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Radiation Induced Synthesis of 2-Hydroxyethylmethacrylate-co-Vinylbenzyltrimethylammonium Chloride Binary Hydrogel System-II: Dynamic Swelling Studies

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2-Hydroxyethylmethacrylate-co-vinylbenzyltrimethylammonium chloride (HEMA-co-VBT) hydrogels were synthesized using ^{60}Co gamma radiation. The dynamic swelling of the binary hydrogel system was investigated gravimetrically. The morphology and pore structure of various gels was studied using scanning electron microscopy (SEM). Incorporation of ionic monomer VBT into the HEMA gel matrix resulted in a highly porous structure. Effect of various experimental variables like gel composition, temperature of the swelling medium, ionic strength, presence of biologically important additives (Glucose, Urea), surfactants (Triton-X, 7-Deoxycholic acid) and monovalent anionic dyes acid blue 25 (AB25), acid yellow 99 (AY99) and Congo red (CR) on swelling kinetics of hydrogels has been reported. The dynamic swelling parameters such as swelling exponent (n), diffusion coefficient (D) and mean swelling time (MST) were evaluated and the possible transport mechanism has been suggested. The activation energy for diffusion (E_D) of water into gels was evaluated to be 15-40 kJmole^{-1}.

Keywords gamma radiation, 2-hydroxyethyl methacrylate, vinylbenzyltrimethyl ammonium chloride, hydrogels, dynamic swelling, Fickian, anomalous

Introduction

Hydrogels are three dimensional crosslinked polymer structures, which are able to swell in the aqueous environment without dissolving or losing their structural integrity (1). The network is often formed by covalently crosslinked polymers, but ionic bonds and van der Waals forces can also lead to water swellable materials (2, 3). The water imbibing properties of hydrogels enable them to be employed as a potential device for a great number of applications in biomedical science such as soft contact lenses (4), dialysis

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membranes (5), artificial implants (6), burn dressings (7), drug delivery systems (8), sensors, separation membranes, adsorbents, etc.

The conventional thermo-chemical method, gamma irradiation or electron beam irradiation has been utilized to synthesize binary or tertiary co-polymer hydrogels to combine the desired properties of all the parent components in the form of an interpenetrating polymer network (IPN), grafted matrices or random copolymers gels (9–13). Radiation induced synthesis of hydrogels has several advantages over conventional methods viz. high purity products, easy process control, wide range of temperature of synthesis and possibility of sterilization during synthesis (14–16). The judicious choice of the components of binary hydrogels can lead to hydrogels that exhibit a combination of unique physiochemical properties, thus permitting their wide-range of applications and often exceptional possibilities for practical applications. For radiation-synthesized gels, gel properties may be programmed by the choice of the main polymer that forms the framework and the co-monomer, its content, and the radiation dose (9–13). Poly (2-hydroxyethyl methacrylate) (PHEMA) based gels have been the subject of interest for scientists and technologists because of its versatile properties like biocompatibility, good mechanical strength, high gel fraction, and ease of synthesis. However, low swelling of non-ionic polymer matrix like PHEMA at higher crosslinking extent restricts their applications where high swelling is desired. This problem can be overcome by either functionalization of the base matrix or by co-polymerization with ionic monomers. Apart from the increase in the swelling, introduction of ionic polymers provides stimuli-responsive property against external stimuli like pH, ionic strength, temperature, and electric field, depending on the chemical nature of the ionic polymer (17–20). Ionizable hydrogels have excellent potential as bio-responsive networks because changing the charge density or the nature of the ionic moieties in the polymer and composition of the swelling medium can control the magnitude of their response. Factors affecting the swelling or solute transport through these ionic hydrogels have gained increasing attention as they facilitate better understanding of the relevant parameters (21).

This part of the study describes the detailed investigation carried out on dynamic swelling behavior of cationic copolymer gels obtained by radiation copolymerization of HEMA, a non ionic type of monomer and vinylbenzyltrimethylammonium chloride (VBT), a cationic type of monomer. Dynamic swelling kinetics of hydrogels containing different amounts of VBT was investigated under various experimental conditions and in the presence of different solutes. Equilibrium swelling of these copolymer gels has been recently reported by us as the first part of this study (22).

Experimental

Materials

2-Hydroxyethyl methacrylate (HEMA), mol wt. 130.14 from Aldrich Chemicals (purity $>$ 97%), was further purified by vacuum distillation at 78°C and 5 mmHg pressure. Only the middle 70% of the distillate was collected. Cuprous chloride was added to the distillation flask to inhibit polymerization during distillation.

