

Studies on thermal and swelling properties of Poly (NIPAM-co-2-HEA) based hydrogels

Suman Shekhar, M. Mukherjee and Akhil Kumar Sen*

Department of Chemical and Polymer Engineering, Birla Institute of Technology, Mesra, Ranchi, Jharkhand, India

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Abstract. Thermoresponsive hydrogels based on N-Isopropylacrylamide (NIPAM) and 2-Hydroxyethylacrylate (HEA) were prepared by free radical polymerization. The hydrogels were characterized by elemental (CHN) analysis, differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). DSC thermogram showed two endothermic transitions which are due to hydration of water present in different environments. One near 0°C called melting transition of ice and was used to calculate the quantitative determination of the amounts of freezing and non freezing water. The other transition above the ambient temperature was due to the combination of hydrophobic hydration and hydrophilic hydration which changes with the copolymer compositions. Swelling and deswelling studies of the hydrogels were carried out using the aqueous media, salt and urea solutions. The experimental results from swelling studies revealed that copolymers have lower rates of swelling and deswelling than the homopolymer.

Keywords: NIPAM; HEA; DSC; TGA; swelling

1. Introduction

Hydrogels are three dimensional cross linked polymeric structures which can take up a considerable amount of water inside its nanoscopic network, but do not dissolve in it. Hydrogels can be stimuli responsive material, whose dynamic characteristics enables them to be applied in a multitude of sectors including bioengineering, biotechnology, agriculture, food industry, pharmacy etc (Kumar *et al.* 2007, Guiseppi-Elie *et al.* 2001, Chunyue *et al.* 2008). The properties of hydrogels change at different environmental conditions such as temperature (Campillo *et al.* 2008), pH (Gyenes *et al.* 2008), solvent composition (Aykara and Dogmus 2004), electrical stimulus (Kulkarni and Biswanath 2009) etc. This simultaneous alternation in the macroscopic properties of the hydrogels is mainly dependent on weak molecular interactions like Van-der-Waals, hydrogen bonding, hydrophobic interaction, dipolar interactions, etc. These interactions give rise to osmotic pressure that together with the elastic stress of the hydrogel determines the swelling properties (Shibayama and Tanaka 1993).

Among many types of stimuli responsive polymer, thermoresponsive polymers are the most common. Poly (N-Isopropylacrylamide) (PNIPAM) has been widely studied as a thermo responsive

*Corresponding author, Ph. D., E-mail: akhilsen@bitmesra.ac.in

polymer due to its sharp volume phase transition (VPT) near ambient temperature (33°C) (Hirokawa and Tanaka 1984). Linear polymer shows lower critical solution temperature (LCST) at this temperature. Above this temperature the gels are collapsed and below this temperature gels are swelled. This is due to thermally induced dissociation of polymer solvent hydrogen bonds resulting in destroying the solvate shell of polymeric chains and thus reinforcing the polymer-polymer hydrophobic interaction.

In recent times, thermoresponsive hydrogels based on PNIPAM have been extensively investigated and reported by the several authors (Otake *et al.* 1990, Li and Tanaka 1992). The PNIPAM based hydrogels are used in controlled drug delivery, artificial muscle, sensor system, immobilization of the enzyme and separation process. Such a wide range of practical applications depends upon the swelling and deswelling behavior of the polymer network. Tokuyama *et al.* (2007) have studied the effect of synthesis medium on the swelling and elastic properties of the PNIPAM hydrogels and observed that the hydrogels synthesized in aqueous medium showed more rigid structures compared to those synthesized in organic solvents.

The biomedical and biotechnological applications of the gels usually need the modification of PNIPAM gels. These modifications are performed by introducing some reactive functional groups to improve the swelling behavior, mechanical strength etc. In this work HEA monomer has been selected as it is hydrophilic, non-toxic and more economic. It has also been successfully employed in tissue engineering and drug delivery applications (Mu *et al.* 2011, Spanoudaki *et al.* 2006).

In the present study, the authors wish to report the effect of hydrophilic HEA on the thermal and swelling properties of crosslinked PNIPAM. PNIPAM based homopolymer and its copolymer with HEA were prepared by free radical polymerization at room temperature. The compositions of the synthesized hydrogels were determined by elemental (CHN) analysis. TGA and DSC techniques were used to study the thermal properties of the hydrogels. The swelling and deswelling behavior of hydrogels were studied at various temperatures in water. The swelling behaviors of hydrogels were also studied in salt and urea solutions to investigate the effect of ionic strength and hydrogen bond interaction.

2. Experimental

2.1 Materials

The monomer N-Isopropylacrylamide (NIPAM) was purchased from ACROS Organic Chemicals and the comonomer 2-Hydroxyl ethyl acrylate was obtained from Sigma Aldrich, USA. Other chemicals used in the work were, *N, N* Methylene bis-acrylamide (MBA) from SISCO Research Lab, India, as cross linking agent, potassium per sulphate (KPS) from Titan Biotech Ltd., India as the initiator and the *N,N,N,N*, Tetra Methylene diamine (TEMED) from Central Drug House Ltd, India as an accelerator. All the reagents were of AR grade and double distilled water was used throughout the experiment for swelling and deswelling studies.

