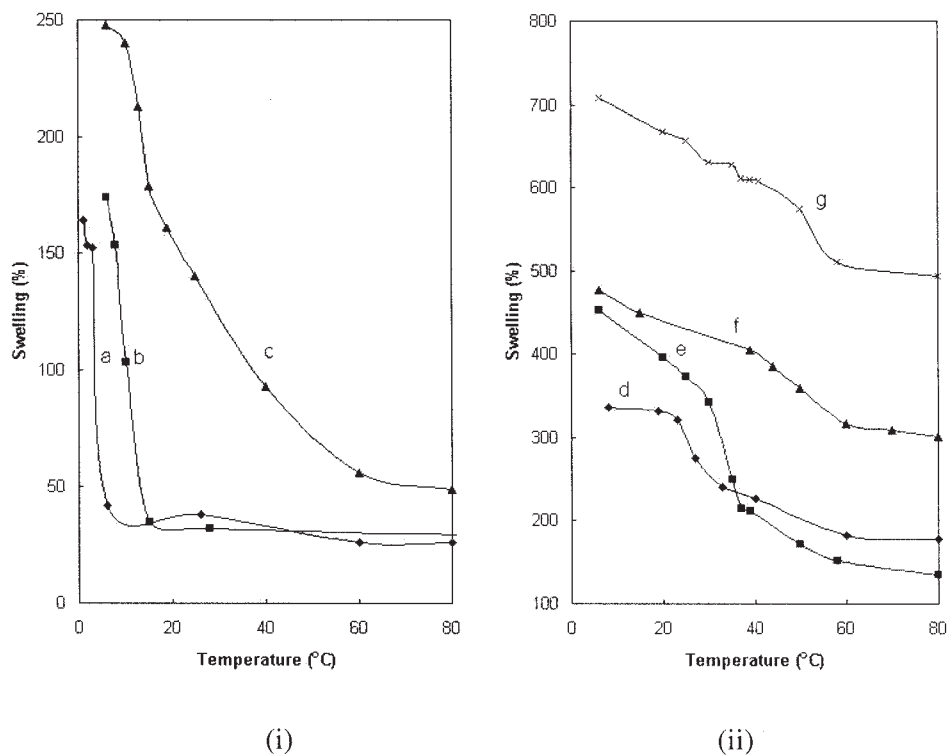
values reported. The crosslinked copolymers (hydrogels) show a significant decrease in swelling percentage at transition temperatures. The sharp decrease in swelling percentage above the transition temperature is attributed to the collapse of the swollen polymer network. The gels show sharp transitions and complete reversibility without significant hysteresis. As detailed in Table I, the transition temperature varied between 2 and 58°C for copolymer gels containing 75 mol % to 11 mol % of NTBA. The transition temperatures (the inflection in swelling % versus temperature curves) for gel copolymers were found to be very close to those observed in their linear counterparts. This suggests that both linear and gel copolymers have similar distribution of comonomers.

The results shown in Figures 5 and 6 indicate that the transition temperature increases with increase in acrylamide content in the copolymers. The temperature sensitivity of polymer solutions or gels is associated with the temperature dependency of hydrogen bonding and hydrophobic interactions.<sup>26</sup>

At lower temperatures, hydrogen bonding between hydrophilic segments of the polymer chain and water molecules dominate, leading to enhanced dissolution/swelling of linear copolymers/hydrogels. Above the transition temperature, the hydrophobic interactions are strengthened, while the hydrogen bonding becomes weaker. The net result is shrinking of hydrogels due to

interpolymer chain association through hydrophobic interactions, and the absorbed water is expelled. As the gel loses water, it shrinks, becomes stiff, and turns translucent or opaque. With increase in hydrophilicity of copolymers at higher Am content, the transition becomes broad and shifts to higher temperature.

