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Radiation induced synthesis and swelling characterization of thermo-responsive *N*-isopropylacrylamide-co-ionic hydrogels

Virendra Kumar, C.V. Chaudhari, Y.K. Bhardwaj *, N.K. Goel, S. Sabharwal

Radiation Technology Development Section, Bhabha Atomic Research Center, Room No. S-1, HIRUP Building,
Trombay, Mumbai 400085, India

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Abstract

Two-component thermo-responsive hydrogels poly(*N*-isopropylacrylamide)-co-vinylbenzyltrimethylammonium chloride (NIPA-co-VBT) and poly(*N*-isopropylacrylamide)-co-*p*-sodium styrene sulphonate (NIPA-co-SSS) were prepared by using high energy gamma radiation. The gels were characterized by Fourier transformed infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and sol–gel analysis. The presence of ionic monomers in NIPA leads to lower gel content. Introduction of ionic components in the matrix enhanced swelling extent but caused slower volume transition. The swelling studies in alcohol indicated that swelling extent was function of polarity of the swelling medium and all gels followed the order water > methanol > ethanol > iso-propanol. In mixed co-solvents (water–alcohol), they exhibit complex reentrant behavior. The co-polymer gels containing VBT swelled faster and to higher extent than those containing SSS. The dynamic swelling studies indicated that diffusion of water in PNIPA gel shifts from Fickian for PNIPA to anomalous for NIPA-co-ionic gels also the mean swelling time (MST) decreases for gels containing ionic monomers.

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Keywords: Radiation; Thermo-responsive; *N*-Isopropylacrylamide; Ionic monomer; Equilibrium; Dynamic; Swelling

1. Introduction

Hydrogels are two or multicomponent, three-dimensional network of polymer chains imbibing significant amount of water. They are being considered as most promising biomaterials in form of contact lens, burn dressings, artificial corneas, soft tissues substances etc. [1]. A special class of hydrogels, stimuli–responsive hydrogels exhibit a sudden change in solvent-swollen weight in response to a small change in external stimuli such as pH, temperature, ionic strength, light sensitivity and electric field [2]. The crosslinked gels of *N*-isopropylacrylamide, vinylmethyl ether, vinyl acetate-co-vinyl alcohol, *N*-vinylcaprolactum and *N*,*N*′-dimethylaminoethyl methacrylate have been shown to exhibit discontinuous volume transitions with temperature in aqueous medium [3–7]. Among the various thermo-responsive gels poly(*N*-isopropylacrylamide) (PNIPA) is probably the most widely studied [8–10]. Linear PNIPA exhibits a lower critical solution temperature

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* Corresponding author. Tel.: +91 022 2559 0175/0178; fax: +91 22 2550 5151.

E-mail addresses: ykbhard@magnum.barc.ernet.in, ykbhardwaj2001@yahoo.co.in (Y.K. Bhardwaj).

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(LCST) of 33 °C and its crosslinked gel undergoes temperature induced phase transitions at this temperature [8,10]. It has been suggested both for practical applications as well as model for theoretical examination of phase transitions in gels. It has been studied for biotechnological applications, as controlled drug delivery device, recyclable adsorbents, for immobilizations of enzymes and cells, dewatering of protein molecules [11–16]. Practical applications of PNIPA usually involve its chemical modi- fication which has been achieved by its co-polymerization with anionic monomers [17,18], neutral monomers [19–21] and cationic monomers [22–24]. Lu et al. [25] synthesized IPN hydrogel of PNIPA-co-PMMA to improve the mechanical strength of parent matrix. Temperature as well as pH sensitive hydrogels have been prepared by co-polymerizing PNIPA with acrylic acid [26]. It has been documented that introduction of small amount of ionic moieties into PNIPA matrix enhances the swelling extent at the expense of thermo-response of the gel [26].

The aim of the present study was to design a clean matrix with good extent of swelling having a fast response to change in temperature and ionic concentration. This report presents the effect of incorporating ionic monomers on extent of swelling, swelling mechanism, response time and LCST of PNIPA gel. The effect of electrolyte concentration, solvents and pH has also been reported. Clean PNIPA and poly(NIPA-co-ionic) gels for these investigation were prepared using high-energy gamma radiation.

2. Experimental

2.1. Material

N-Isopropylacrylamide (NIPA) (mol. wt. = 113.16, purity > 99%), vinylbenzyltrimethyl ammonium chloride (VBT) (mol. wt. 211.74, purity > 99%), *p*-sodium styrene sulphonate (SSS) (mol. wt. 206.20, purity > 99%) from Aldrich chemicals and *N*,*N*-methylene-bis-acrylamide (MBA) (mol. wt. 154.2) from Sigma chemicals were used as received. All other chemicals used were of AnalaR grade. Double distilled water (conductivity 1.9 μS cm^{-1}) was used for preparing all solutions and for swelling studies.

2.2. Radiation induced synthesis of hydrogels

The gels were synthesized by radiation-induced crosslinking of aqueous NIPA solution containing 0.3% (w/v) of MBA and varying amount of VBT and SSS. The monomer/monomers were dissolved in water, stirred and filled in glass vials (ID = 1.0 cm, l = 7–8 cm). The vials were deoxygenated under 10^{-3} Torr vacuum at liquid nitrogen temperature and sealed. Polymerization was carried out by irradiating the sealed samples in ice temperature bath with gamma rays from a ^{60}Co source in a gamma chamber GC-5000 supplied by M/s BRIT, INDIA. The gels were synthesized by delivering radiation dose of 1.25 kGy at a dose rate of 1.6 kGy h^{-1}, as measured by Fricke dosimetry. After irradiation the glass vials were break opened to retrieve polymer/copolymer gels in cylindrical form. The gels samples were rubbery and transparent at room temperature. These samples were cut into 0.5–1.8 mm thick disks with a sharp edged blade and soxhlet extracted with double distilled water to remove residual monomers. Swelling-drying cycles were carried out 3–4 times and finally the disks were left for drying at room temperature. The dried samples were stored in a desiccator for further use.

2.3. Equilibrium swelling measurement

The increase in the mass of samples immersed in aqueous solutions was monitored gravimetrically using Mettler analytical measurements (Accuracy 10 μg) at 26 ± 1 °C. Preweighed samples were immersed in water, the swelled samples were removed periodically, blotted free of surface water using high quality tissue paper, weighed and returned to the swelling medium. Measurements were taken until the samples reached a constant weight. The swelling ratio and equilibrium degree of swelling (EDS) of the gels were determined gravimetrically using following equations:

$$\text{Swelling ratio} = W_\mathrm{s}/W_\mathrm{d} \tag{1}$$

$$\text{Equilibrium degree of swelling(EDS)} = (W_\mathrm{s} - W_\mathrm{d})/W_\mathrm{d} \tag{2}$$

where W_s and W_d are the weights of gel in swollen and dry states.