2.2 Copolymer preparation

PNIPAM/HEA hydrogels with different compositions were prepared by free radical polymerization. A typical procedure for the preparation of copolymer is as follows. NIPAM and HEA were dissolved in double distilled water in a test tube (internal diameter 15 mm) at room

Table 1 Compositions of homopolymer and copolymers and its nomenclature

NIPAM/HEA (Molar ratio)	MBA (in moles) × 10 ⁴	KPS (in moles) × 10 ⁴	Water (ml)	TEMED (20 vol%) Soln (ml)	Nomenclature
100/0	6.49	1.85	6	0.25	PNIPAM
75/25	6.49	1.85	6	0.25	NIPHEA7525
50/50	6.49	1.85	6	0.25	NIPHEA5050
25/75	6.49	1.85	6	0.25	NIPHEA2575

temperature followed by addition of cross linking agent MBA (1 mole% in terms of total monomers) in solution mixture. After complete dissolution of above reagent the initiator KPS (1 mole% in terms of total monomer) was added and shaken for dissolution. Then, the accelerator TEMED (0.25 ml aqueous solution of 20% v/v) was mixed and the test tube was kept under tap water to control the initial heat build-up. The total monomer concentration in the mixture was kept constant at 0.0225 moles and the total volume of the reaction mixture was maintained at 10 ml for all the compositions. The reaction mixture was sealed and allowed to stand for 24 hours to complete the reaction. The prepared hydrogel was removed from the test tube and cut into small pieces and washed in distilled water for several times followed by SOXHLET extraction with 1-4 dioxane to remove the unreacted monomer, the linear homopolymer present, if any and physically entrapped chemicals within the gel. Then the gels were recovered and air dried at room temperature followed by drying in the vacuum oven for minimum 48 hrs at about 80°C until a constant weight was attained for each sample. The total mole number of the monomers in the solvent was kept constant for all the compositions and the molar ratio of NIPAM and HEA were changed accordingly to obtain hydrogels of different thermoresponsive properties and swelling capacity. The conditions for the synthesis of Poly (NIPAM-HEA) copolymers are summarized in Table 1.

3. Characterizations

3.1 Elemental analysis (CHN)

The CHN analysis of dried hydrogels was carried out by an elemental analyzer (Elementar, Germany model: Vario EL111) to determine the CHN content in dried samples.

3.2 Differential scanning calorimetry (DSC)

DSC instruments (model: DSCQ10) manufactured by TA Instrument was used to study the thermal characteristics of the hydrogels in N₂ atmosphere. Equilibrium swollen hydrogels were taken for measurements. Excess water was removed by blotting the surface of the hydrogels with filter paper. Samples (7-13 mg) were then loaded in aluminum cells, and sealed hermetically. Thermogram for each sample was obtained for temperature range from -30°C to 85°C at the heating rates of 1°C min⁻¹. For analysis the thermogram was divided into two parts; one from -30°C to 15°C and another from 15°C to 85°C.

3.3 Thermo gravimetric analysis (TGA)

TGA analysis was performed on Thermogravimetric Analyzer (model: DTG 60, Shimadzu Corporation, Japan). Thermograms were recorded from room temperature (27°C) to 700°C at the heating rate of 10°C min⁻¹ with nitrogen gas flow rate of 30 ml min⁻¹.

3.4 Swelling studies at various temperatures in water

Temperature dependent swelling measurement was carried out at constant temperature water bath supplied by JULABO. The dried gel pieces were swollen up to equilibrium in distilled water over a range of temperatures (5-60°C). After a certain time interval, the swollen hydrogels were taken out from the swelling media, and weigh after removing excess surface water with filter paper, the corresponding weight being m_t . The swelling percentage was defined by using following Eq. (1), where m_d is the dry weight of hydrogel.

$$\%swelling = \frac{m_t - m_d}{m_d} \times 100 \quad (1)$$

3.5 Deswelling behavior

The deswelling kinetics of hydrogel was also followed gravimetrically in a constant temperature water bath at the different temperatures (50°C and 60°C). Hydrogels swollen till equilibrium at room temperature were transferred into a constant temperature water bath of different temperature, then after a certain time, hydrogels were surface dried with filter paper and weighed. The weight changes of the hydrogels were recorded during the course of deswelling at different time intervals. The percentage water retention (W_r) was calculated according to the Eq. (2).

$$W_r = \frac{m_{td} - m_d}{m_e - m_d} \times 100 \quad (2)$$

Where m_e is the equilibrium swelling weight at room temperature and m_{td} is the weight of hydrogel at a given time.

3.6 Swelling studies in salt and urea solutions

The swelling of respective cross linked gels were studied in salt solutions (NaCl) and non-ionic urea solutions separately at 10°C. The dry gels were swollen in different specified solute concentrations and equilibrium swelling percentage was calculated using Eq. (1).