Vinylbenzyltrimethylammonium chloride (VBT), mol wt. 211.74, purity $>$ 99%, in solid form, from Fluka Chemicals, anionic dyes acid blue 25 (dye content $\sim$ 45%, mol. wt. 416.39), acid yellow 99 (dye content $\sim$ 40%, mol. wt. 496.35) and Congo red (dye content $\sim$ 40%, mol. wt 696.66) from Aldrich were used as received. All other

chemicals used were of AnalaR grade. Double distilled water was used for preparing all solutions and for swelling studies.

Radiation Induced Synthesis of Gels

The monomers HEMA and VBT were mixed in water in various compositions. The solutions were stirred and then filled in glass tubes (inner dia = 2 cm and length = 7–8 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 gamma rays from a ^{60}Co source at a dose rate of 5 kGyh^{-1}. After irradiation, the glass vials were broken to get polymer/copolymer in cylindrical form. The samples were rubbery and transparent at room temperature. 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, if any and 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 and stored in a desiccator for further use. The composition of various gels used for swelling studies is shown in Table 1.

Swelling Measurements

The progress of the swelling process was followed gravimetrically by monitoring the increase in the mass of samples at different time intervals. In a typical swelling experiment, a pre-weighed circular piece of gel was immersed into a definite volume of swelling media, taken out at different time intervals, the surface water was blotted using laboratory tissue paper, weighed and returned to the swelling medium. The swelling ratio (SR) and equilibrium degree of swelling (EDS) of the gels were determined using the following equation:

$$SR = \frac{Ws - Wi}{Wi} \tag{1}$$

$$EDS(\%) = \frac{(Weq - Wi)x100}{Wi} \tag{2}$$

where *Wi*, *Ws*, and *Weq* are the initial weight of dry gel, weight of swelled gel at a particular time, and weight of gel swelled to equilibrium respectively.

Table 1
Composition and properties of HEMA-co-VBT gels synthesized at a dose rate of 5 kGyh^{-1}

S. No.	[VBT] (% Mol)	[HEMA] (% Mol)	Dose (kGy)	EDS (%)
HV0	0	100	6.1	65.24
HV1	9.25	90.75	6.1	669.93
HV2	19.67	80.33	6.1	1809.76
HV3	31.66	68.34	6.1	2824.87
HV4	45.00	55.00	6.1	3440.36
HV5	31.66	68.34	2.5	4068.39

Data Analysis

Alfrey et al. (23) 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 chains.

a. Fickian diffusion, also known as Case I diffusion, occurs when the rate of diffusion (k_d) is significantly slower than the rate of relaxation (k_r) 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 most simple and 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:

$$\frac{M_t}{M_\infty} = kt^n \tag{3}$$

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 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 (24).

Equation 3 is applied to the initial stages of swelling and the plots of $\ln(M_t/M_\infty)$ vs. $\ln(t)$ yield a straight line up to almost a 60% increase in the mass of the hydrogels. The n and k values were obtained from the slope and intercept of the plot, respectively.

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 the 'short time approximation method', which is generally valid only for the first 60% of the swelling. For calculating the diffusion coefficient of water in the hydrogels, the following relation (4) was used (25):

$$\frac{M_t}{M_\infty} = 4(Dt/\pi l^2)^{0.5} \tag{4}$$

Where D is the diffusion coefficient of water (cm^2s^{-1}) and l is thickness of the dry gel. The diffusion coefficient for the initial portion of swelling was calculated from the slope of the M_t/M_∞ vs. $t^{0.5}$ plot. In order to characterize the swelling rate of different water swellable gels, the mean swelling time (MST) was estimated according to the following equation (5) (26):

$$MST = \left(\frac{n}{1+n}\right)k^{-1/n} \tag{5}$$

Where n and k having the same meaning as in power law, Equation (3).

Scanning Electron Microscopy

SEM of the pure HEMA and its copolymer with VBT was carried out using Scanning Electron Microscope VEGA MV2300T/40 (TS 5130 MM) equipment (TESCAN) to understand the inner morphology and pore structure of the gels. The hydrogel samples for SEM were prepared by initially lyophilizing the gel 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 a gold using vapor deposition technique. The gel surfaces were scanned at 2000 magnification.

Results and Discussion

The morphology of gels is shown in Figure 1. 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. It is clear from Figure 1 that pure HEMA had intact architecture with poor porosity. The pore size of the gels increased with an increase in VBT content of the gel and, at higher ionic monomer content, lump structure with highly porous architecture appeared. The copolymer gels with higher ionic monomer content exhibited uneven mass distribution compared to pure HEMA gel. There was significant difference in the inner gel morphology of HV3 and HV5 gels having the same VBT content, but irradiated to a different radiation dose. HV5 gel showed a more porous structure as compared to HV3, higher porosity might be attributed to low cross-linking extent of HV5 as it was exposed to low radiation dose.