3. Results and discussion

Introduction of a small amount of ionic monomer into the non-ionic matrices affects properties like EDS [23,27,28] and LCST for stimuli responsive systems [18,19]. In the present study, effect of introducing two monomers one which provides polycationic character to gel by furnishing anion to the medium (VBT) and other which provides polyanionic character to gel by furnishing cation to the medium (SSS) into NIPA matrix has been investigated.

The composition of various gels studied is given in Table 1. The FTIR of these gels performed on FTIR spectrophotometer FT/IR-610 from JASCO, JAPAN in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 25 scans is shown in Fig. 1. Peaks at 1640 and 1551 cm^{-1} are due to C=O

Table 1
Compositions and irradiation parameters of co-polymer gels prepared at a dose rate of 1.6 kGy h^{-1}, [MBA] = 20 mg/ml, total dose 1.24 kGy

Sample	NIPA (% mole)	VBT (% mole)	SSS (% mole)
N	100	0	0
S1	99.30	0	0.70
S2	98.49	0	1.51
S3	96.70	0	3.30
V1	99.30	0.70	0
V2	98.53	1.51	0
V3	96.78	3.30	0

in amide group (amide I and amide II bands) present in PNIPA. Doublet at 1010 and 1040 cm^{-1} was attributed to the stretching frequency of sulphonate group in NIPA-co-SSS gel. Presence of VBT in the NIPA-co-VBT gel was confirmed by appearance of extra absorption peaks at 1425, 1490 and 1221 cm^{-1}. Peaks at 1425 and 1490 cm^{-1} belong to the C–H bending of methyl groups and scissoring of methylene groups, respectively, whereas, 1221 cm^{-1} peak was attributed to C–N of tertiary ammonium group.

SEM of the pure NIPA and its co-polymers was investigated using scanning electron microscope VEGA MV2300T/40 (TS 5130 MM) equipment (TESCAN) to understand the inner morphology of the gels. The hydrogel samples for SEM were prepared by initially lyophilizing the samples swelled to equilibrium in liquid nitrogen. The lyophilized hydrogel samples were then fractured carefully and mounted on the base plate by carbon tape and coated with gold using vapour deposition technique. The gel surfaces were scanned using magnification of 2800 to investigate their pore structure.

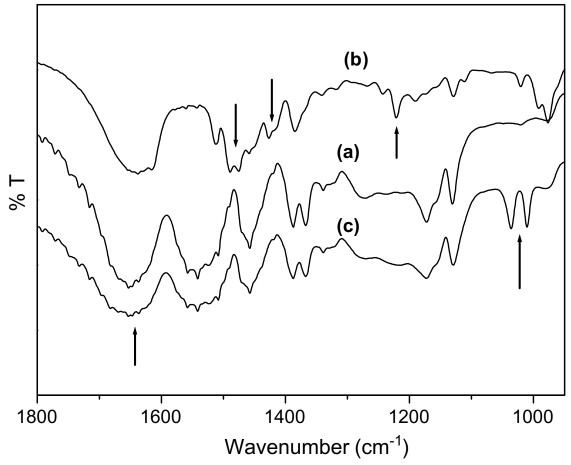

Fig. 1. FT-IR spectra of co-polymer gels: (a) PNIPA; (b) NIPA-co-VBT; (c) PNIPA-co-SSS.

Although, the freeze-drying of hydrogel may lead to some structural artifacts of the specimens, the dramatic differences in the morphology observed between hydrogels are presumably of intrinsic nature since the fixation procedures were identical among all hydrogels. The morphology of gels is shown in Fig. 2. As clear from SEM PNIPA gel showed fibrous morphology with less porous architecture. As the ionic monomer content in the gel increased, the pore size also increased and the fibrous structure gradually disappeared at higher ionic monomer content and lump structure appeared. The co-polymer gels with higher ionic monomer content exhibited uneven mass distribution compared to pure PNIPA gel. It was found that co-polymer gel exhibits more porous structure in presence of VBT than in the presence of SSS, which can be attributed to the higher water uptake capacity of PNIPA-co-VBT gel as compared to PNIPA-co-VBT gel.

3.1. Equilibrium swelling study

3.1.1. Effect of ionic monomer on gel fraction

The radiation sensitivity of aqueous NIPA solution in presence of VBT and SSS was studied by irradiating aqueous NIPA solution containing different amounts of VBT or SSS. The gels formed were analyzed for their sol–gel content. As shown in Fig. 3 for a given radiation doses the gel content was maximum for pure NIPA solution and it decreased as the ionomers content increased in the range (0–8.5 mol%). The extent of decrease in gel fraction was more in case of SSS in comparison to VBT. The decrease in the gel fraction in presence of these monomers may be attributed to two reasons first the presence of aromatic rings in these monomers provides them inherent poor radiation sensitivity due to resonance stabilization of radical generated as reported for styrene [29] and second the segments of ionic monomers in NIPA co-polymer chain would hinder inter-crosslinking of chains due to bulkier pendant rings associated to these segments. Also it has been reported that PVBT and PSSS predominantly undergo degradation in aqueous solution under steady state irradiation condition [30,31].

3.1.2. Effect of ionic monomers on the thermo-responsive behavior of PNIPA gels

Thermo-response of pure PNIPA at different temperature is shown in Fig. 4. From the inflexion point on the profile the LCST was estimated to be 34 °C which is very close to that reported by earlier workers [8]. The LCST temperature was further confirmed by DSC thermogram of pure swelled PNIPA gel (inset, Fig. 4). Thermo-response of NIPA-co-VBT and NIPA-co-SSS gels are shown in Figs. 5 and 6. As clear from the figures EDS increases significantly in their presence but gel loose their abruptness of volume phase transition and the

