

Swelling Behavior of Radiation-Polymerized Polyampholytic Two-Component Gels: Dynamic and Equilibrium Swelling Kinetics

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ABSTRACT: Polyampholytic hydrogels, with varying degrees of crosslinking and ionic content, were prepared by radiation polymerization of *p*-sodium styrene sulfonate (SSS) and vinyl benzyl trimethylammoniumchloride (VBT). These gels were investigated for their dynamic and equilibrium swelling kinetics. Dynamic swelling of these gels established that the gels containing equal amounts of SSS and VBT strictly follow Fickian diffusion. The hydrogels containing excess of SSS followed the case II type of diffusion, whereas those containing excess of VBT followed anomalous diffusion. Equilibrium swelling kinetics of these gels in aqueous system, ethanol–water mixture, at different pHs, and in the presence of solutions of biological interest was studied. It was seen that gels containing equal amounts of SSS and VBT show the lowest equilibrium swelling. Swelling of the polyampholytic gel decreased with an increase in the radiation dose imparted and the amount of crosslinking agent incorporated in the gel. The gels having an excess of VBT showed higher equilibrium swelling in comparison to those having an excess of SSS. Differential scanning calorimetry (DSC) studies showed that crosslinking of the gels

decreases equilibrium swelling but increases the bonded nonfreezable water content of the gels. The organic solvents like ethanol cause abrupt collapse of the polyampholyte gels containing excess of SSS and those containing equal amounts of both the monomers at some critical ratio of water and ethanol in swelling medium. However, the deswelling in the water–ethanol mixture was gradual for gels containing an excess of VBT and the extent of deswelling was also low for these gels in comparison to other gels. The swelled gels of all compositions deswelled when they were transferred to solutions at pH in the range 2–12. Biologically important solutes like urea, glucose, and surfactants like Triton-X tend to further swell the polymer matrices, whereas NaCl causes their deswelling. The additive effect is more prominent for polyampholyte gels containing excess of either of the monomers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 730–742, 2003

Key words: radiation; hydrogels; swelling kinetics; dynamic swelling; diffusion; simulations; equilibrium swelling; crosslinking

INTRODUCTION

In recent years, phase transition, a critical phenomenon in polymer gels, has attracted much attention because of its scientific interest and technological importance.¹ Phase transitions accompanied by a reversible, discontinuous volume change, as large as 500-fold, have been observed in various gels made of synthetic and natural polymers.^{2–6} Polyampholyte gels, because of their similarity to biopolymers, have been considered as role models for understanding the molecular interactions in biopolymers.⁷ The changes in the conformation of biopolymers may be due to either all of the forces like hydrogen bonding, hydrophobic interactions, van der Waals forces, or to coulombic interactions.⁸ Among these various forces, the first three are considered to be the reason for the phase transition observed in the majority of the gels; how-

ever, coulombic interaction, which is comparatively a long-range interaction, is solely observed in heteropolymers like polyampholytes gels, where two types of charges are involved.⁹ Due to their ionic nature, polyampholytes show rapid swelling before reaching equilibrium swelling, which is a function of type and amount of ions present in the swelling medium. The presence of strong coulombic interactions in polyampholytic gels results in a complicated dynamic swelling behavior as compared to their nonionic counterparts.¹⁰ We have recently reported the change in equilibrium and dynamic swelling behavior of a nonionic parent matrix due to introduction of two types of ionic moieties in the parent matrix.^{11,12}

In the present work, dynamic and equilibrium swelling behavior of a wide range of high-purity polyampholytic gels obtained by radiation copolymerization of *p*-sodium styrene sulfonate (SSS), a cation exchange type of monomer, and vinyl benzyl trimethyl ammonium chloride (VBT), an anion exchange type of monomer, has been reported. Equilibrium swelling of these polyampholyte gels in different solvent mixtures and additives has also been reported.

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EXPERIMENTAL

Materials

SSS (mol wt = 206.20), VBT (mol wt 211.74), and *N,N*-methylene-bis-acrylamide (MBA) in powder form, from Aldrich were used as received. Double-distilled (DD) water (conductivity $1.9 \mu\text{S cm}^{-1}$) was used for making solutions and all swelling experiments.

The monomers SSS and VBT with or without MBA were mixed in water in various compositions with total monomer concentration fixed at 2M. The solutions were stirred and then filled in glass tubes (ID = 2 cm and $l = 7\text{--}8$ cm), deoxygenated at less than 10^{-3} torr vacuum at liquid nitrogen temperature, and sealed. Polymerization was carried out by irradiating the sealed samples at room temperature with γ -rays from a 10,000 Curie Cobalt-60 source at a dose rate of 10 kGy h^{-1} . The samples were irradiated to doses of 5 and 10 kGy, which was sufficient to achieve almost complete conversion of monomer/monomer mixture to polymer gels. After irradiation, the glass vials were broken to get polymer/copolymer in cylindrical form. The samples were rubbery at room temperature and their appearance varied from transparent and colorless to opaque and white depending on the ratios of the monomers in the solution. These samples were cut into 0.6–1.8 mm thick disks with a sharp-edged blade and left in double-distilled water to remove residual monomers, and then dried in an oven at 30°C. Swelling–drying cycles were carried out 3–4 times and finally the disks were dried under vacuum to constant weight.

Fourier transform infrared (FTIR) spectra of dried polymers and copolymers were performed on Jasco FTIR-420 spectrometer operating in the external mode. Spectra were obtained in the region $7500\text{--}4000 \text{ cm}^{-1}$ and acquired with a resolution of 4 cm^{-1} and a total of 90 accumulations. The spectra did not show any peaks at about 6200 or 4750 cm^{-1} corresponding to $>\text{C}=\text{CH}-$, indicating absence of monomers in the polymer matrices.

Sorption measurements

The increases in the mass of samples, immersed in distilled water at $28 \pm 1^\circ\text{C}$ were monitored gravimetrically. Preweighed samples were placed in a 200-mesh stainless steel compartment and immersed in excess distilled water. The swelled samples were periodically removed, blotted free of surface water using laboratory tissue paper and weighed on Mettler analytical balance (accuracy 0.00001 g), and returned to the swelling medium. Measurements were taken until the samples reached a constant weight. The swelling ratio and equilibrium water content (EWC) of the gels swelled to equilibrium were determined using simple equations:

$$\text{Swelling ratio} = \text{Swelled weight}/\text{Initial weight} \quad (1)$$

$$\text{EWC} = \frac{\text{Mass of water absorbed by gel}}{\text{Mass of swollen gel}} \times 100\% \quad (2)$$

DSC studies

For DSC studies, 5–10 mg of gels samples swelled to equilibrium were weighed in aluminium crucibles covered with a lid carrying two pin holes. The samples were heated between -50 and 200°C at a heating rate of $5^\circ\text{C}/\text{min}$ in a dynamic N_2 atmosphere. The amount of freezable water was calculated by comparing heat of fusion of water in the gel to that of pure water (334 J/g). Bound water contents were calculated by taking the difference of freezable water and the total water content determined gravimetrically.

Data analysis

The dynamic swelling property of a polymer includes the solvent sorption rate, the rate of approach to equilibrium, and the transport mechanism controlling the solvent sorption. These characteristics were evaluated by the following methods.