An interesting observation was made in transitions shown by linear and crosslinked copolymers. Though only a few compositions of linear copolymers show a visible transition from complete solubility to insolubility (marked by the appearance of turbidity), gel copolymers show clear transitions for many more compositions. This may be because of the fact that the linear copolymer compositions having extremely high content of either NTBA (hydrophobic groups) or acrylamide (hydrophilic groups) are unable to transform their solubility in water. However, in gel form, the same compositions are able to associate with different amounts of water molecules due to the change in relative hydrophilicity of the copolymer network at the transition temperature. The change in hydrophilicity in such copolymers is significant as evident from the sharp decrease in swelling % at the transition temperature. This suggests that detecting transitions in many cases of linear SSPs based only on appearance/disappearance of turbidity may be difficult and inconclusive.



**Figure 6** (i) Dependence of swelling percentage of SSP copolymers on temperature: (a) B80 : A20, (b) B70 : A30, and (c) B60 : A40. (ii) Dependence of swelling percentage of SSP copolymers on temperature: (d) B50 : A50, (e) B40 : A60, (f) B30 : A70, and (g) B20 : A80.

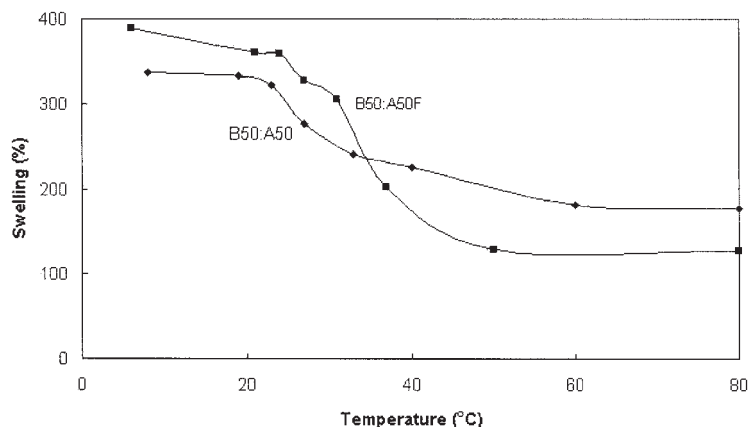
The copolymer-gel prepared by adding a full dose of both the monomers at the start of the reaction, B50 : A50F, showed a broad transition evenly spread over a range of 30°C, while the copolymer-gel prepared with regulated feed, B50 : A50, showed transition in essentially one step with the majority of change taking place in a less than 10°C interval (Fig. 7). Similarly, their linear counterparts also showed different transitional behavior between them, with only the copolymer prepared with regulated dosing exhibiting clearly defined LCST. These observations may be attributed to formation of blocks of different compositions in copolymers prepared without regulated dosing. Since DSC studies reveal two clear  $T_g$ s for the single dose B50 : A50F copolymer, our explanation for broad transition based on blocks of different composition is reasonable.

#### Swelling/deswelling kinetics of copolymer gels

The swelling and deswelling kinetics of copolymer gels were studied by recording the change in swelling percentage with time for copolymer gels (2mm thick discs). For swelling studies the gels were immersed in a water bath at temperature below the transition temperature (6°C), while the deswelling was recorded by subjecting the gels to 80°C. These temperatures were chosen as they are the extreme temperatures on both

sides of the expected transition temperatures for all copolymers except B80 : A20. The swelling-deswelling curves for varying compositions of copolymer gels are plotted in Figures 8 and 9. The kinetic studies were followed for the first (Fig. 8) and third cycle (Fig. 9). As seen from the figure, the rate of swelling of gels in the first cycle was found to be slower than in the subsequent cycles. In the first cycle, the crosslinked gels took about 20 h to attain equilibrium swelling, while in the third cycle approximately 2 h were required to attain equilibrium. The equilibrium swelling percentage was also observed to increase with increase in the Am content in the copolymer hydrogel. The maximum swelling increased from 42 to 689% with increase in Am content in copolymers from 25 to 89 mol %. The equilibrium swelling values below transition for B80:A20 could not be achieved because the temperature used (6°C) in these experiments was higher than the transition temperature of the copolymer.