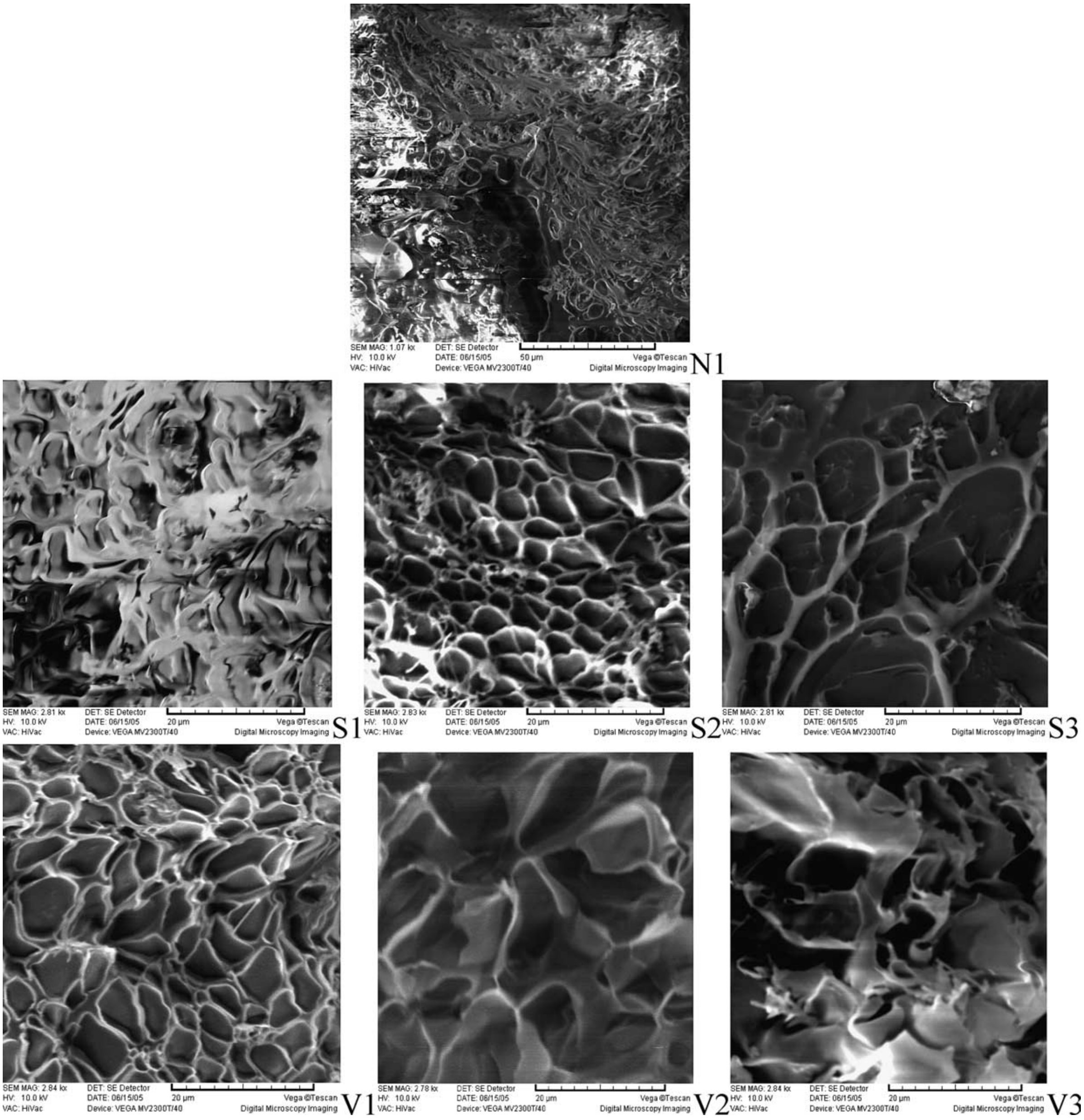

Fig. 2. SEM micrographs of swollen pure PNIPA, PNIPA-co-SSS and PNIPA-co-VBT hydrogels.

weight loss is more gradual. Also the extent of deswelling decreases in presence of ionic monomers. The amount of water absorbed by an ionic hydrogel is a function of the hydrophilicity of the polymer, the cross-linking of network structure and the number of ionized groups on the polymer. To understand the swelling of NIPA-co-ionic gels within the framework of Flory–Rehner equation the osmotic pressure π of a hydrogel during swelling is given by the sum of the pressures due to polymer–solvent mixing (mix), due to deformation of network chains to a more elongated state(el) and due to the non-uniform distribution of mobile counter ions between the gel and the external solution(ion) [32].

$$\pi = \pi_{\text{mix}} + \pi_{\text{el}} + \pi_{\text{ion}} \tag{3}$$

According to Flory–Huggins theory, π_{mix} is given by [32]

$$\pi_{\text{mix}} = -RT/V_1\{\ln(1 - v_2) + v_2 + \chi v_2^2\} \tag{4}$$

where R is gas constant, T is temperature, V_1 is molar volume of solvent (water) and v_2 is volume fraction of polymer. To describe the elastic contribution π_{el} to the

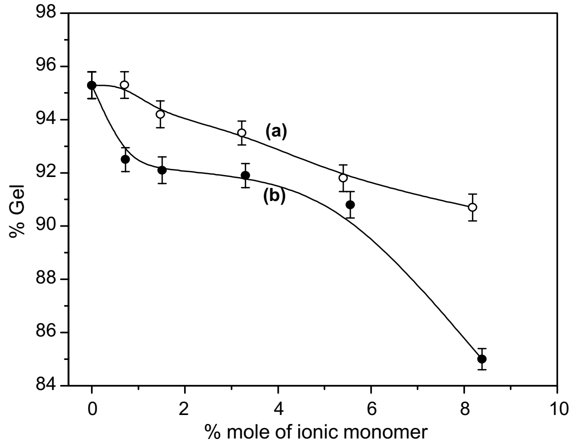

Fig. 3. Effect of concentration of VBT and SSS on the gel fraction of PNIPA co-polymer hydrogels: (a) VBT; (b) SSS.

swelling pressure simplest affine network model is used to describe the behavior of our gels [32]

$$\pi_{\mathrm{el}} = -(RT/V_1)N^{-1}\{v_2^{1/3}(v_2^0)^{2/3} - v_2/2\} \tag{5}$$

where N is number of segments between two successive crosslinks of the network. Ionic contribution π_{ion} to the swelling pressure is caused by the concentration difference of counter ions between the gel and the outer solution. The ideal Donnan theory gives π_{ion} as the pressure difference of mobile ions inside and outside the gel [32]

$$\pi_{\mathrm{ion}} = RT\sum(C_i^{\mathrm{g}} - C_i^{\mathrm{s}}) \tag{6}$$

where C_i^{g} and C_i^{s} are the concentrations of the mobile ions of species i inside and outside the gel, respectively. Thus the parameters π_{mix} and π_{elas} are themselves related to crosslink density and Flory–Huggins parameter (χ) and hence are the key parameters that determine the swelling of non-ionic gel in a solvent [29]. If the gels contain ionizable groups, the contribution by the term π_{ions} becomes significant [32].