4. Results and discussion

4.1 Elemental analysis

The elemental (CHN) analysis of dried samples was carried out to determine the composition of the gels. The theoretical C/N ratio is based on the feed ratio and the experimental C/N ratios for the different Poly (NIPAM-HEA) composition are presented in Table 2. These results indicate that the

Table 2 Comparison of theoretical and experimental *C/N* ratio of PNIPAM and its copolymers

Sample	Theoretical <i>C/N</i> ratio (Based on feed ratio)	Experimental <i>C/N</i> ratio (Based on elemental analysis result)
PNIPAM	5.01	5.112
NIPHEA7525	6.57	6.664
NIPHEA5050	9.42	9.985
NIPHEA2575	18.0	18.53

C/N ratio is increased with increasing the HEA content in hydrogel. This is expected as the HEA monomer does not contain any nitrogen, whereas NIPAM contains nitrogen in each monomer unit, hence the incorporation of HEA monomer will increase the *C/N* ratio. The experimental *C/N* ratios are comparable with the theoretical value. The slightly higher values of experimental results are due to the hydrolysis of the amide group during the synthesis and purification (Thomas 1964).

4.2 Differential scanning calorimetry (DSC)

Two endothermic transitions are obtained from DSC curve, one at lower temperature range and another at ambient temperature range. Thermal changes at two different temperature ranges are explained separately.

4.2.1 Thermal changes at lower temperature

Water behaves differently in constrained nanoscopic structures and three different forms of water have been detected (Drost-Hansen 1969, Casillas *et al.* 1989). One is free water, which does not take part in hydrogen bonding with polymer molecules. It has a similar transition temperature (enthalpy) in DSC curve as that of normal water. Second is interfacial or freezing water, which is weakly bound and exhibits a melting transition near 0°C. Third is bound or non-freezing water, which is strongly associated and its melting transition cannot be detected even at a temperature as low as -100°C (Katime *et al.* 2000). Hence they will not show any endothermic peak in the studied range. Therefore, of the three types only free and interfacial water can be detected using DSC (Huglin *et al.* 1986, Li *et al.* 2005, Davis *et al.* 1988).

Fig. 1 shows the DSC thermogram of PNIPAM and its copolymer with HEA having the different molar ratio (75:25, 50:50 and 25:75). The endothermic transition starts around -10°C and ends within 5°C, with the peak value observed near 0°C. This corresponds to the melting point of free and interfacial water. Shifting in melting point is due to the change in the environment of the water molecules, which is observed in many hydrogel systems (Huglin *et al.* 1986, Anna and Sen 2010). Here the positions of peaks are almost constant but the starting and ending point changing with the copolymer composition. Consequently, the peak area shifted from below 0°C to beyond this temperature. In case of PNIPAM the peak area above 0°C is almost 50% of the total peak area, whereas for copolymers this is shifted to below 0°C. This may be due to the difference in hydrophilic and hydrophobic balance of the side chain functional group. NIPAM has both hydrophilic (amide) and hydrophobic (isopropyl) group (Fig. 2(a)) and they are segregated each other but the comonomer HEA has the mainly hydrophilic (ester and alcohol) group (Fig. 2(b)).

The physicochemical properties of a hydrogel depend not only on the molecular structure, gel

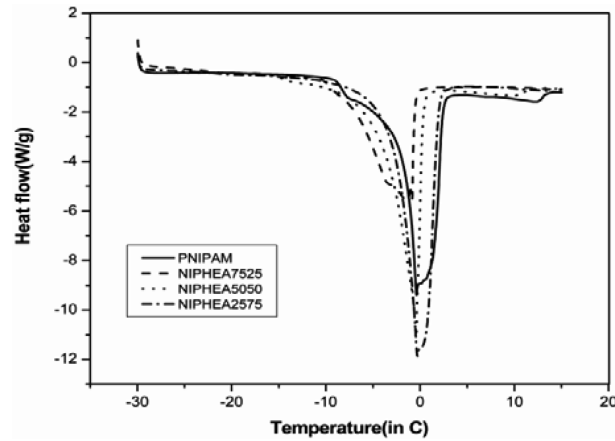


Fig. 1 DSC thermogram of Poly (NIPAM) and Poly (NIPAM-HEA) copolymers at lower temperature