The dynamic swelling properties of a polymer include solvent sorption rate, the rate of approach to equilibrium, and the transport mechanism controlling the solvent sorption. The nature of water transport through polymer matrices is important for understanding the transport phenomena of aqueous solute through these matrices. In particular, the release of drugs incorporated into an originally glassy hydrogel depends on the diffusion of water to enhance their mobility within the matrix. The case II transport mechanism desirable for constant release is a rare phenomenon for hydrogels, whereas, anomalous diffusion is commonly encountered in glassy polymers.

Effect of Gel Composition on Dynamic Swelling

As reported in the first part of the study, the EDS of the gels increased with VBT content and radiation dose delivered to gels (22) indicating the swelling extent of ionizable gels is governed by ionic monomer content and crosslinking density of the gel. Swelling kinetics and time dependent swelling behavior of HEMA-co-VBT gels containing different amounts of VBT at 28°C is shown in Figure 2. It can be seen that the swelling ratio and rate of swelling of gel increased with the increase in the VBT content in the gel matrix. In order to have more realistic insight into the effect of ionic monomers, the experimental swelling data was analyzed using the power law (3). The n and k values were obtained from the slope and intercept values of $\ln(M_t/M_i)$ vs. $\ln(t)$ plot, respectively. The dynamic swelling parameters of different HEMA-co-VBT gels in aqueous medium are presented in Table 2. It has been reported that n value for pure poly(HEMA) prepared by different methods under different conditions remain 0.5 (27, 28). For HVD gel also it was found to be 0.5 indicating the diffusion through the gel which does not contain any VBT, is Fickian however, for gel HV1 $n = 0.61$ indicating that the presence