For thermo-responsive gels like PNIPA at temperature <LCST the gel remains in equilibrium swollen state due to critical balance of hydrophobic and hydrophilic groups on the polymer chains. At low temperature (<LCST) strong hydrogen bonding between hydrophilic groups and the surrounding water molecules enables good solubility of polymer in water. However, with increasing temperature the hydrogen bonding weakens and at temperature >LCST hydrophobic interactions become dominant and the refolding of polymer chains causes phase separation of the polymer from the aqueous solution [34]. Incorporation of ionic monomers in NIPA matrix provides ionic character to the gel and contribution to extent of swelling due to electrostatic interaction becomes significant as like charges generated on the polymer chains due to ionization repel each other, and this repulsion tends to stretch polymer chains to extended state from closed coiled state, which causes opening of the polymer chains and over all swelling of the hydrogels. The electrostatic force would cancel out the hydrophobic interaction that determines the phase

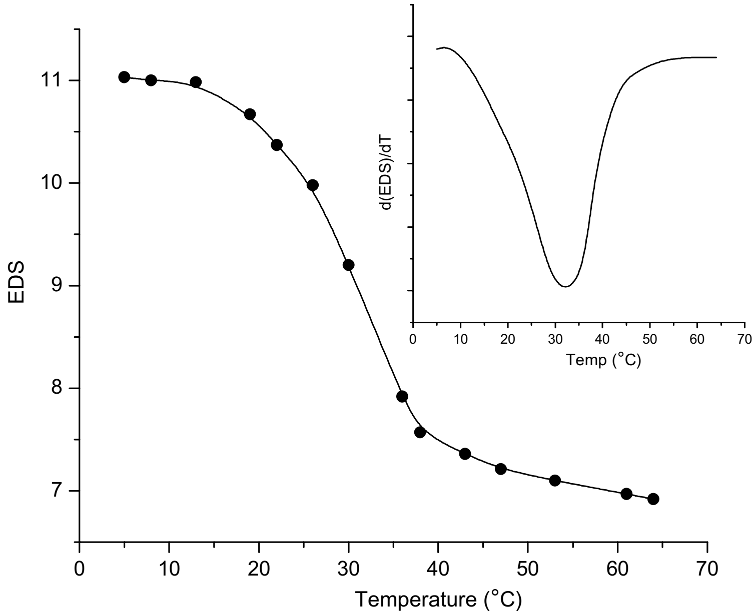

Fig. 4. Thermo-sensitivity of PNIPA hydrogel synthesized by gamma irradiation. Inset: derivative of EDS vs temperature.

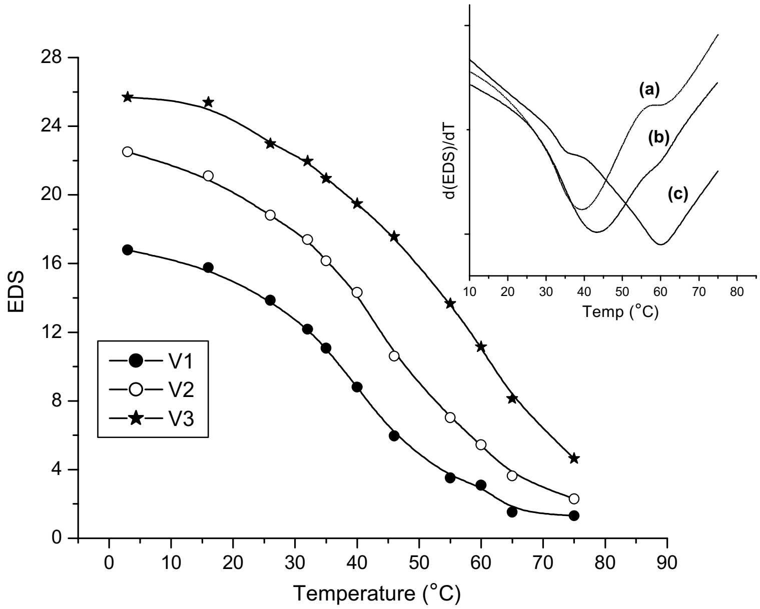

Fig. 5. Thermo-sensitivity of PNIPA-co-VBT hydrogel synthesized by gamma irradiation. Inset: derivative of EDS vs temperature: (a) V1; (b) V2; (c) V3.

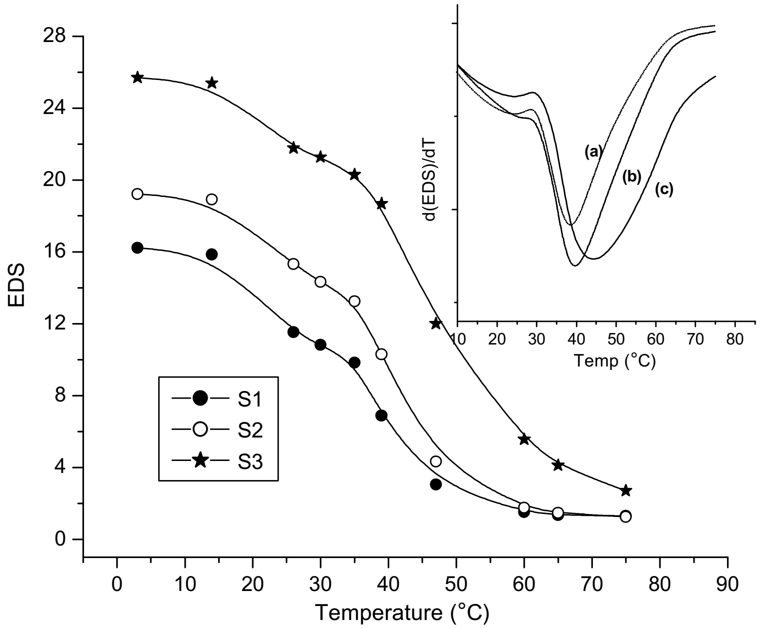

Fig. 6. Thermo-sensitivity of PNIPA-co-SSS hydrogel synthesized by gamma irradiation. Inset: derivative of EDS vs temperature: (a) S1; (b) S2; (c) S3.

transition of PNIPA when VBT or SSS are present in the matrix. The shift in LCST to higher temperature coupled with loss in abruptness of transition in presence of ionic monomers can be assigned to better solvation of polymer chains due to stronger interactions between ions on polymer chains and water molecules. As clear from the figure the volume phase transition completely disappears at ionic monomer concentration of 8.3 mol%. The strong attractive forces probably require higher temperature to overcome the force of attraction as well as slower removal of several layers of water held inhibits the hydrophobic interactions to become strong enough to cause abrupt collapse of gel above LCST. It was interesting to observe that the shift in LCST is more for co-polymer gels containing VBT which may be due higher water holding capacity of quaternary ammonium group in VBT compared to sulphonate group in SSS. The ions like tetra-alkylammonium ions are known to have net structure making effect [35]. Their high electric fields not only polarize, immobilize and electrostrict nearest neighbour molecules but also induce additional order beyond the first layer of water molecules. On the other hand, ions like SO_3^- cannot induce the multi-layer immobilization of water molecule. The higher attractive field that can be felt to several layers in case of $-N^+(CH_3)_3$ group probably causes more layers of water associated to the first layer, which is in immediate vicinity of polymer in comparison to $-SO_3^-$ group and hence more water uptake is seen in gels containing residual VBT containing $-N^+(CH_3)_3$ groups. Similar behavior of PNIPA in presence of other ionic monomers like acrylic acid and (diethyldiamino)ethylmethacrylate has been reported [23]. From Figs. 5 and 6 it is clear that the LCST of the co-polymer gels can be easily controlled depending on the content and type of ionic monomer in the co-polymer gel.