The transport mechanism, which indicates the relative importance of diffusion and relaxation, was identified through the empirical eq. (3)¹³:

$$M_t/M_\infty = Kt^n \quad (3)$$

where M_t is the mass of solvent absorbed at time t , M_∞ is the mass of the solvent absorbed at equilibrium, K is the rate constant, n is an empirical number called the transport exponent. The transport exponent values were obtained by linear regression of the $M_t/M_\infty < 0.6$ vs t^n plot. A value of $n = 0.5$ was taken as an indication that the process is diffusion controlled (Fickian diffusion) or case I transport, whereas transport was considered to be relaxation controlled (case II) for $n = 1.0$ and as anomalous when the value of n lies between 0.5 and 1.0. The utility of eq. (3) for directly comparing the rates of sorption for different materials is limited because of dependence of the rate constant K on the transport exponent n . Direct comparison of K values can only be made provided all the polymer samples have same value of n .

It has been suggested that for the cases of Fickian transport, the rate of approach to equilibrium can be characterized by a diffusion coefficient value D , which can be calculated from eq. (4)¹⁴:

$$M_t/M_\infty = 4/\pi^{0.5}(Dt/L_0^2)^{0.5} \quad (4)$$

where D is the diffusion coefficient in a polymer-fixed reference frame and L_0 is initial thickness of the sample. The presence of dimensionless time factor (Dt/L_0^2) in this equation also suggests that a plot of M_t/M_∞ vs $t^{0.5}/L_0$ (diffusion plot) should be independent of sample thickness. This criterion was also used to confirm the transport mechanism of copolymer gels.

A simulated sorption curve was computed from eq. (5)¹³ using the D value obtained experimentally, and compared with the experimentally determined diffusion plot.

$$M_t/M_\infty = 1 - \sum_{n=0}^{\infty} \{8/(2n+1)^2 \pi^2\} \times \exp\{- (2n+1)^2 \pi^2 (Dt/L_0^2)\} \quad (5)$$

RESULTS AND DISCUSSION

Dynamic swelling kinetics

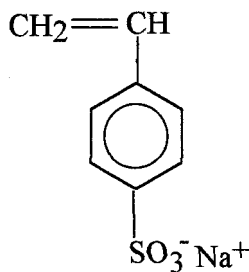
The kinetic response of gels depends both upon the history of a given gel sample and its chemical composition, e.g., the swelling kinetics of gels are reported to change with the initial anisotropy of the matrix^{14,15} as well as changing the constituent of the matrix, particularly introducing ionic monomers in the parent gels.^{16,17}

For a nonionic gel in equilibrium with the solvent, the osmotic swelling pressure is given by

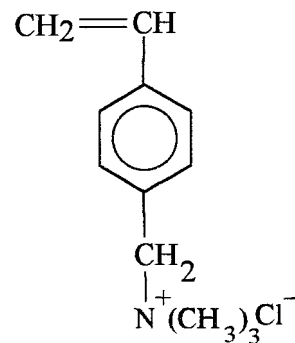
$$\pi_{\text{tot}} = \pi_{\text{mix}} + \pi_{\text{elas}} \quad (6)$$

where π_{tot} is the total osmotic pressure, π_{mix} is osmotic pressure due to mixing of polymer chains with solvent molecules, and π_{elas} is osmotic pressure due to elastic response to changes in the configuration of the polymer network. The parameters π_{mix} and π_{elas} are themselves related to the crosslink density and the Flory-Huggins parameter (χ). Thus the key parameters that determine the swelling of nonionic gel in a solvent are the crosslink density and Flory-Huggins parameter (χ).¹⁸ If the gels contain ionizable groups, the additional ion-related term π_{ions} has to be included in eq. (6).¹⁹

Unlike poly(acrylic acid), polymers of SSS and VBT (Structure 1 and Structure 2) are highly ionized salt.



Structure 1 *p*-Sodium styrene sulfonate.



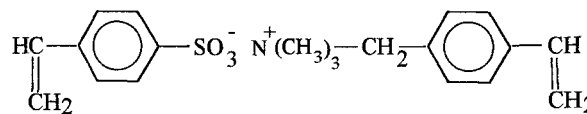
Structure 2 Vinyl benzyl trimethyl ammonium chloride.

If a polyampholyte gel is prepared by copolymerizing two ionic monomers, one of which ionizes to positively charged species and other leads to negatively charged species in aqueous solution, then the type of ionic group available on the copolymer gel depends on the ratio of two monomers taken initially in the feed solution. These gels, which may be totally neutralized, or which ionize to cationic or anionic species, may swell at different time scales, i.e., their dynamic sorption kinetics may be different. In order to understand this phenomenon, dynamic swelling kinetics of radiation-polymerized polyampholyte gel of SSS and VBT crosslinked to different extents were investigated.

Swelling behavior of SSS-co-VBT containing SSS and VBT in the ratio (1:1)

When SSS and VBT are taken in equal ratios in an aqueous solution, a neutralized species of structure as shown in Structure 3 is formed. This neutral molecule, unlike its parent monomer molecule, which is bifunctional, is a multifunctional molecule like MBA or ethylene glycol dimethacrylate (EGDMA). So practically irradiating an aqueous solution containing SSS and VBT in equal amounts is like irradiating a multifunctional monomer, which results in gels of high crosslink density and better strength. In fact, gels obtained were of very good strength and easy to handle but comparatively low swelling ratio.

Figure 1 shows changes in the swelling extents of these polyampholytic gels due to their further crosslinking by addition of different amounts of MBA to the mixture. As expected, increasing amounts of crosslinking agents in the copolymer matrix leads to more crosslinked structure and hence lower equilib-



Structure 3

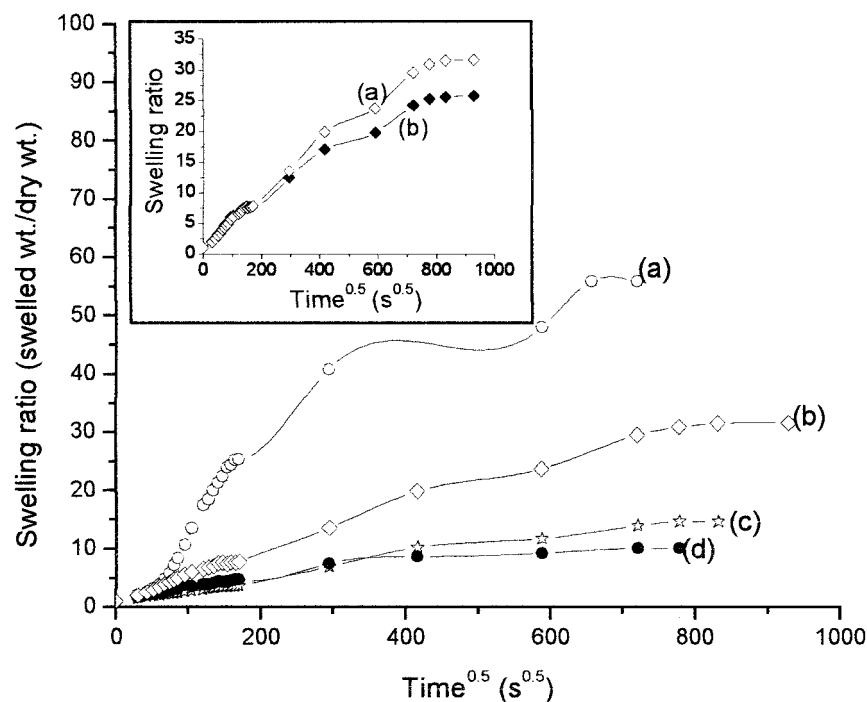


Figure 1 Swelling of SSS-co-VBT gel {[SSS]:[VBT]; 1M:1M}. (a) No MBA, (b) 10 mM MBA, (c) 25 mM MBA, and (d) 50 mM MBA. Total dose kGy. Inset: (a) 10 mM MBA and 5 kGy; (b) 10 mM MBA and 10 kGy.

rium swelling and swelling ratio. The inset of Figure 1 shows the swelling ratio of a polyampholytic gel of same compositions synthesized for two different total doses. The lower swelling ratio for a gel synthesized by irradiating the gel beyond radiation dose of 5 kGy increases the extent of crosslinking of the gel.