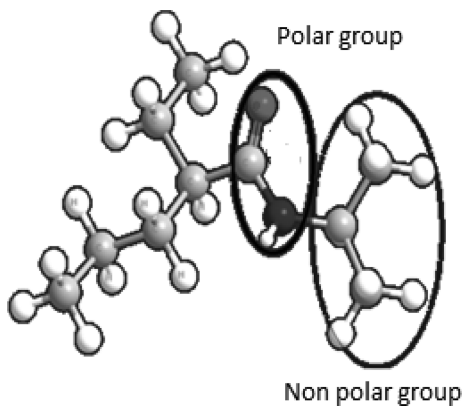


Fig. 2(a) 3D picture of PNIPAM

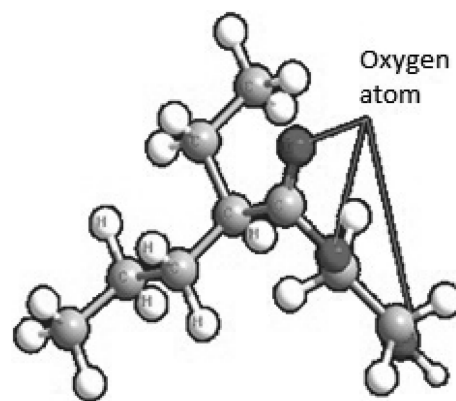


Fig. 2(b) 3D picture of PHEA

structure, degree of cross linking and water content but also on the relative amount of free and interfacial water. The enthalpy of melting for interfacial and free water is determined from the area under the endothermic peak of the DSC curve. Hence the amount of the free and interfacial water can be obtained from the ratio of $\Delta H_m/\Delta H$, where ΔH_m is the total enthalpy of swollen gel and ΔH is the latent heat of pure water, which is 321.17 J/g (Katime *et al.* 2000). The ratio $\Delta H_m/\Delta H$ represents the free and interfacial water per unit mass of the gel. The total water content of the gel is obtained from swelling studies. The bound water can be calculated as the difference between the total water content of the sample and free and interfacial water in the gel. Table 3 shows the fraction of free and interfacial water, bound water and total water in the hydrogel system.

It is seen that amount of total water and the bound water are highest in case of PNIPAM homopolymer than copolymers. The reason behind this is the substantial amount of the hydrophobic portion (isopropyl group) in addition to hydrophilic part (amide) of the PNIPAM homopolymer. Water molecules are known to structure around non polar hydrophobic solutes through the formation of a hydrophobic layer. Due to this reason, more water molecules are needed to form the hydrophobic layer around the isopropyl group. This enhances the osmotic effect and increases the

Table 3 The amount of bound water, total water, free and interfacial water for PNIPAM and its copolymers

Sample	Total water (in g/g of gel)	Free and interfacial water (in g/g of gel)	Bound water (in g/g of gel)	Bound water/ Total water
PNIPAM	0.766	0.545	0.221	0.288
NIPHEA7525	0.516	0.307	0.209	0.405
NIPHEA5050	0.658	0.454	0.204	0.310
NIPHEA2575	0.727	0.584	0.143	0.197

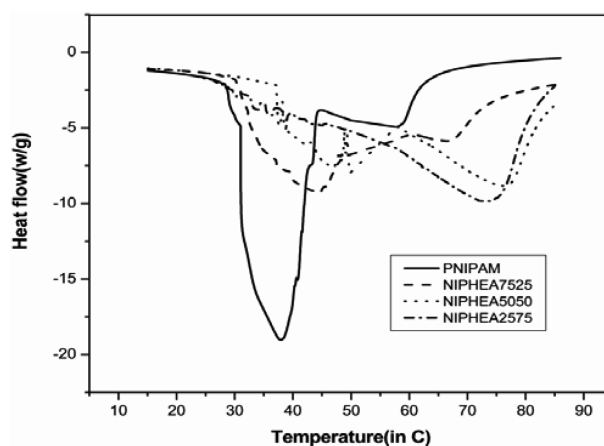


Fig. 3 DSC thermogram of poly (NIPAM) and poly (NIPAM-HEA) copolymers at higher ambient temperature

bound water and as well as total water content in the hydrogels. On the other hand, the comonomer HEA has mainly hydrophilic part (ester and alcohol). Substitution of NIPAM monomer with HEA monomer decreases the hydrophobic content in the hydrogel. So, the amount of bound water is decreased but the free and interfacial water content increased in copolymers.

4.2.2 Thermal change above ambient temperature

The DSC thermogram of poly (NIPAM) and poly (NIPAM-HEA) copolymers are shown in Fig. 3 from 15°C to 85°C. All the samples show the large endothermic transition in the studied range. The peaks are overlapping in nature. Simple mathematics is used to segregate the peak enthalpy values for different peaks keeping the total enthalpy change constant. The peak positions and the heat (enthalpy) changes are presented in Table 4. In case of PNIPAM two endothermic peaks are observed. The first peak starts from 30°C and ended at 45°C. This endothermic transition may be due to the hydrophobic hydration of the isopropyl group as the LCST of linear PNIPAM homopolymer is near 33°C where phase separation takes place (Hirokawa and Tanaka 1984). The second peak starts at 45°C and ended near 65°C. This may be due to the hydrophilic hydration of the amide group. The significant feature is that the hydrophobic and hydrophilic hydration shows the distinct transition separately for PNIPAM hydrogel, although they are present side by side.