Deswelling was initiated at 1200 min (Figs. 8 and 9) by increasing the temperature of the water bath to 80°C, as explained in the experimental section. The rate of deswelling was found to be faster than the rate of swelling. The copolymer hydrogel took 1–2 h to attain the equilibrium collapsed-state. This may be attributed to faster diffusion at higher temperature and reduction in internal stresses during the deswelling process.



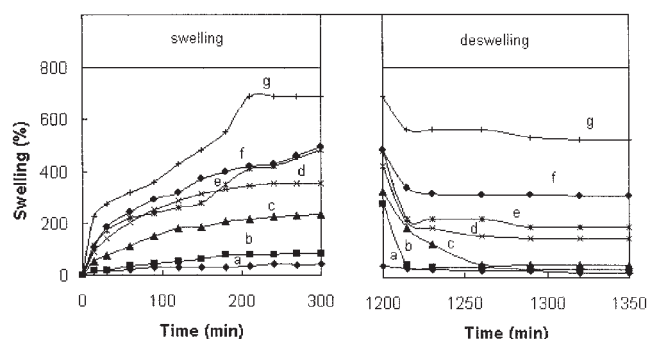
**Figure 7** Transition behavior of copolymer gel (a) prepared with single dosing of monomers (B50 : A50F) and (b) regulated dosing of monomers (B50 : A50).

### Reversibility of copolymer gels

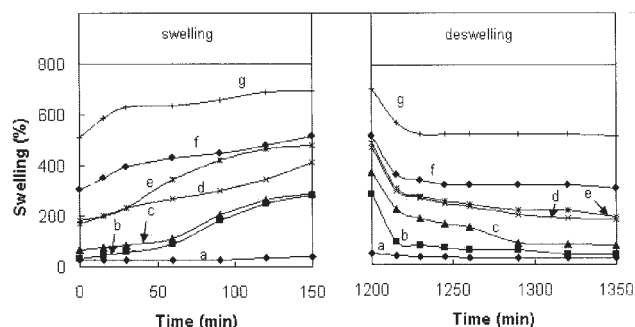
To study the reversibility of transition in copolymer gels, the samples were subjected to repeated swelling and deswelling. This was achieved by placing them in water at 6°C and at 80°C, respectively, for three cycles. The samples were first placed at the low temperature and then changed to the high temperature. The cycle was followed until constant weight was attained. Figure 10 shows the repeated swelling and deswelling behavior of copolymer gels (gel disc thickness 2 mm). As seen in the figure, all copolymer gels were found to reverse perfectly between the swollen and collapsed state. This is in contrast with the earlier study<sup>17</sup> where only one copolymer hydrogel containing 60 mol % NTBA (actual incorporation 67 mol % NTBA) showed a clear and reversible transition. The copolymers with higher Am content in that study were shown to remain swollen. The authors attributed this observation to hydrolysis of the Am moieties. No such phenomenon was observed in any of our copolymers. As discussed earlier, to obtain random copolymers of NTBA and Am, which have widely different reactivity ratios,

copolymerization should be carried out under regulated dosing of Am. The earlier study has not taken this fact into consideration.

As indicated in the previous section, the equilibrium swelling percentage was also observed to increase with increase in the acrylamide content in the copolymer hydrogel. The maximum swelling increased from 42 to 689% with increase in the Am content in copolymers from 25 to 89 mol %. This indicated that the hydrophobic tertiary butyl groups were responsible for the reduced interaction of water with the copolymer. Due to the hydrophobic nature of the tertiary butyl groups of NTBA, the deswelling was found to occur to a greater extent for copolymers with higher NTBA content. For copolymers with NTBA content in excess of 38 mol %, almost complete deswelling was observed with a residual swelling percentage of 20–40%. In comparison the copolymer with 89 mol % Am could only be deswollen to a residual swelling of 500%. The swelling values of B80 : A20 in Figure 10 are lower than equilibrium swelling values (>160% at 2 °C) because the transition temperature of this copolymer is lower than the experimental temperature of 6°C used here.