Table I shows swelling characteristics of these gels. For all these gels, the transport exponent value (n) was found to be 0.5, indicating Fickian diffusion. Figure 2 shows the experimentally observed diffusion curve for one of the polyampholyte gels of this family. Figure 2 also shows a computed plot (solid curve) from the theoretical eq. (5) using a constant diffusion coefficient value $D = 9.77 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. The experimental sorption data and the simulated sorption data are

in good agreement during initial stages; however, at a later time scale the experimental data lies above the simulated diffusion curve, signifying an acceleration in swelling rates as reported in the earlier studies^{20–22} for other systems. This acceleration in swelling rates has been attributed to the dimensional rearrangements after the disappearance of glassy core, which decreases the thickness (diffusional path length) of the polymer but increases the diffusional area of the sample. Both of these effects may therefore accelerate the diffusion process.

The diffusion through these gels was further studied by swelling the copolymers of different thicknesses and plotting reduced absorption curves for them. The results of this study are shown in Figure 3.

TABLE I
Swelling Characteristics of SSS-co-VBT Polyampholytic Gels Containing Equal Amounts of SSS and VBT in Double-Distilled Water

Sample no.	Matrix composition			Dose (kGy)	Swelling ratio ^a	Transport exponent (n)	D ($\times 10^9 \text{ cm}^2 \text{ s}^{-1}$) ^a
	SSS (M)	VBT (M)	MBA (mM)				
1	1	1	0	5	57.42 ± 1.29	0.5	17.02 ± 2.22
2	1	1	0	10	55.89 ± 1.00	0.5	13.40 ± 1.67
3	1	1	10	5	31.55 ± 1.43	0.5	13.73 ± 1.55
4	1	1	10	10	25.74 ± 1.43	0.5	7.97 ± 1.63
5	1	1	25	5	14.67 ± 0.52	0.5	9.77 ± 1.22
6	1	1	25	10	9.31 ± 0.93	0.5	7.91 ± 0.83
7	1	1	50	5	10.14 ± 0.87	0.5	3.96 ± 0.53
8	1	1	50	10	7.26 ± 0.27	0.5	3.69 ± 0.56

^a Average of at least five values.

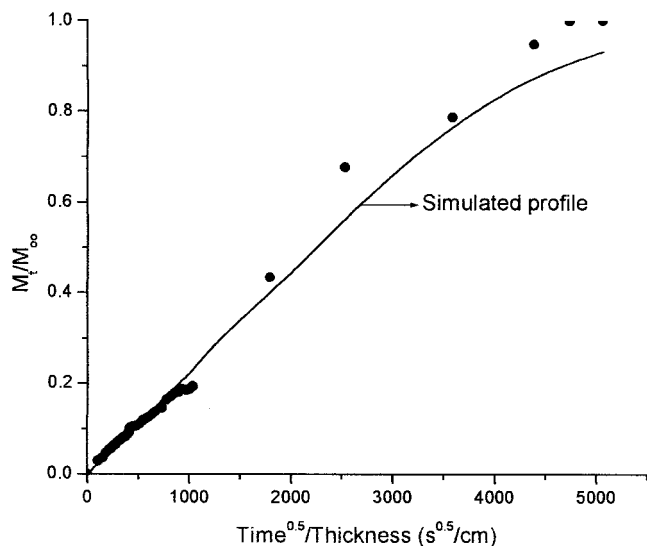


Figure 2 Water sorption kinetics of poly(SSS-co-VBT + 25 mM MBA) gel {[SSS]:[VBT]; 1M:1M}. Dose 5 kGy. Solid line: Simulated diffusion curve with $D = 9.77 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for sample of initial thickness 0.16 cm.

From Figure 3 it is clear that for samples of different initial thicknesses the experimental data overlaps very well and a computed curve can be fitted [using eq. (5)] with $D = 9.77 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ into the experimental data. The simulated profile curve fits very well into the experimental data at initial timings, and at later times the experimental data lies above the simulated profile.

From these studies it could be conclusively established that the diffusion through copolymer polyampholytic gels containing SSS and VBT in equal amounts essentially remains Fickian.

Swelling behavior of SSS-co-VBT containing excess SSS

Table II shows swelling characteristics of gels containing higher amounts of SSS. For all such gels the transport exponent value was found to be 1, i.e., induction of extra SSS in the polyampholyte gel changes the diffusion to a case II type of diffusion from Fickian diffusion for a polyampholyte gel containing equal amounts of SSS and VBT. Case II type diffusion indicates that for these gels the rate of diffusion overtakes the rate of relaxation of the polymer chains, whereas it is the reverse for the Fickian type of diffusion.

This change in type of diffusion was caused by the excess SSS (which remained non-neutralized) in the polyampholyte gel. We have recently reported that on irradiation in aqueous solution SSS undergoes very fast polymerization²³ and its polymer predominantly undergoes radiolytic degradation²⁴ to radiation doses as high as 1000 Kgy. It seems incorporation of more SSS in the copolymer gel results in comparatively less

crosslinked matrix, which allows faster diffusion of swelling medium into the matrix. Comparing the diffusion values for polyampholyte gels containing the same amounts of crosslinking agent (MBA) from Tables I and II, it can be seen that D values are 30–40 times higher for gels containing higher amounts of SSS. Higher diffusion rates are probably sufficient to overtake the rate of relaxation of chains and hence the case II diffusion in these polyampholytic gels. Moreover, the diffusion process may be further enhanced when SSS gets ionized in diffusion medium and the ionized segments due to charge repulsion further tend to open up the gel for much faster ingress of the diffusion medium into the matrix. Figure 4 shows experimental diffusion profiles for one such gel. The figure also shows a computed (solid curve) from the theoretical eq. (5) using a constant diffusion coefficient value $D = 3.72 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. It can be seen that the experimental and simulated profiles do not overlap even initially; later the experimental data lies above the simulated profile drawn from initial diffusion rates; however, in the final stages of swelling (near equilibrium swelling) again the simulated profile lies above the experimental profile. This type of disagreement between the two profiles indicates that dynamic swelling of such gels is not of the conventional type as observed by earlier workers for other nonionic gels.^{18,22,25} The disagreement between the two profiles indicate that the diffusion rates for these type of matrices always keep changing as the swelling of the matrix progress to equilibrium swelling. In order to probe this observation further, the diffusion values obtained using eq. (4) were plotted at different times.