In the presence of hydrophobic compound water molecules tend to form a cage like structure around the hydrophobe with minimum destruction of hydrogen bonds (Isreachvilli 1998). This is known as hydrophobic effect (Tanford 1980). Thus two different orientations of the water molecules

Table 4 The peak positions and the heat (enthalpy) changes of PNIPAM and its copolymers

Sample	Peak 1 (Hydrophobic)	ΔH_1 (J/g)	Peak 2 (Hydrophilic)	ΔH_2 (J/g)	Total enthalpy change ΔH_{Total} (J/g)
PNIPAM	38°C	1010	57°C	272	1282
NIPHEA7525	45°C	464	68°C	300	766
NIPHEA5050	50°C	338	75°C	540	878
NIPHEA2575	No peak	300	76°C	1020	1320

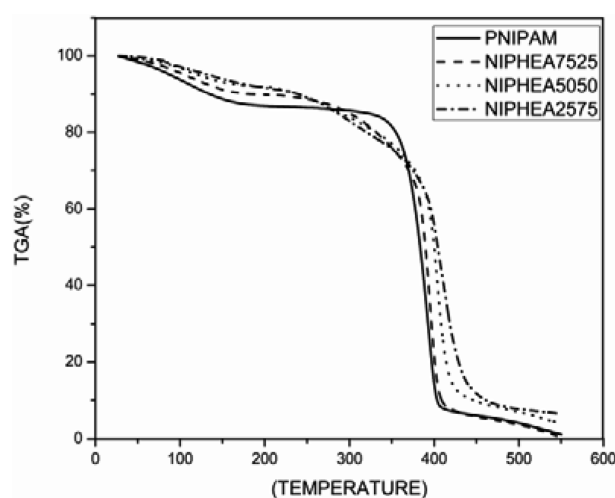


Fig. 4 TGA thermogram of poly (NIPAM) and poly (NIPAM-HEA) copolymers

are possible one near the hydrophobic group and another near the hydrophilic group. Water molecules present near the hydrophobic (isopropyl) group is defined as hydrophobic hydration and the water molecules present near the hydrophilic (amide) group is defined as hydrophilic hydration. The interesting point is that the enthalpy change for PNIPAM near 38°C (hydrophobic hydration) is almost four times of the enthalpy change of the second peak at 57°C (hydrophilic hydration). As the comonomer concentration increases in the copolymer the hydrophobic hydration decreases and the hydrophilic hydration increases. This is due to the presence of hydrophilic group in the HEA comonomer. The peak positions for the two transitions are shifted to higher temperatures in the copolymer.

4.3 Thermo gravimetric analysis

The thermal behaviors of PNIPAM and its copolymers are shown in Fig. 4 from 27°C to 600°C. In case of PNIPAM the weight loss below 200°C is due to loss of water. From 200°C to 325°C there is no weight loss. In the range of 325°C-410°C the weight loss may be due to the degradation of side chain functional group and back bone structure. This is in analogy of Van Dyke *et al.* (1993) reported TGA data of poly (acrylamide) homopolymer. With incorporation of HEA, the weight loss of copolymer takes place in slightly different way. Initially the weight loss takes place slowly up to

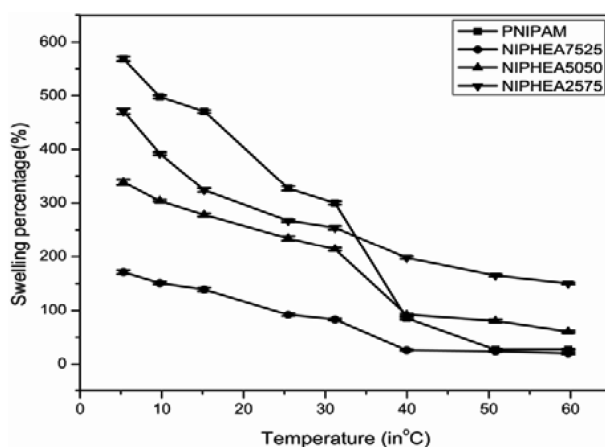


Fig. 5 Percentage swelling of poly (NIPAM) and poly (NIPAM-HEA) copolymers at different temperatures

250°C this may be due to loss of moisture. Weight loss in the temperature range of 250°C-400°C may be due to side chain functional group and above 400°C the main backbone chain degradation takes place. Thus, incorporation of HEA does not affect much the thermal stability of the copolymer within 150°C which is required for separation process.

4.4 Swelling behavior

4.4.1 Swelling studies with respect to temperature

The temperature dependency on the percentage equilibrium swelling of PNIPAM cross-link gels and its copolymer with HEA are shown in Fig. 5. As usually the percentage equilibrium swelling decreases with increase in temperature for all the samples. In case of PNIPAM the major change takes place in between 30-40°C. This is due to the increase in hydrophobic forces at higher temperature which leads to phase separation of the polymer. Swelling in hydrogel depends on the co-operative phenomena of elastic forces and osmotic forces for a particular cross link density. Here the backbone chains are similar and the amount of cross linking agent is constant but the pendant groups are different. Hence the elastic forces are comparable between the two polymeric structures. The osmotic effect depends on the amount of hydrophilic and hydrophobic hydration of the pendent functional group. In case of PNIPAM, hydrophobic hydration is highest in addition to hydrophilic hydration (Fig. 3 and Table 4) so it is showing maximum swelling characteristics. On the other hand, comonomer has mainly hydrophilic hydration. Hence the swelling of copolymers is lower than PNIPAM.