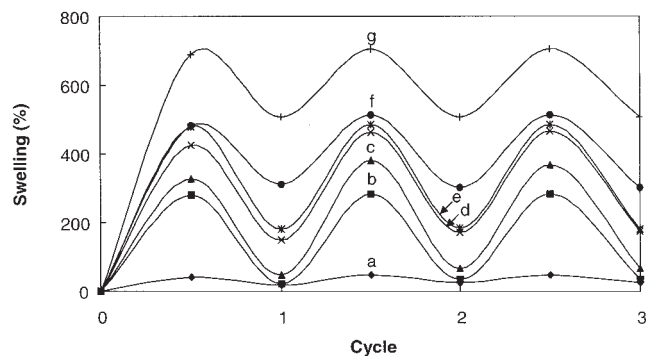


**Figure 8** (i) Rate of swelling at 6°C in the first cycle; (ii) Rate of deswelling at 80°C in the first cycle for the SSP copolymers: (a) B80 : A20, (b) B70 : A30, (c) B60 : A40, (d) B50 : A50, (e) B40 : A60, (f) B30 : A70, and (g) B20 : A80.



**Figure 9** (i) Rate of swelling at 6°C in the third cycle; (ii) Rate of deswelling at 80°C in the third cycle for the SSP copolymers: (a) B80 : A20, (b) B70 : A30, (c) B60 : A40, (d) B50 : A50, (e) B40 : A60, (f) B30 : A70, and (g) B20 : A80.





**Figure 10** Repeated swelling and deswelling of the copolymer gels over three cycles: a) B80:A20, b) B70:A30, c) B60:A40, d) B50:A50, e) B40:A60, f) B30:A70, g) B20:A80.

## CONCLUSION

A new series of temperature sensitive linear and crosslinked poly(*N*-*tert*-butylacrylamide-*ran*-acrylamide) were synthesized by free radical copolymerization in methanol at 50°C. For synthesis of copolymer hydrogels, MBA was used as a crosslinker. The copolymers with varying feed ratios of NTBA and Am (80 : 20 to 20 : 80 mol %) were synthesized and characterized. The following conclusions were drawn:

1. Regulated dosing of Am, having a higher reactivity ratio ( $r_{Am} = 1.5$ ) than NTBA ( $r_{NTBA} = 0.5$ ), was found to be necessary for obtaining random copolymers exhibiting a single glass transition temperature. The incorporation of the NTBA comonomer in the copolymers was found to be lower than the feed because of the lower reactivity of NTBA and non quantitative yields.
2. The linear copolymers and their crosslinked gels exhibited single sharp transition. The transition temperature decreased with increase in NTBA content in the copolymer. With increasing content of NTBA from 27 to 38 mol %, the LCST/transition temperature of the linear and crosslinked copolymers decreased from  $\sim 38$  to 17°C. The swelling percentage of crosslinked gels also decreased from 480 to 327% for the above NTBA content. Copolymer gels with a wider range of transition from 2 to 58°C were obtained on varying NTBA content from 75 to 11 mol %.

3. The conditioned gel discs (2 mm thickness) were found to take about 2 h to attain equilibrium swelling. The rate of deswelling was found to be significantly faster than the rate of swelling. The copolymer gels reversed perfectly and repeatedly between the swollen and deswollen state.

These NTBA/Am based linear copolymers could be used for processing into fine films and other desirable structures that could be subsequently crosslinked using amide side groups and suitable crosslinkers. The gel copolymers may serve as interesting alternatives for well known polymer systems based on poly(*N*-isopropylacrylamide) for various applications.

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