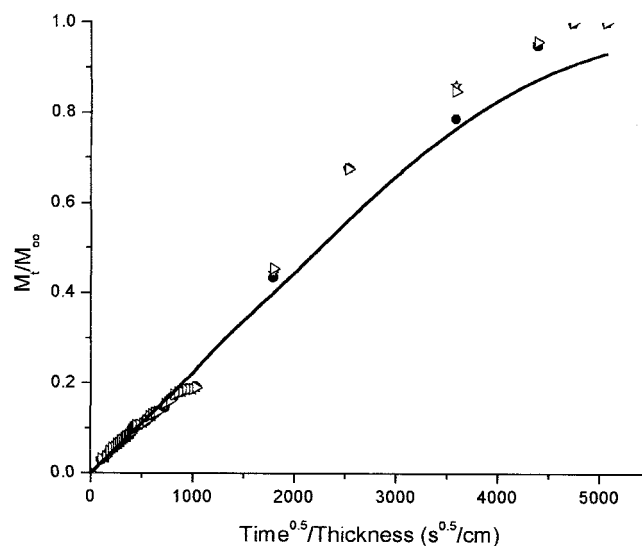


Figure 3 Water sorption kinetics of poly(SSS-co-VBT + 25 mM MBA) gels {[SSS]:[VBT]; 1M:1M} as a function of thickness. Initial thickness (cm): (●) 0.16, (▷) 0.08, and (☆) 0.12. Dose 5 kGy. Solid line: Simulated diffusion curve with $D = 9.77 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

TABLE II
Swelling Characteristics of SSS-co-VBT Polyampholytic Gels Containing Excess SSS in Double-Distilled Water

Sample no.	Matrix composition			Dose (kGy)	Swelling ratio ^a	Transport exponent (<i>n</i>)	<i>D</i> ($\times 10^9 \text{ cm}^2 \text{ s}^{-1}$) ^a
	SSS (M)	VBT (M)	MBA (mM)				
1	1.5	0.5	10	5	270.64 \pm 5.53	1	61.21 \pm 2.18
2	1.5	0.5	10	10	147.97 \pm 4.33	1	56.53 \pm 2.00
3	1.5	0.5	25	5	88.28 \pm 3.42	1	55.93 \pm 1.28
4	1.5	0.5	25	10	56.55 \pm 1.20	1	47.51 \pm 1.49
5	1.5	0.5	50	5	44.46 \pm 2.00	1	45.22 \pm 2.12
6	1.5	0.5	50	10	32.67 \pm 1.05	1	36.10 \pm 0.69
7	1.25	0.75	10	5	81.85 \pm 3.27	1	39.24 \pm 1.83
8	1.25	0.75	10	10	64.43 \pm 2.67	1	37.03 \pm 1.02
9	1.25	0.75	25	5	49.88 \pm 1.91	1	37.20 \pm 0.85
10	1.25	0.75	25	10	42.44 \pm 1.42	1	31.33 \pm 1.12
11	1.25	0.75	50	5	41.00 \pm 2.39	1	29.64 \pm 1.39
12	1.25	0.75	50	10	27.15 \pm 1.18	1	21.91 \pm 1.85

^a Average of at least five values.

The inset of Figure 4 shows the profile for this study. It is evident from the profile that the diffusion values initially increase and then decrease almost exponentially for these gels, and therefore probably the anomaly between the two profiles was observed for these types of polyampholyte gels.

Swelling behavior of SSS-co-VBT containing excess VBT

Table III shows swelling characteristics of gel containing higher amounts of VBT. For all such gels transport exponent values were between 0.5 and 1, i.e., the diffusion was non-Fickian or anomalous in the pres-

ence of higher amounts of VBT in the polyampholytic gels. Anomalous diffusion is characterized by comparable rates of diffusion and relaxation. Polyampholytic copolymer gels containing higher amounts of VBT result in segments in the gel matrix, which can get ionized in aqueous medium. Virendra et al.²⁶ have recently reported that on irradiation in aqueous solution VBT, like SSS, undergoes very fast polymerization; however, its polymer, unlike polySSS, predominantly undergoes crosslinking on radiolysis. Thus, though incorporating extra VBT causes higher hydrophilicity of the matrix due to more binding site in the matrix, its crosslinking nature does not affect the

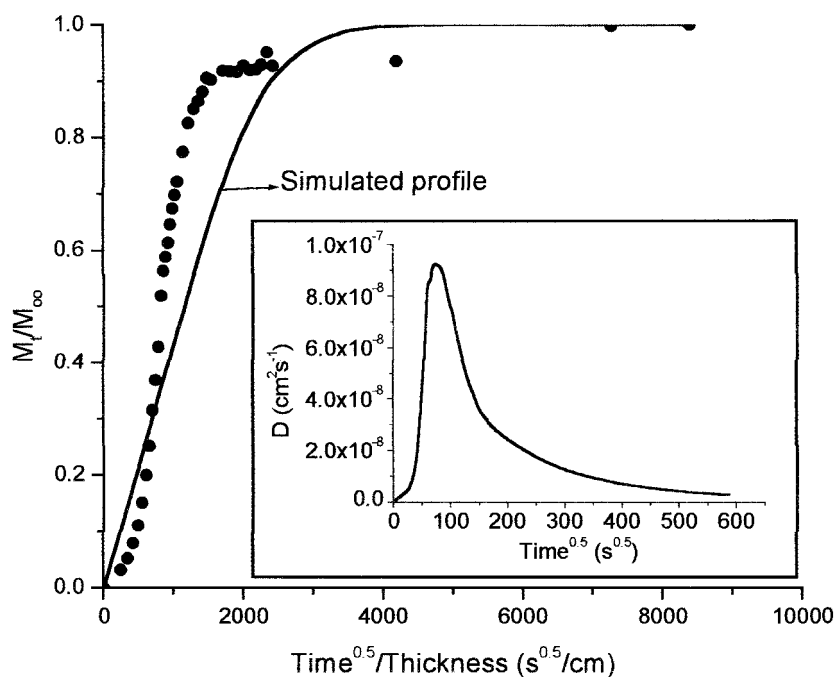


Figure 4 Water sorption kinetics of poly(SSS-co-VBT + 25 mM MBA) gel ([SSS]:[VBT]; 1.25M:0.75M). Dose 5 kGy. Solid line: Simulated diffusion curve with $D = 3.72 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for sample of initial thickness 0.07 cm.