The hydrophilic hydration decreases with increase in temperature (Varghese 2001). Furthermore, it is also mentioned in literature that the PNIPAM polymer can form an Intramolecular hydrogen bond in collapsed state (Lee and Chen 2001). All these factors affect the swelling at higher temperatures. At the higher temperatures, the hydration force reduces and the hydrophobic force helps the molecules to form a globular structure. Due to this reason phase separation takes place above a certain temperature which is called LCST of polymer.

The lowest swelling is observed in case of lower (25%) HEA concentration in the copolymer and the swelling increases with the increase in HEA concentration in copolymers. This is in

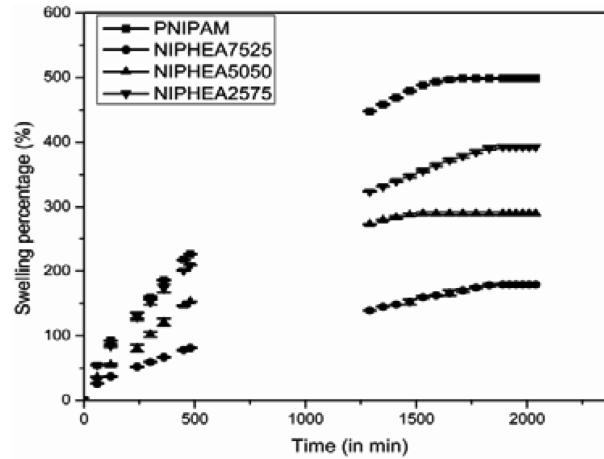


Fig. 6 Dynamic swelling at 10°C of poly (NIPAM) and poly (NIPAM-HEA) copolymers

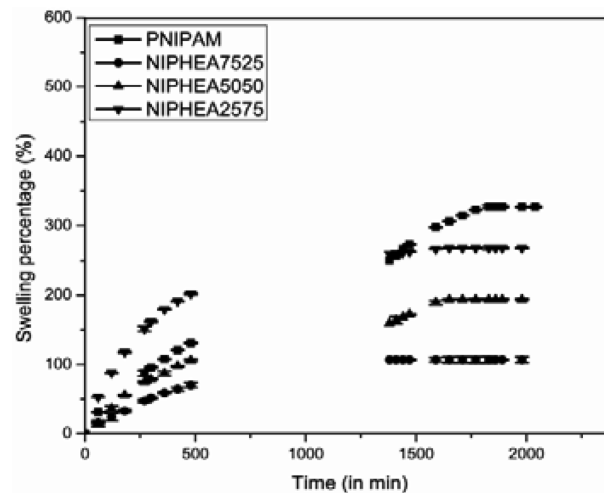


Fig. 7 Dynamic swelling at 25°C of poly (NIPAM) and poly (NIPAM-HEA) copolymers

similar with the copolymer of NIPAM and acrylamide compositions where swelling increases with the increase in acryl amide compositions (Kim 2003). The drastic change in swelling with incorporation of HEA (25%) may be explained on the basis of the dipole moment. The dipole moment of the amide group ($3.6D$) is higher than the ester group ($1.79D$) (Weast and Astle 1982). These dipoles are present in the vinyl group containing polymers, which experiences strong repulsion (Manning 1969, Sen *et al.* 2007). Water has also a dipole moment of $1.87D$ (Weast and Astle 1982) and the molecules try to orient themselves to reduce this dipole-dipole repulsion. This may also be a reason for the swelling of PNIPAM to be the highest. As the HEA incorporated into the copolymer the dipole-dipole repulsion decreases also the hydroxyl groups of HEA may take part in the hydration layer. Hence the swelling reduces for copolymer. As the comonomer concentration increases in the copolymer the hydrophilic hydration increases and the swelling increases.