3.1.3. Swelling behavior of PNIPA-co-ionic polymer gels in different organic solvents

EDS of PNIPA and its co-polymers was studied as a function of ionic monomer content in various solvents viz. methanol, ethanol and iso-propanol. The results of the study are shown in Figs. 7 and 8 for VBT and SSS, respectively. The swelling study of these gels in different solvent showed that the EDS of ionic co-polymer gels were in the order of water > methanol > ethanol > iso-propanol i.e. in accordance with decreasing polarity. However, the increase in swelling of co-polymer gels was significant only in polar solvents (water and methanol), whereas the ionic content did not affect the swelling extent in less polar solvents like ethanol and iso-propanol. This was on expected lines as higher the ionic content in matrix more will be the effect on swelling extent in polar solvents. As described in Section 3.1.2, swelling of gels containing VBT was higher than those containing SSS.

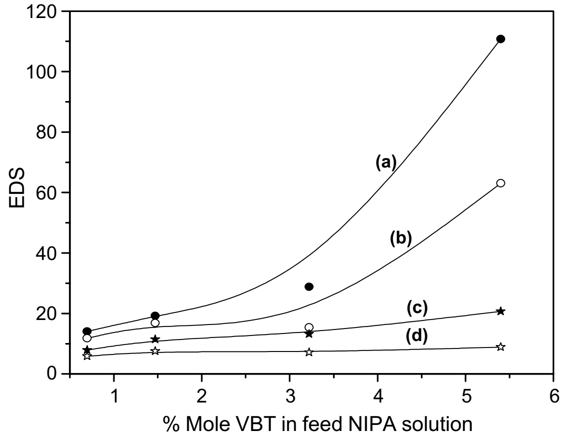

Fig. 7. Swelling behavior of NIPA-co-VBT hydrogels containing different extent of VBT in different solvents. (a) Water, (b) methanol, (c) ethanol, (d) iso-propanol.

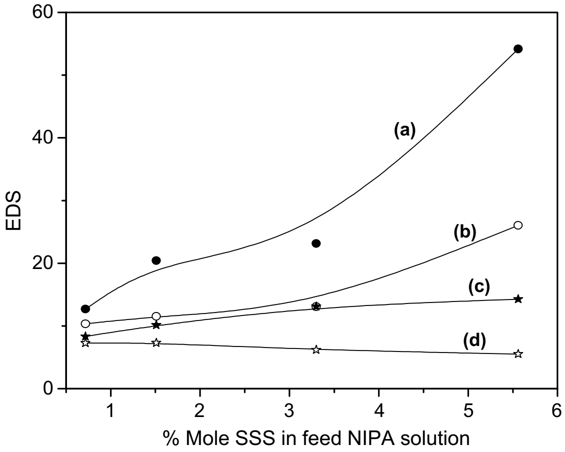

Fig. 8. Swelling behavior of NIPA-co-SSS hydrogels containing different extent of SSS in different solvents. (a) Water, (b) methanol, (c) ethanol (d) iso-propanol.

3.1.4. Swelling behavior of PNIPA-co-ionic polymer gels in mixed solvents

Very interesting results on decrease in LCST or swelling extent of PNIPA have been reported in mixed solvents. It has been shown that for water–methanol mixture PNIPA does not precipitate even at boiling temperature [36]. A combined collapse-swelling behavior has been reported on addition of lower alcohols to an aqueous dispersion of PNIPA. The PNIPA chains collapse to a minimum globular size from extended size in the water rich region and then reswell on further addition of alcohol [37]. The co-non-solvency of mixed solvents for linear PNIPA has been manifested as reentrant volume phase transition (deswelling–swelling) in the crosslinked PNIPA hydrogels [38,39]. The effect of presence of ionic segments in the PNIPA hydrogels on the reentrant swelling behavior was investigated in water–ethanol mixed solvent systems. Results are shown in Figs. 9 and 10, respectively. As reported earlier [40,41] pure PNIPA hydrogel showed reentrant swelling behavior, i.e. initially on addition of ethanol, the equilibrium volume of a PNIPA decreases drastically unto (40% v/v) of ethanol in water and reswells gradually with further

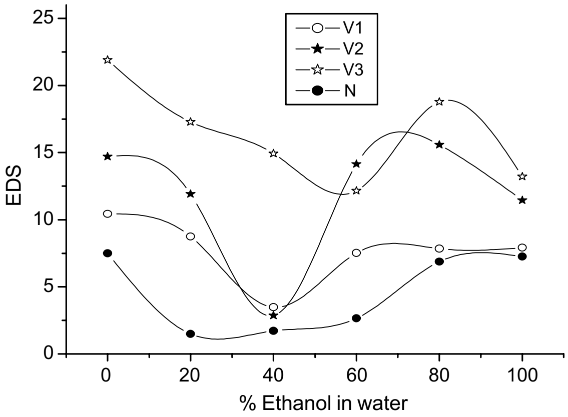

Fig. 9. Swelling behavior of NIPA-co-VBT hydrogels containing different amounts of VBT in water–ethanol mixture.

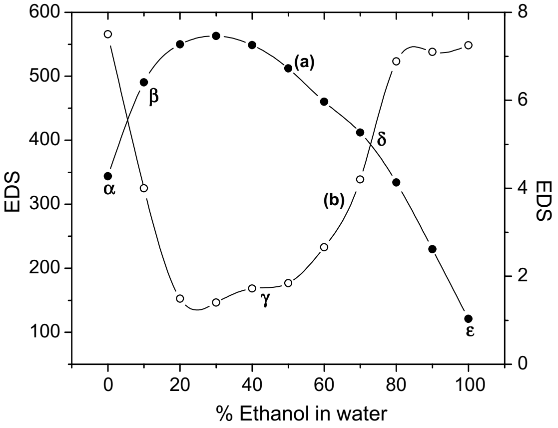

Fig. 11. Swelling of gels: (a) [SSS]:[VBT]; 0.5 M:1.5 M + 1 mM MBA, dose 5 KGy; (b) PNIPA gel.