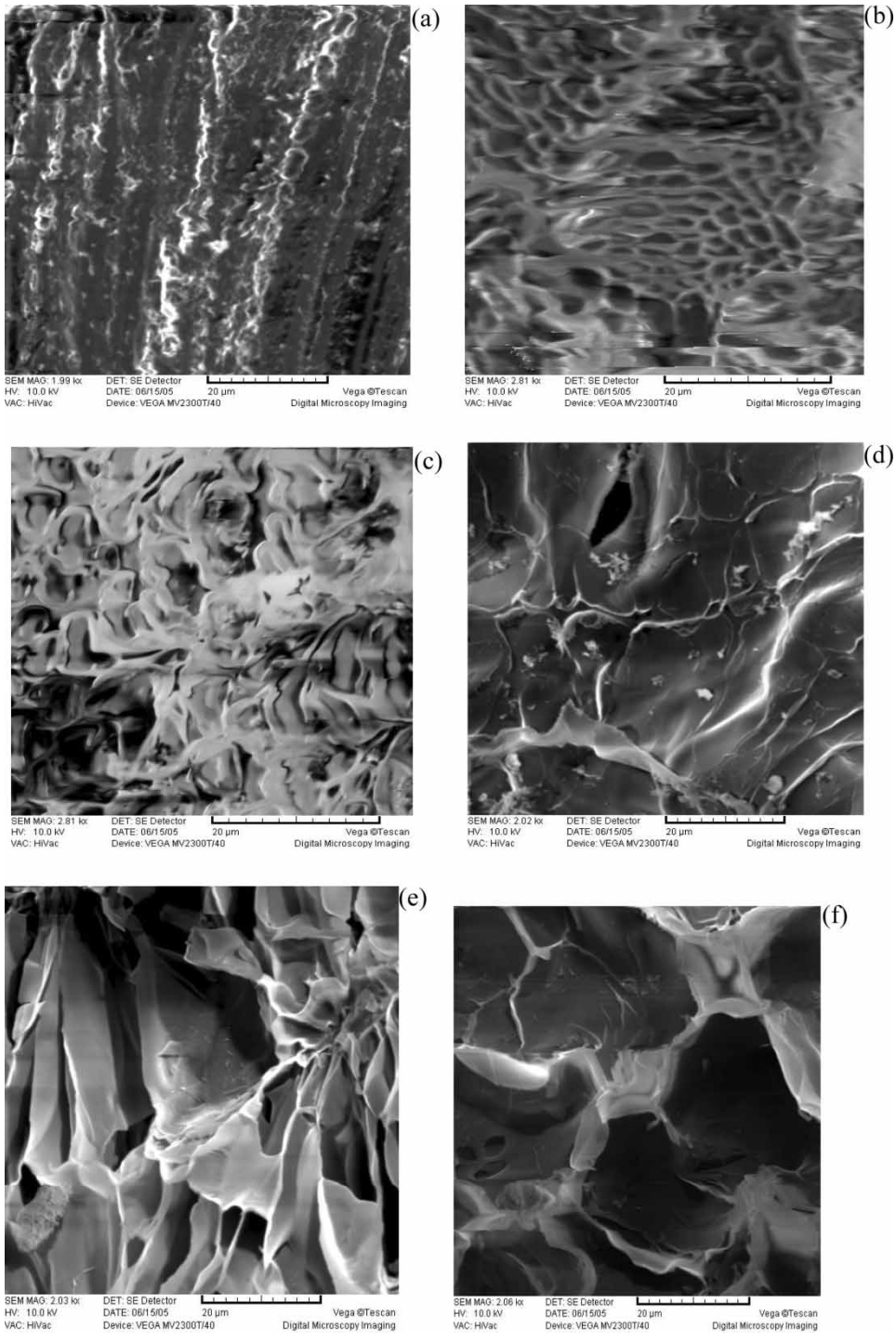

Figure 1. SEM micrographs of (a) HV0, (b) HV1, (c) HV2, (d) HV3, (e) HV4, (f) HV5.

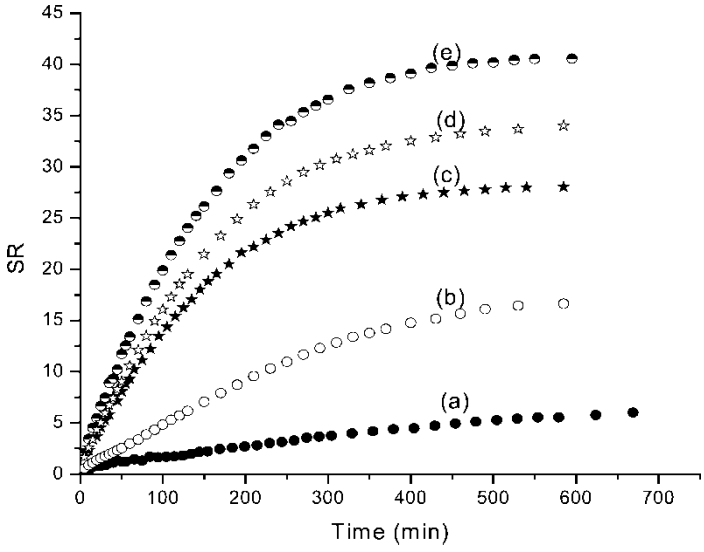

Figure 2. Swelling kinetics of different HEMA-co-VBT gels in double distilled water at 28°C. (a) HV1, (b) HV2, (c) HV3, (d) HV4, (e) HV5.

of VBT even in small amounts in HEMA matrix causes shifting of swelling from Fickian to anomalous. The anomalous diffusion is characterized by the rate of diffusion (k_d) $\approx$ rate of relaxation (k_r), whereas for Fickian diffusion $k_d \ll k_r$. Thus, the presence of VBT either increases k_d to match with k_r or k_r decreases to become comparable to k_d. The first possibility is more likely as k_d may increase because of two reasons: 1) VBT segments present in the matrix on ionization will repel each other to open up the matrix and cause faster diffusion of water into the matrix, and 2) the k_d will also be enhanced due to the increase in concentration gradient of counter ions inside and outside of the gels as reported for several other ionic gels (29, 30). These two factors contribute to an increase in k_d which is supported by the experimentally observed fact that n values further increased with an increase in VBT content for other gels and also by SEM's of the gels.

To further support our observation, the mean swelling time (MST) using Equation (5) and D values were estimated and are given in Table 2 and 3, respectively. MST values

Table 2
Dynamic swelling parameters of HEMA-co-VBT gels in distilled water

	28°C		37°C		50°C	
S. No.	n	MST (h)	n	MST (h)	n	MST (h)
HV1	0.61	5.46	0.74	3.00	0.77	2.10
HV2	0.78	3.87	0.80	2.64	0.85	1.83
HV3	0.74	1.90	0.80	1.78	0.82	1.63
HV4	0.79	1.94	0.81	1.21	0.76	1.18
HV5	0.77	1.84	0.89	1.65	0.85	1.24

Table 3
D and E_D values for different gels at different temperatures

	D (cm^2s^{-1}) × 10^7			
S. No.	28°C	37°C	50°C	E_D (kJ/mole)
HV1	2.6	5.4	7.6	38.43
HV2	4.3	5.9	9.6	29.60
HV3	4.8	7.5	9.9	26.10
HV4	5.5	8.4	10.4	22.86
HV5	10.1	11.6	16.0	17.10

decreased and *D* values increased monotonously with the amount of VBT in the gel, once again confirming that the presence of VBT in the HEMA matrix facilitates the diffusion process. It has been reported that the transport mechanism is related to the SR of gel. Transport mechanism tends to shift from Fickian to non-Fickian after a certain threshold value of SR for a hydrogel (31).