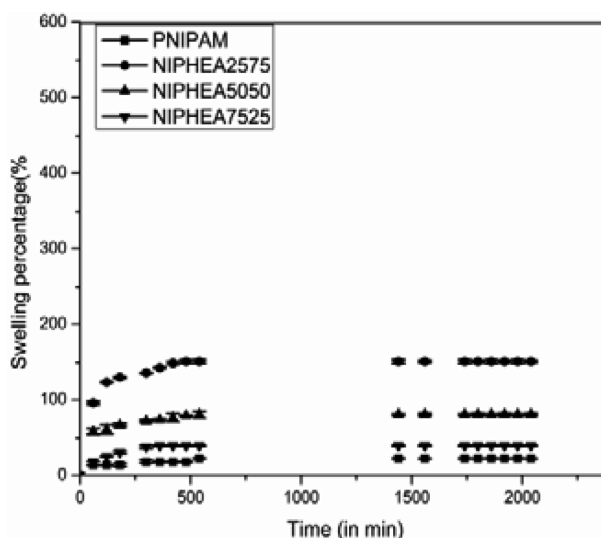


Fig. 8 Dynamic swelling at 50°C of poly (NIPAM) and poly (NIPAM-HEA) copolymers

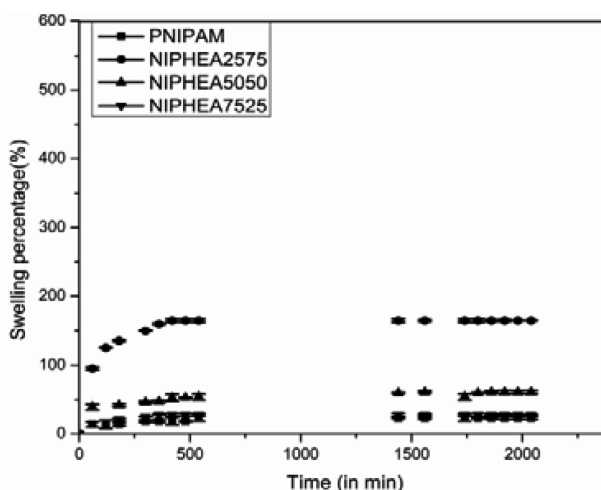


Fig. 9 Dynamic swelling at 60°C of poly (NIPAM) and poly (NIPAM-HEA) copolymers

4.4.2 Dynamic swelling of hydrogels in water

Dynamic swelling of PNIPAM and its copolymer are shown in Figs. 6-9 at 10°C, 25°C, 50°C and 60°C respectively. It is observed that the swelling rate of PNIPAM is higher than copolymers at 10°C. This is due to the high osmotic forces produced by hydrophobic and hydrophilic hydration of the PNIPAM. At 25°C the rate of swelling of PNIPAM is initially lower than the copolymer having 75% HEA content, but equilibrium swelling is higher than copolymers. For higher temperature both the rate of swelling and the equilibrium swelling for PNIPAM is lower than copolymers. This is due to phase transition of PNIPAM. An interesting point to be noted here is that the copolymers maintain a same order of swelling up to 60°C but in case of PNIPAM the rate of swelling changes which can be attributed to its thermoresponsive nature.

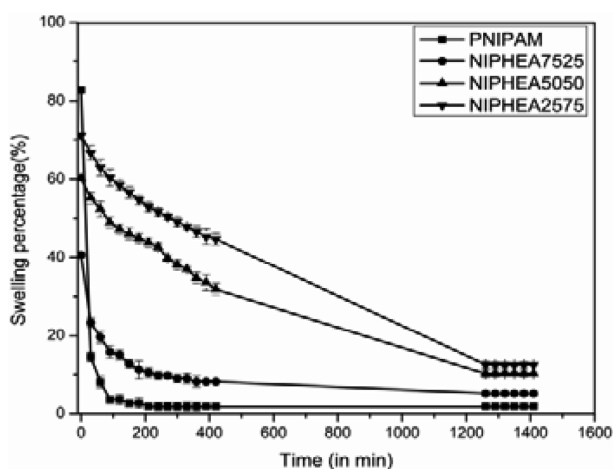


Fig. 10 Deswelling at 50°C of poly (NIPAM) and poly (NIPAM-HEA) copolymers

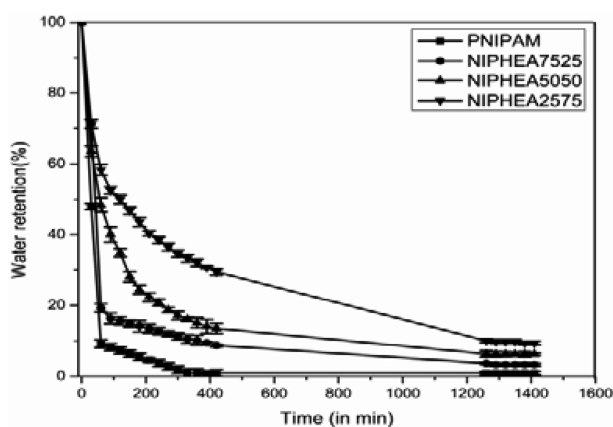


Fig. 11 Deswelling at 60°C of poly (NIPAM) and poly (NIPAM-HEA)

4.5 Deswelling kinetics of hydrogels

Figs. 10 and 11 show the percentage water retention by PNIPAM and its copolymers at 50°C and 60°C. The percentage water retention decreases with increase in temperature for all types of hydrogels. The rate of deswelling is highest in case of PNIPAM and decreases with an increase in the HEA concentration. This is due to presence of hydrophobic force in PNIPAM beyond its LCST. On the other hand, HEA is hydrophilic in nature and the incorporation of HEA enhances the hydrophilicity of the hydrogel and reduces the deswelling. So, the water retention is highest for the copolymer having the highest concentration of HEA and least for PNIPAM.