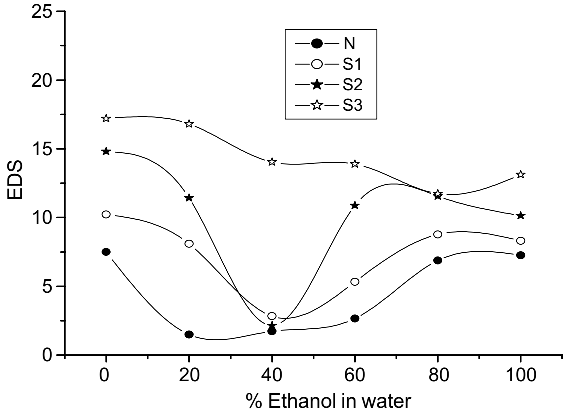

Fig. 10. Swelling behavior of PNIPA-co-SSS hydrogels containing different amounts of SSS in water–ethanol mixture.

addition of organic solvent. It seems initially at low ethanol concentration water–polymer hydrogen bonding is perturbed leading to strong polymer–polymer interactions reflected as desorption of water by gels, and later at higher ethanol concentration, when ethanol–polymer interaction overtake polymer–polymer interaction the gels re-swell. However, an interesting observation about swelling of NIPA-co-ionic gels was that the co-polymer hydrogels showed a complex "reentrant' swelling behavior i.e. the gels deswelled–swelled and again deswelled in pure ethanol. The complex reentrant swelling of co-polymer gels is clearly due to ionic component in PNIPA gel. It has been reported earlier that swelling of SSS-co-VBT gels containing residual SSS or VBT in ethanol–water co-solvent show initially increase in swelling and later deswelling at higher concentration of ethanol [42]. The swelling profile for these types of gels is concave towards solvent [42] as shown in Fig. 11 unlike for pure PNIPA, which is convex to x-axis. The co-polymer seems to follow swelling behavior which is a overlap of these two profiles as shown by stretch α to β, β to δ through γ and finally to ε which indicate that in water–ethanol co-solvent the overall swelling of the co-polymer matrix is governed at lower ethanol concentration by swelling of ionic component than by that of PNIPA component and finally again by that of ionic component.

3.1.5. Swelling in NaCl solution

In an electrolyte solution, the phase transition of NIPA-co-ionic gels is determined by various coexistent intra and intermolecular forces such as van der Waals force, hydrogen bonding, hydrophobic interaction and electrostatic forces [38]. These forces can exert counter effects or co-effects on the co-polymer gels [39,43,44], and depending on the conditions, some forces can dominate the behavior of gels. The NIPA-co-VBT or NIPA-co-SSS hydrogels unlike PNIPA will exhibit behavior of polyelectrolytes, therefore electrolytes may affect there swelling. The majority of biotechnological applications involve buffered aqueous solution which contain more than one active agent therefore we studied the swelling of these gels in presence of NaCl a fairly weak salting out agent. The results of these studies are shown in Figs. 12 and 13. From the figures, it is clear that PNIPA as well its co-polymer gels swell to lower extent in presence of NaCl in the swelling medium. Salts are known to change the structure of water and thus the free energy of interaction between the polymer and water. The change of water structure may strongly affect the hydrophobic interaction of the hydrophobic pendant isopropyl group and thus may cause volume phase transition of PNIPA gel as reported for PNIPA gels in presence of other electrolytes [45]. Also expected is the decreased swelling ratio of hydrogels with increasing salt concentration in the external solution due to decrease in the

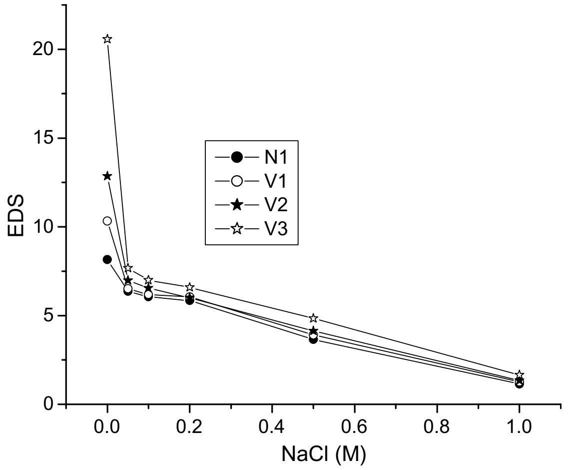

Fig. 12. Swelling of NIPA-co-VBT hydrogels in NaCl solution.

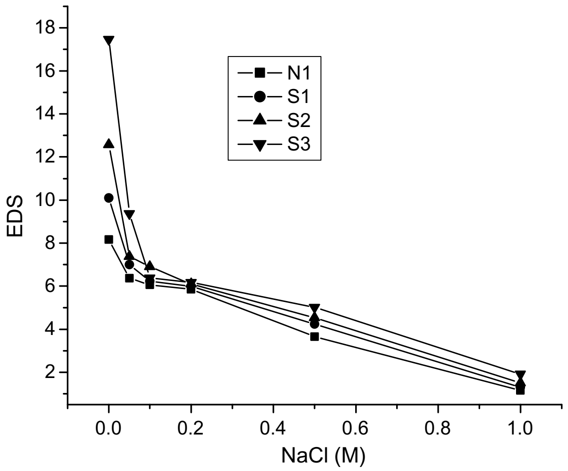

Fig. 13. Swelling of PNIPA-co-SSS hydrogels in NaCl solution.

concentration difference of counter ions inside and outside the hydrogel. The decrease in swelling ratio is rapid initially and then gradual at higher NaCl concentration. Thus the contribution due to π_{ion} to π (Eq. (3)) will be more when for given NaCl concentration the gel has more ionic monomer content or conversely for a gel of known composition when NaCl concentration will be low as observed in these studies.

3.2. Dynamic swelling studies

The dynamic swelling properties of a polymer include the solvent sorption rate, the rate of approach to equilibrium and the transport mechanism controlling the solvent sorption. Alfrey et al. [46] have proposed that the diverse responses of polymers to the presence of a penetrant may be categorized into three classes based on the relative rates of diffusion and relaxation of the polymer:

(a) Fickian diffusion, also known as Case I diffusion, occurs when the rate of diffusion is significantly slower than the rate of relaxation of the polymer chains.
(b) Case II diffusion arises when the rate of diffusion is greater than the rate of the relaxation of the polymer chains. The main feature of this second limiting model is the establishment of a sharp boundary between the glassy core and the swollen shell that advances at a constant velocity.
(c) Non-Fickian or anomalous diffusion occurs when the rates of diffusion and polymer relaxation are comparable and is connected with the transition region between the two limiting cases of Case I and Case II.