TABLE III
Swelling Characteristics of SSS-co-VBT Polyampholytic Gels Containing Excess VBT in Double-Distilled Water

Sample no.	Matrix composition			Dose (kGy)	Swelling ratio ^a	Transport exponent (<i>n</i>)	<i>D</i> ($\times 10^9$ cm ² s ⁻¹) ^a
	SSS (M)	VBT (M)	MBA (mM)				
1	0.50	1.50	10	5	343.86 \pm 6.82	0.8	25.74 \pm 2.07
2	0.50	1.50	10	10	157.21 \pm 5.29	0.7	24.00 \pm 2.31
3	0.50	1.50	25	5	131.73 \pm 4.46	0.7	32.04 \pm 2.86
4	0.50	1.50	25	10	74.54 \pm 3.29	0.7	26.51 \pm 1.23
5	0.50	1.50	50	5	49.26 \pm 3.84	0.9	10.61 \pm 0.61
6	0.50	1.50	50	10	33.12 \pm 1.25	0.8	9.73 \pm 0.75
7	0.75	1.25	10	5	120.67 \pm 2.88	0.8	52.33 \pm 1.08
8	0.75	1.25	10	10	98.29 \pm 1.36	0.9	48.32 \pm 1.90
9	0.75	1.25	25	5	72.94 \pm 2.23	0.6	30.20 \pm 1.62
10	0.75	1.25	25	10	55.90 \pm 2.45	0.8	22.81 \pm 1.45
11	0.75	1.25	50	5	46.19 \pm 1.41	0.9	12.44 \pm 1.40
12	0.75	1.25	50	10	33.36 \pm 1.29	0.8	11.31 \pm 1.40

^a Average of at least five values.

crosslinking extent of the polyampholyte matrix appreciably. However, as the extra non-neutralized VBT can get ionized to similar charge in the close vicinity which tend to open up the matrix owing to repulsive force, this may cause faster diffusion as the ionization proceeds while swelling. The increased diffusion rates (due to ionization of VBT) probably match the relaxation rates of chains and cause anomalous diffusion. Figure 5 shows diffusion profiles for one of such gels. The disagreement between the simulated and the experimental profile was as in the above case. The diffusion values changed as the swelling progressed (inset, Fig. 5); however, the change in the *D* values was

not so high as in the case where an extra amount of SSS was incorporated in the polyampholyte gel.

Equilibrium swelling kinetics

The amount of water absorbed by a hydrogel is a function of the hydrophilicity of the polymer, the crosslinking of network structure, and the number of ionized groups on the polymer. As swelling degree is central to any application of hydrogel, it is important to examine changes in its swelling degree due to composition of gels as well as due to swelling medium. As described earlier in a polyampholyte gel, the type and

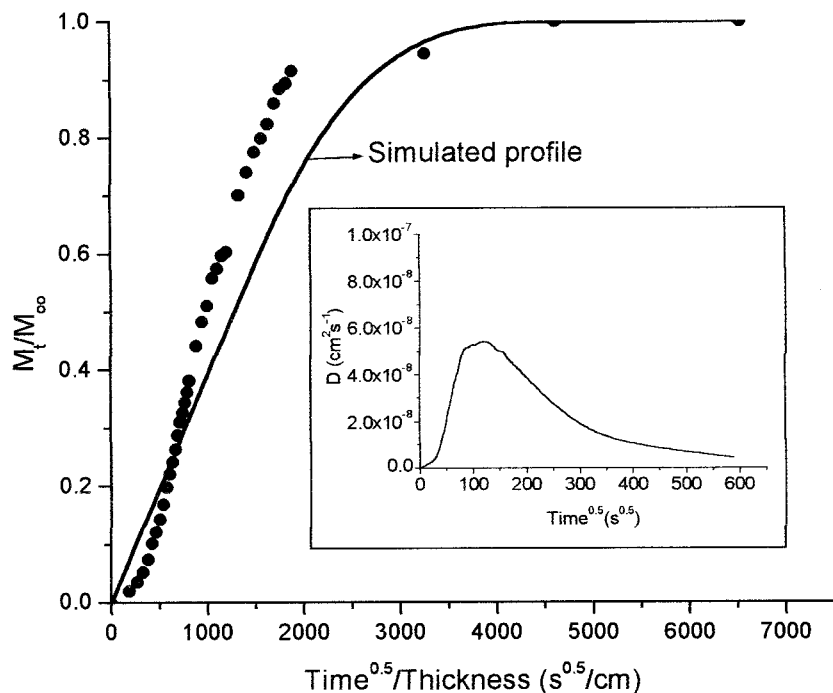


Figure 5 Water sorption kinetics of poly(SSS-co-VBT + 25 mM MBA) gel ([SSS]:[VBT]; 0.75M:1.25M). Dose 5 kGy. Solid line: Simulated diffusion curve with $D = 3.02 \times 10^{-8}$ cm² s⁻¹ for sample of initial thickness 0.09 cm.

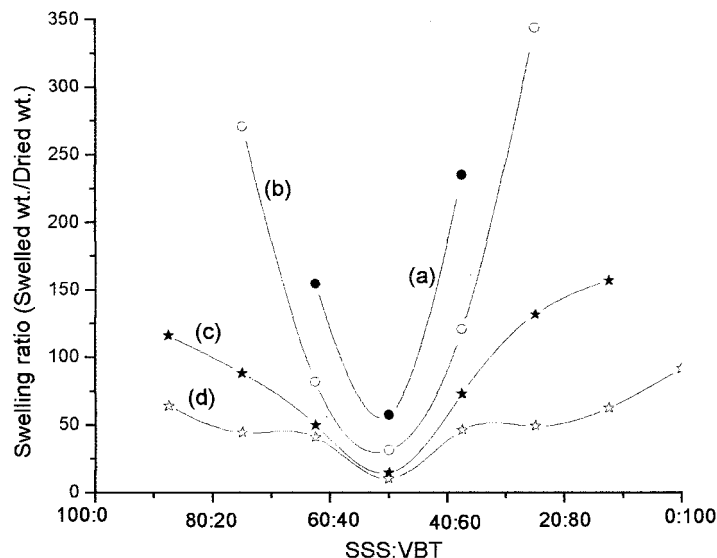


Figure 6 Swelling of SSS-co-VBT gel. (a) No MBA, (b) 10 mM MBA, (c) 25 mM MBA, and (d) 50 mM MBA. Total dose 5 kGy.

amount of residual charge determines its equilibrium swelling extent. In order to understand the changes in the swelling extent of polyampholyte gels due to residual charges on the gels, the equilibrium swelling of the radiation polymerized gel of SSS and VBT crosslinked to different extents were investigated.

Swelling in aqueous medium

Figure 6 shows swelling ratio as a function of composition of radiation-polymerized SSS-co-VBT polyampholyte gels. It can be seen that for all series of gels crosslinked to different extents by incorporating different amounts of the crosslinking agent MBA, the swelling ratio was minimal for those having equal amounts of SSS and VBT in the gels. The swelling ratio increased rapidly as this balance deviated from perfect neutrality. Another interesting feature of the result is that introducing excess SSS or VBT in same proportions does not affect swelling ratio to the same extent. It is higher for polyampholyte gels containing excess VBT. This can be attributed to the different types and natures of water binding sites $-\text{SO}_3^-$ and $-\text{N}^+(\text{CH}_3)_3$ in SSS and VBT respectively. Ions like tetra-alkylammonium ions are known to have a net structure making effect.²⁷ Their high electric fields not only polarize, immobilize, and electrostrict nearest neighbor molecules, but they also induce additional order beyond the first layer of water molecules. Ions like SO_3^- ; however, can immobilize the water molecules of only the first layer. The higher attractive field that can be felt to several layers in the case of $-\text{N}^+(\text{CH}_3)_3$ probably causes many more layers of water to be associated to the first layer, which is in the immediate vicinity of the polymer in comparison to SO_3^- group, and hence more water uptake is seen in gels containing residual VBT containing $-\text{N}^+(\text{CH}_3)_3$ groups.