4.6 Swelling studies in salt and urea solutions

Fig. 12 shows the variation of swelling percentage of respective cross linked hydrogels in different sodium chloride solutions. It shows that the percentage swelling decreases with increasing

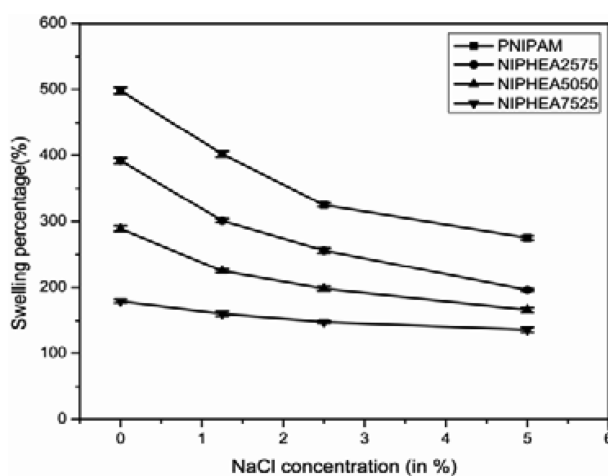


Fig. 12 Effect of swelling of PNIPAM based gels at different NaCl concentration

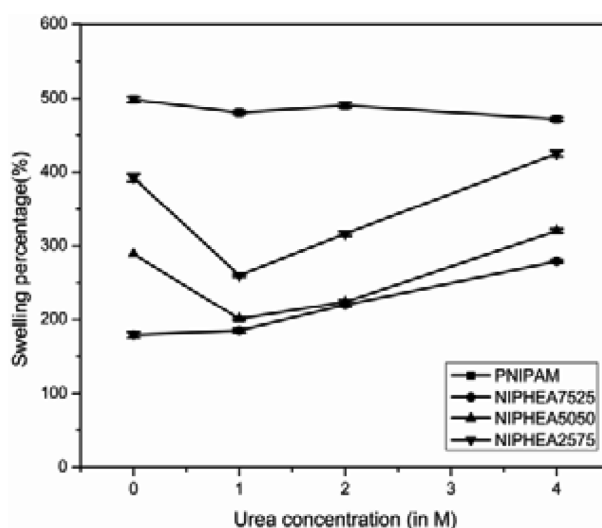


Fig. 13 Effect of swelling of PNIPAM based gels at different urea concentration

the NaCl concentration (ionic strength) of the swelling medium. The decrease in rate of swelling is much larger for the PNIPAM than the copolymers. This is due to the change in chemical potential in the solution surrounding the gels. Equilibrium is maintained mainly by diffusion of water into the gel. The diffusion of solute into the gel network may be possible, but it is restricted by entropy of Na^+ and Cl^- ions present in solution. At equilibrium the osmotic pressure of the solution becomes equal to the turgor pressure of the gel which is governed by the contractibility of the polymer network. Similar behaviors have also been reported in 2-hydroxyethyl methacrylate gels (HEMA) in different NaCl concentrations (Wang and Wu 2005, Wood *et al.* 1981).

Fig. 13 represents the percentage swelling of the PNIPAM based hydrogels for different urea concentrations. It is observed that the PNIPAM hydrogel does not show any change in percentage swelling up to the 4 M urea solution. This may be due to the similar functional group of PNIPAM

and urea so that urea could not change the hydration inside the PNIPAM hydrogel. Conversely, copolymers show different swelling behavior in urea solution. The percentage swelling of the copolymer gels increases above 1 M urea solution. This may be due to the diffusion of urea molecules inside the gel structure by breaking the intra-molecular hydrogen bonds between the amide and hydroxyl groups of the copolymer. Similar type of interaction mechanism was also found in poly (HEMA) gels with 0.5 M urea solution (Ratner and Miller 1972). Copolymer having lowest HEA (25%) content remained unchanged in 1 M urea concentration while others having the higher amount of HEA concentration showed diminution in swelling.

5. Conclusions

PNIPAM based crosslinked hydrogels with different content of HEA were prepared by free radical polymerization and their thermal and swelling characteristics were studied. The copolymer composition was found to be almost similar to the feed composition as found in CHN analysis. DSC thermogram of PNIPAM revealed two endothermic transitions, one near 38°C which was due to hydrophobic hydration and the other peak near 55°C, due to the hydrophilic hydration. The thermogram also showed that the enthalpy change due to hydrophobic hydration was about four times than hydrophilic hydration for PNIPAM. The hydrophobic hydration decreased and the hydrophilic hydration increased with decrease in NIPAM concentration and increase in HEA content in the copolymer. The peak value for hydrophobic and hydrophilic hydration in copolymers was shifted towards higher temperature. TGA thermogram also clarified that the thermal stability of the copolymer did not change much in comparison with PNIPAM. Swelling studies of the hydrogels showed that PNIPAM has higher rate of swelling at lower temperature but it decreases as temperature rises. Swelling percentage of copolymers increases with increasing the HEA content. The experimental results of swelling in urea solution suggested that hydrogen bond interactions were present in copolymers between amide and hydroxyl groups.

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