The mechanisms of the transport of solvents into polymers can be determined by a variety of experimental techniques, the simplest and most common one is the sorption technique. In a sorption experiment (including both absorption and desorption), the polymer is exposed to a penetrant and the gain or loss in mass of the polymer, M_t, is monitored as a function of time, t. When this quantity, M_t, is normalized to the mass of the polymer at its equilibrium hydration level, M_∞, and analyzed according to

$$M_t/M_\infty = kt^n \tag{7}$$

where k is a constant incorporating characteristic of polymer network and the solvent, n is an empirical number called as transport or diffusion exponent, which is the indicative of the transport mechanism. A value of $n = 0.5$ for planar systems is indicative of Fickian diffusion, while non-Fickian or anomalous behavior is characterized by an exponent lying between 0.5 and 1.0, with a limit of $n = 1.0$ identifying Case II transport [33].

Eq. (7) is applied to the initial stages of swelling and the plots of $\ln(M_t/M_i)$ vs $\ln(t)$ yield straight line up to almost 60% increase in the mass of the hydrogels. The n and k values were obtained from the slop and intercept of the plot, respectively [33].

The study of diffusion phenomenon in hydrogels is of great interest as it clarifies the polymer swelling behavior. The diffusion coefficient of hydrogels can be calculated by ‘short time approximation method’, which is generally valid only for the first 60% of the swelling [47]. For calculating diffusion coefficient of water into the hydrogels, the following relation (4) was used [47]:

$$M_t/M_i = 4(D_t/\pi l^2)^{1/2} \tag{8}$$

where D is the diffusion coefficient of water ($\mathrm{cm}^2\,\mathrm{s}^{-1}$) and l is thickness of the dry gel.

In order to characterize the swelling rate of different water swellable gels, the mean swelling time (MST) was estimated according to following Eq. (5) [48]:

$$\mathrm{MST} = [n/(1+n)](k)^{-1/n} \tag{9}$$

where n and k having same meaning as in power law Eq. (7).

The rate of swelling at different temperatures was evaluated in terms of the penetration velocity (V) of solvent, determined by weight-gain method as described elsewhere [49,50]. The penetration velocity was calculated from the slope of the initial portion of water uptake curve by following equation:

$$V = (1/\rho A) \times (\mathrm{d}W/\mathrm{d}t) \tag{10}$$

where $\mathrm{d}d/\mathrm{d}t$ is the slope of the weight gain vs time curve, ρ is the density of the solvent, A is the area of one face of the disc.

Figs. 14 and 15 show the dynamic swelling kinetics of NIPA-co-VBT and NIPA-co-SSS hydrogels, respectively, in water at room temperature as a function of ionic monomer content. It was found that not only the extent of gels containing VBT was higher but also their rate of approach to equilibrium was faster. The transport exponent values and other parameters evaluated for various gels (using Eq. (3)) are tabulated in Table 2. From these studies it was observed that transport exponent value, which was 0.5 for NIPA increased monotonically with the increase in the ionic monomer content in the co-polymer gels and were in the range 0.54–0.71. This indicated that the diffusion which was Fickian for PNIPA gel switched to anomalous diffusion in presence of the ionic components. The mean swelling time (MST) for co-polymer hydrogels decreased with increase in concentration of ionic monomer, this may be attributed to strong electrostatic repulsion between the polymer chains. The charge on polymer chain allows electric double layer to develop around the polymer chains, which consequently increases the hydrodynamic size of the chains by expanding them from compact ones to expanded coil form. The MST for NIPA-co-VBT hydrogels were found to be lower than the NIPA-co-SSS hydrogels containing same amount of ionic monomer content, which is attributed to the higher water binding capacity of VBT compared to SSS as described in Section 3.1.2. The faster rate of swelling in presence of ionic monomers is also supported by the "D" values estimated from experimental results (Table 2). The D values for NIPA-co-VBT hydrogels were higher than NIPA-co-SSS hydrogels. The penetration velocities obtained from the initial swelling data increased with the increased in the ionic content in the hydrogel and found to be higher for NIPA-co-VBT. The higher D values and faster penetration velocity for NIPA-co-VBT gels is supported by

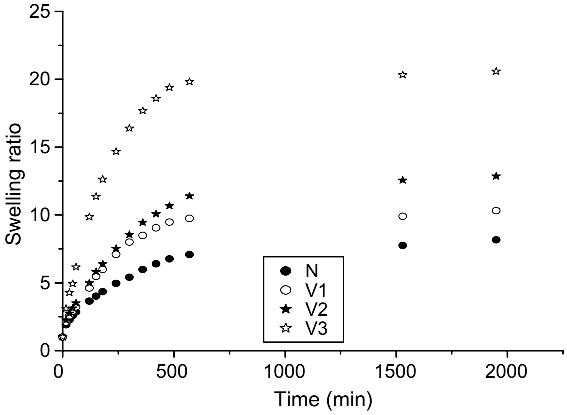

Fig. 14. Dynamic swelling of PNIPA-co-VBT hydrogels in water at room temperature.

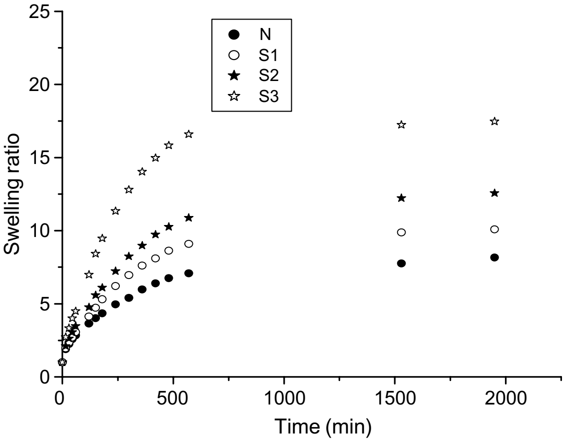

Fig. 15. Dynamic swelling of NIPA-co-SSS hydrogels in water at room temperature.

Table 2
Diffusion parameters derived for swelling using Eq. (7)

Sample	n	k	MST (min)	$D \times 10^8$ (cm^2/s)	Penetration velocity ($V \times 10^4$) (cm/s)
N	0.52	2.86×10^{-2}	319	4.03	2.69
S1	0.54	2.83×10^{-2}	258	4.23	3.19
S2	0.63	1.63×10^{-2}	265	5.86	4.38
S3	0.67	1.49×10^{-2}	212	6.80	5.89
V1	0.63	1.79×10^{-2}	251	6.05	3.56
V2	0.62	2.02×10^{-2}	207	6.47	4.42
V3	0.71	1.50×10^{-2}	154	7.00	7.50

the SEM studies where the gels containing VBT were observed to be more porous.