It has been suggested that water in natural macromolecular gels^{28,29} or in synthetic hydrogels³⁰ can be of three types—namely, bulk water, interfacial water, and bound water, and they have been conveniently determined by techniques like dilatometry, specific conductivity, and differential scanning calorimetry.³¹ For all practical purposes the three types of water have been grouped in two classes as freezable (bulk) water and nonfreezable (bound) water.³² The DSC technique was used to determine the two types of waters in these gels. Results of these studies are presented in Table IV. The data presented clearly indicates that EWC as well as freezable water content of the gels increases as excess of SSS or VBT is incorporated in the polyampholyte gel. The enhanced crosslinking of the gels, though, decreases EWC but increases the ratio of nonfreezable to freezable water content of the gels. The increase in this ratio is not just because of the gradual decrease in the freezable water; there is an increase in the nonfreezable water content of the gels as well. This may be due to increased water binding sites generated due to introduction of the crosslinking agent MBA, which itself has sites available for hydrogen bonding with water. The higher ratio of nonfreezable to freezable water content for polyampholytic gels containing excess VBT confirms high electric fields, which lead to the net structure making effect in the gels.

Effect of crosslinking agents on swelling of polyampholytic gels

Crosslinking of polymers, though, improves the strength of the matrices; it restricts the swelling of the matrix. Figure 7 shows a decrease in the swelling ratio of the polyampholytic gels as the amount of crosslinking agent is increased. Expectedly, the gels synthe-

TABLE IV
Percentage of Total, Free, and Bound Water Normalized with Respect to Weight of Polyampholytic Hydrogel Synthesized for Total Radiation Dose of 5 kGy

Sample no.	Matrix composition			Dose (kGy)	W (%)	W_f (%)	W_{nf} (%)	W_{nf}/W_f
	SSS (M)	VBT (M)	MBA (mM)					
1	1	1	0	5	98.21	73.52	24.69	0.336
2	1	1	10	5	96.83	68.00	28.83	0.424
3	1	1	25	5	93.18	59.73	33.45	0.560
4	1	1	50	5	90.14	54.07	36.07	0.667
5	1.25	0.75	0	5	99.35	76.75	22.60	0.294
6	1.25	0.75	25	5	97.99	67.75	30.24	0.446
7	1.25	0.75	50	5	97.56	64.43	33.13	0.514
8	0.75	1.25	0	5	99.59	74.27	25.32	0.340
9	0.75	1.25	25	5	96.88	65.32	33.31	0.510
10	0.75	1.25	50	5	99.59	62.64	35.20	0.562

W_f : water freezable (free); W_{nf} : water nonfreezable (bound).

sized for total higher radiation dose had lower swelling ratio, indicating that the SSS-co-VBT matrix undergoes further crosslinking as it is irradiated to higher radiation dose $>5\text{kGy}$ (inset, Figure 7).

Swelling of polyampholytic gels in ethanol-water mixture

Three main forces that govern the swelling or collapse of the polymer network have been identified as rubber elasticity, polymer-polymer affinity, and hydrogen ion pressure.³³ The balance of these forces is easily

perturbed by composition of the matrix and external factors like temperature and type of solvent. For a polyampholyte gel, the coulombic interactions are stronger in organic solvents than in water, and the solvent quality is poorer than in water with respect to noncoulombic interactions. In order to study the effect of these forces on swelling of SSS-co-VBT polyampholyte gels, their swelling behavior was investigated in water-ethanol mixtures of different compositions. Figure 8 shows the swelling of totally neutralized gels crosslinked to different extents. For all these gels it can

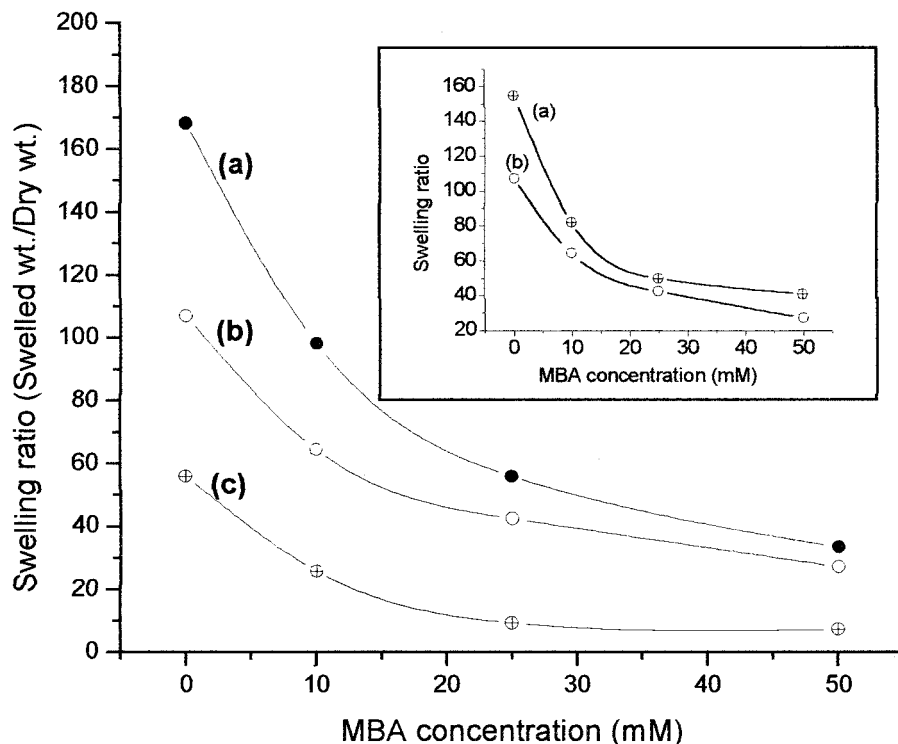


Figure 7 Effect of crosslinking on swelling of SSS:VBT polyampholyte gels synthesized for a total dose of 10 kGy. (a) [SSS]:[VBT]; 0.75M:1.25M. (b) [SSS]:[VBT]; 1.25M:0.75M. (c) [SSS]:[VBT]; 1.0M:1.0M. Inset: [SSS]:[VBT]; 1.25M:0.75M; (a) 5 kGy and (b) 10 kGy.

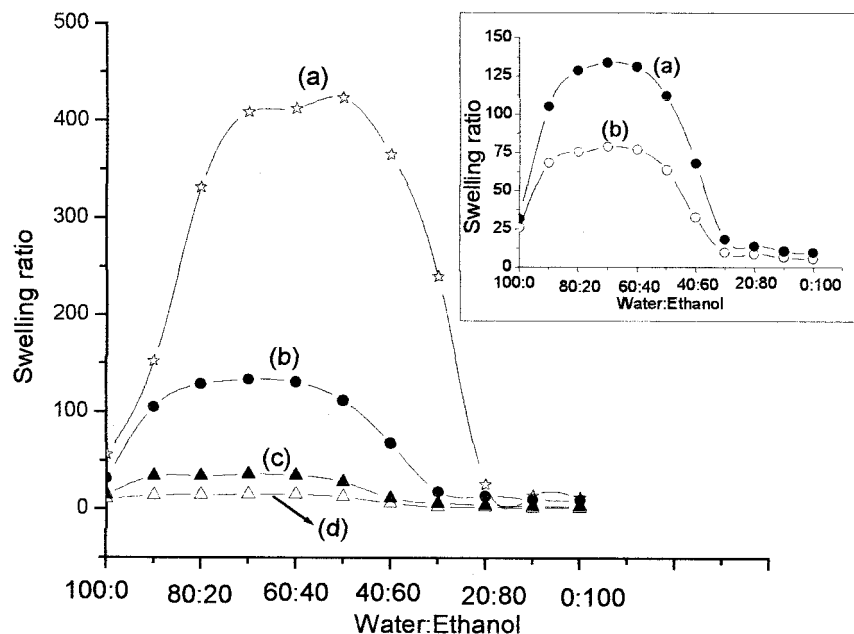


Figure 8 Swelling of poly([SSS]:[VBT]; 1M:1M) polyampholyte gel crosslinked to different extents in a water-ethanol mixture. (a) No MBA, (b) 10 mM MBA, (c) 25 mM MBA, (d) 50 mM MBA. Inset: ([SSS]:[VBT]; 1M:1M) + 10 mM MBA; (a) 5 kGy and (b) 10 kGy.

be seen that swelling ratio initially increases as the content of ethanol is increased in the swelling mixture to 50%. However, the gels start deswelling as the ethanol content is increased beyond 50% in the swelling mixture and finally the gel collapses at ethanol concentration $>75\%$. Similarly, initial swelling followed later on by deswelling at higher concentrations of ethanol was observed for other gels containing excess of SSS or VBT. It is worth noting that the changes in the swelling ratio are not rapid or sudden in terms of time—they are abrupt only in the sense that they can be provoked by an arbitrary small change in the composition of solvent.

Swelling and shrinking of gels containing ionizable groups can be induced by augmenting electrostatic swelling forces associated with these ionizable charged groups present on the gel matrix.³⁴ For non-ionic gels like poly(2-hydroxyethyl methacrylate) PHEMA, further swelling beyond equilibrium swelling, has been ascribed to disruption of attractive hydrophobic interactions in the covalently crosslinked gels.³⁵ It seems for the neutralized polyampholyte gels of SSS and VBT initially at lower concentrations of ethanol in the swelling mixtures the hydrophobic forces of attraction between the polymer chains are disrupted, causing further swelling of the gels. But beyond 50% concentration of ethanol the polymer chains are surrounded more by ethanol than water, and the polymer-polymer affinity overtakes the polymer-solvent interaction, resulting in deswelling and the gel collapses.

It was interesting to see that the increase in the swelling ratio due to introduction of ethanol in the

swelling medium at lower concentrations decreased as the crosslink density of the gels increased. Also, the deswelling phenomenon became a gradual process for highly crosslinked gels, unlike an abrupt phenomenon for gels sheerly crosslinked through charge-neutralized bridges. The slower deswelling for comparatively more crosslinked gels may be because of formation of more rigid gel structure due to higher crosslink density, resulting in restriction of polymer chain movements. The pore size of the gels will decrease due to enhanced crosslinking, which may again contribute to hindered outflow of water from the gel. Figure 8 (inset) shows the swelling response of a gel synthesized for two different total doses. The lower swelling in all proportions of water:ethanol indicates that polyampholyte undergoes further crosslinking beyond 5 kGy at least up to a dose of 10 kGy at which low swelling gel was synthesized.

Figure 9 shows swelling of totally neutralized gel, a gel containing excess of SSS and of a gel containing excess of VBT. For all these gels the swelling ratio increased initially and at higher ethanol concentrations all of them deswelled. The deswelling of gels containing excess of SSS was quite abrupt; however, for the gels containing excess of VBT it was more of a gradual phenomenon. The gels containing excess SSS almost shrunk to their initial dry weight; however, the gels containing excess VBT even in pure ethanol held some water. Lower extent of deswelling for gels containing excess VBT confirms strong binding of water in gels containing free trimethyl ammonium groups because of their strong electric field.

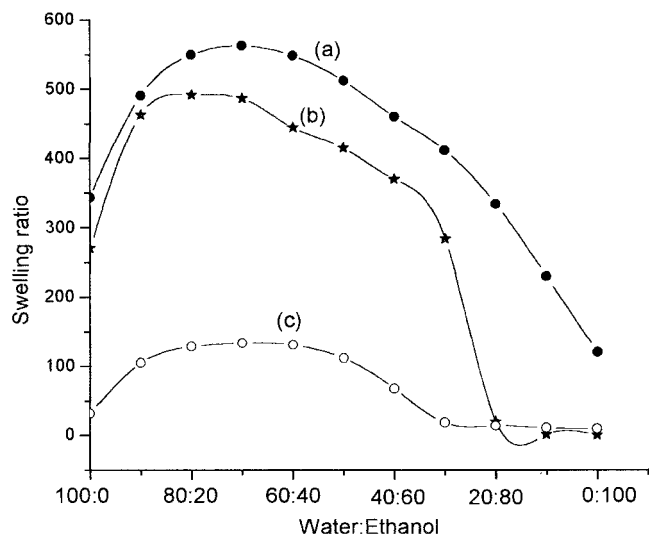


Figure 9 Swelling in water/ethanol mixtures for gel synthesized for total radiation of 5 kGy with 10 mM MBA. (a) [SSS]:[VBT]; 0.5M:1.5M. (b) [SSS]:[VBT]; 1.5M:0.5M. (c) [SSS]:[VBT]; 1.0M:1.0M.

Swelling of polyampholytic gels at different pHs

Swelling of gels containing ionizable groups in their constituent macromolecules is generally a function of pH because the conformation of the polymer changes as they go from the nonionized to ionized state or vice versa.³⁶ Among these ionizable polymers, sulfonates³⁷ and trialkyl ammonium chlorides³⁸ have been re-

ported to be most chemically stable and relatively insensitive to pH. Accordingly, the neutralized polyampholyte gels or those containing excess of SSS or VBT were expected not to be very sensitive to the pH of the medium. Figure 10 shows results of swelling studies for totally neutralized gels crosslinked to different extents. It can be seen that all of them deswelled when the samples swelled to equilibrium were transferred to any of the pH. The deswelling process was also seen for gels containing excess of any of the two monomers in the gel. It seems for these polyampholyte gels the role of ions used to maintain pH is not significant enough to cause ionization or nonionization of units in the gels, but their presence just causes more of the salting out effect due to a concentration gradient in order to equilibrate the concentration of ions inside the gel and outside in the swelling medium. In order to observe whether the ions used for maintaining pH always caused the same deswelling effect, swelling of gels of different compositions were studied at pH ~ 1 maintained by HCl and by HClO₄ per chloric acid. Figure 10 (inset) shows the result of these studies. It can be seen that though the swelling ratio values are different for the pH maintained by HCl and HClO₄, the shape of the profiles are qualitatively similar. From these results it can be concluded that both ions primarily caused the deswelling due to the concentration gradient. The extent of deswelling was different, as the ions in the solution may interact with water inside the gel to different extents.