4. Conclusion

PNIPA based ionic thermo-responsive hydrogels of good strength can be easily prepared by radiation induced crosslinking of NIPA with VBT and SSS in aqueous solution. The incorporation of small amounts of ionic monomer (VBT and SSS) in the PNIPA matrix enhances its equilibrium swelling drastically without affecting the mechanical strength of the gel. However introduction of ionic monomers shifts LCST to high temperatures as well as the thermo-response of the gel does not remain abrupt particularly at higher ionic monomer components. The swelling in organic solvents indicated that on introduction of ionic monomer the EDS of the gels is governed by ionic content which induce polar nature in the matrix as the extent of swelling of the co-polymer gels was found to be a strong function of polarity of the solvent. These gels showed complex reentrant behavior in co solvents like water–ethanol. The gels containing VBT showed higher and faster swelling than the gels containing SSS.

References

[1] Kaetsu I. Radiat Phys Chem 1985;25:517–28.

[2] Osada Y, Gong JP, Tanaka T. J Macromol Sci Part C: Polym Rev 2004;44(1):78–112.

[3] Panda A, Manohar SB, Sabharwal S, Bhardwaj YK, Majali AB. Radiat Phys Chem 2000;58:101–10.

[4] Inomata GS, Saita CS. Macromolecules 1984;23:4887–91.

[5] Farahani EV, Cooper DG, Vera JH, Weber ME. Chem Eng Sci 1992;47(1):31–40.

[6] Cheng SC, Feng W, Pashikin II, Yuan LH, Deng HC, Zhou Y. Radiat Phys Chem 2002;63:517–9.

[7] Chen YF, Yi M. Radiat Phys Chem 2001;61:65–8.

[8] Gherke SH, Palasis M, Akthar MK. Polym Int 1992;28(4): 1–8.

[9] Hirotsu S, Hirokawa Y, Tanaka T. J Chem Phys 1987;87(2):1392–5.

[10] Baltes T, Garret-flaudy F, Freitag R. J Polym Sci Part A: Polym Chem 1999;37:2977–89.

[11] Yildz B, Isik B, Kis M. Eur Polym J 2002;38:1343–7.

[12] Park TG, Hoffman AS. Biotechnol Bioeng 1990;35:152–9.

[13] Ganorkar CR, Buddys M, Kim SW. J Biomater Polym Edn 2000;11:45–54.

[14] Zhai ML, Yi M, Shu J, Ha HF. Radiat Phys Chem 1998;52:313–7.

[15] Freitas RFS, Cussler EI. Chem Eng Sci 1987;42:97–103.

[16] Kotiyan PN, Vavia PR, Bhardwaj YK, Sabharwal S, Majali AB. Int J Pharm 2004;270:47–54.

[17] Valada JL, Liu Y, Huglin M. Macromol Chem Phys 1998;199:1127–34.

[18] Erbil C, Aras S, Uyanik N. J Polym Sci Part A: Polym Chem 1997;37:1837–55.

[19] Zhai ML, Li J, Yi M, Ha HF. Radiat Phys Chem 2000;58:397–400.

[20] Bhalerao VS, Varghese S, Lele AK, Budiger MV. Polymer 1998;39:2235–60.

[21] Senel S, Yuruksoy IB, Cicek H, Tuncel A. J Appl Polym Sci 1997;64:1775–84.

[22] Park TG, Hoffman AS. J Appl Polym Sci 1992;46:569–71.

[23] Feil H, Bae YH, Feijen J, Kim HW. Macromolecules 1993;26:2496–500.

[24] Yi M, Li J, Zhang JB, Jiang GL, Qiao JH, Ha HF. Radiat Phys Chem 1998;52:261–4.

[25] Lu XQ, Zhai ML, Li JQ, Ha HF. Radiat Phys Chem 2000;57:477–80.

[26] Yoo KK, Sung YK, Lee YM, Cho CS. Polymer 2000;41:5713–9.

[27] Bhardwaj YK, Sabharwal S, Majali AB. J Polym Mater 2000;17(3):239–52.

[28] Bhardwaj YK, Sabharwal S, Majali AB. J Polym Mater 2001;18(1):37–48.

[29] Chapiro A. Radiation polymerization of pure monomers in the homogeneous liquid phase. Radiation chemistry of polymeric systems. New York: Interscience; 1962. p. 159–203.

[30] Kumar V, Bhardwaj YK, Sabharwal S, Mohan H. J Radiat Res 2003;44:161–9.

[31] Bhardwaj YK, Mohan H, Sabharwal S, Mukherjee T. Radiat Phys Chem 2001;62:229–42.

[32] Flory PJ. Phase equilibria in polymeric systems. In: Flory PJ, editor. Principles of polymer chemistry. Ithaca, New York: Cornell University Press; p. 541–4.

[33] Gherke SH, Lee PI. Hydrogels in drug delivery system. Specialised drug delivery systems. New York: Marcel Dekker Inc.; 1990. p. 334–92.

[34] Schild GH, Tirell DA. J Phys Chem 1990;94:4352–6.

[35] Vinogradov SN, Linnell RH. Hydrogen bonding in water, ice and aqueous solutions. Hydrogen bonding. New York: Van Nostrand Reinhold Co.; 1971. p. 198–222.

[36] Nandi AK, Sen UK, Bhattacharys SN, Mandal BM. Eur Polym J 1983;19(4):283–6.

[37] Zhu PW, Napper DH. J Colloid Interface Sci 1996;177(2): 343–52.

[38] De KS, Aluru ND, Johnson B, Crone WC, David JB. J Microelectromech Syst 2002;11(5):544–55.

[39] Takeoka Y, Berker AN, Du R, Enoki T, Grosberg A, Kardar M, et al. Phys Rev Lett 1999;82(24):4863–5.

[40] Katayama S, Hirokawa Y, Tanaka T. Macromolecules 1984;17:2641–3.

[41] Makoto A, Horei K, Yamashitab T. Polym Gels Networks 1995;3(3):281–93.

[42] Bhardwaj YK, Kumar V, Sabharwal S. J Appl Polym Sci 2003;88:730–42.

[43] Subotic DV, Wu XY. Ind Eng Chem Res 1997;36(4): 1302–9.

[44] Chu Y, Varanasi PP, McGlade MJ, Varanasi S. J Appl Polym Sci 1995;58:2161–76.

[45] Dhara D, Chatterjee PR. JMS Rev Macromol Chem Phys 2000;C 40(1):51–68.

[46] Alfrey A, Gurnee EF, Lloyd WG. J Polym Sci 1966;C12: 249–61.

[47] Park GS. The glassy state and slow process anomalies. Diffusion in polymers. London: Academic Press; 1968. p. 141–64.
[48] Mockel JE, Lippold BC. Pharmaceutical Res 1993;90: 1066–70.
[49] Lee WF, Yeh PL. J Appl Polym Sci 1998;68(10):1597–603.
[50] Bajpai AK, Bajpai J, Shukla S, Kulkarni RA. J Macromol Sci A Pure Appl Chem 2004;A41(2):211–30.