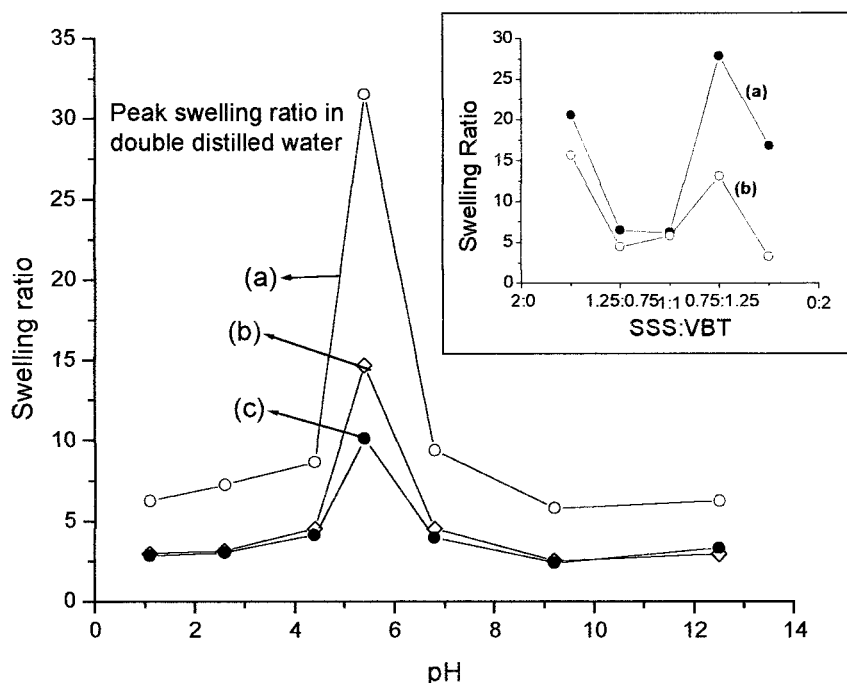


Figure 10 Effect of pH on swelling of [SSS]:[VBT], 1.0M:1.0M, polyampholyte gels: (a) 10 mM MBA, (b) 25 mM MBA, and (c) 50 mM MBA. Inset: Swelling of SSS:VBT polyampholyte gels of different compositions at pH ≈ 1 ; (a) the pH maintained by HCl and (b) the pH maintained by HClO₄.

TABLE V
Effect of Various Solutes on Swelling Behavior

S. no	Matrix composition			Dose (kGy)	Solution	SR ^a	% Change in SR ^b
	SSS (M)	VBT (M)	MBA (mM)				
1	1.5	0.5	10	5	DD Water	147.97	00.00
2	1.5	0.5	10	5	1.5M NaCl	3.74	-97.47
3	1.5	0.5	10	5	0.117M Urea	216.84	+46.54
4	1.5	0.5	10	5	0.5M Glucose	221.05	+49.39
5	1.5	0.5	10	5	0.1% Triton	192.94	+30.39
6	1.0	1.0	10	5	DD Water	31.55	00.00
7	1.0	1.0	10	5	1.5M NaCl	7.53	-76.13
8	1.0	1.0	10	5	0.117M Urea	32.10	+01.74
9	1.0	1.0	10	5	0.5M Glucose	31.55	00.00
10	1.0	1.0	10	5	0.1% Triton	37.60	+19.17
11	1.0	1.0	10	10	DD Water	25.74	00.00
12	1.0	1.0	10	10	1.5M NaCl	6.91	-73.15
13	1.0	1.0	10	10	0.117M Urea	26.20	+01.79
14	1.0	1.0	10	10	0.5M Glucose	25.74	00.00
15	1.0	1.0	10	10	0.1% Triton	27.44	+06.61
16	0.5	1.5	10	5	DD Water	157.21	00.00
17	0.5	1.5	10	5	1.5M NaCl	8.68	-94.48
18	0.5	1.5	10	5	0.117M Urea	212.10	+34.91
19	0.5	1.5	10	5	0.5M Glucose	216.72	+37.85
20	0.5	1.5	10	5	0.1% Triton	223.44	+42.13

^a Swelling ratio.

^b % Change in swelling ratio with respect to swelling ratio in DD water.

Swelling characteristics in presence of additives of biological importance

The swelling behavior of hydrogels like PHEMA is known to be affected by the presence of solutes of biological interest—viz., sodium chloride, urea, and glucose.^{39,40} These results have been explained on the molecular level by proposing the existence of a secondary noncovalent structure based upon hydrophobic interactions between the backbone chains.³⁹ Hydrogels with EWC of around 70% have special significance because of their potential use as extended wear contact lenses, wound dressings, sanitary napkins, and superabsorbent baby napkins. Therefore, the effect of various biologically important additives on SSS-co-VBT polyampholyte gels was investigated. The results are summarized in Table V. It can be seen that NaCl tends to deswell these gels, whereas urea, glucose, and Triton-X tend to further swell the gels. The polyampholyte gels that contain excess of either of the

monomers show significant deswelling in NaCl solution as well as swelling in the presence of other additives. The swelling or deswelling in the presence of these additives was comparatively low for neutral polyampholyte gels. In order to understand how the presence of additives affect the bonded and nonbonded water content, DSC studies of one family of gels swelled/deswelled in these solutions was carried out. Table VI shows the result of these studies. It is clear from the results that NaCl affects the freezable water content of the gel, i.e., its similar to salting out effect of inorganic ions reported earlier for nonionic hydrogels.³⁹ Urea and Triton do not significantly affect the freezable water; however, their presence causes an increase in nonfreezable water. It is well known that urea is able to perturb the hydrophobic attractive interactions in the gels⁴⁰ as a result of their is further uptake of water. It seems when these attractive hydrophobic interactions decrease or diminish, the

TABLE VI
Percentage of Total, Free, and Bound Water Normalized with Respect to Weight of Polyampholytic {[SSS]:[VBT]; 1M: 1M + 10 mM MBA} Gel Synthesized for Total Radiation Dose of 5 kGy

S. no	Solution	EWC (%)	W _f (%)	W _{nf} (%)	W _{nf} /W _f
1.	DD Water	96.83	68.00	28.83	0.424
2.	1.5M NaCl	86.88	29.08	57.80	1.988
3.	0.117M Urea	96.88	62.44	34.44	0.551
4.	0.1% Triton	97.84	60.36	36.98	0.613

W_f: water freezable (free); W_{nf}: water nonfreezable (bound).

polymer chains undergo hydrophobic hydration as explained by earlier workers,⁴¹ resulting in increased nonfreezable bonded water.

CONCLUSION

In summary, our studies show the following for radiation-polymerized polyampholytic gels of SSS and VBT:

1. The copolymer gels containing equal amounts of SSS and VBT demonstrate Fickian swelling.
2. The gels containing excess amounts of SSS show the case II type of diffusion, whereas those containing excess amounts of VBT show anomalous diffusion.
3. For copolymer gels containing excess amounts of either of the monomers, the diffusion rate keeps changing as the swelling progresses to equilibrium.
4. The ratio of the two monomers in the gel affects the equilibrium swelling to a great extent. The gels containing equal amounts of both the monomers swell to a minimum. The swelling extent depends on the type of residual charge on the gel.
5. Crosslinking of the gels decreases the freezable water content but it increases the nonfreezable water content of the gels.
6. The polyampholyte gels undergo abrupt deswelling in water/ethanol mixtures at some critical water/ethanol ratio. The deswelling effect and extent is more pronounced in neutral gels and gels containing excess of SSS.
7. The gels swelled in aqueous medium deswell at all pH in the range 2–12.
8. The presence of additives like NaCl affect the free water in the gels, whereas urea and triton are able to disturb the bonded water content.

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