Effect of Temperature on Swelling Kinetics

Swelling kinetics of HEMA-co-VBT gels at 28°C, 37°C, and 50°C are plotted in Figures 2, 3, and 4, respectively. The dynamic swelling parameters (n and MST) of these gels at different temperatures are given in Table 2. The extent of swelling did not change significantly with temperature. However, the *n* values increased marginally but to the extent that the diffusion remained anomalous. Presumably, due to increased kinetic energy of the water molecules at higher temperature, they are more mobile and their faster diffusion

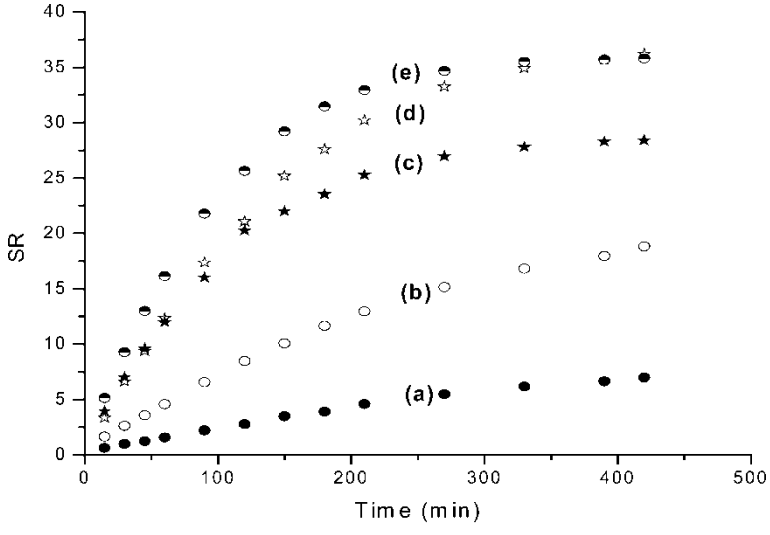

Figure 3. Swelling kinetics of different HEMA-co-VBT gels in double distilled water at 37°C. (a) HV1, (b) HV2, (c) HV3, (d) HV4, (e) HV5.

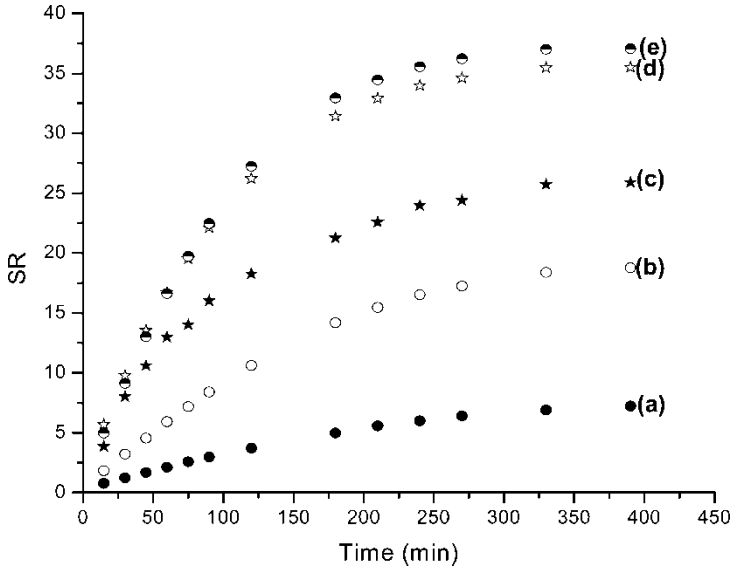

Figure 4. Swelling kinetics of different HEMA-co-VBT gels in distilled water at 50°C. (a) HV1, (b) HV2, (c) HV3,(d) HV4, (e) HV5.

into the gels causes a further increase in the rate of diffusion which decreases mean swelling time (MST) of different gels (Table 2).

The enhancement in k_d values with an increase in temperature was also obvious from the maximum shift of n value of most loosely crosslinked gel HV5.

At much higher temperatures, when $k_d \gg k_r$ n value may become 1, i.e., it will be relaxation controlled diffusion. Figure 5 shows diffusion plot (M_t/M_∞ vs $t^{0.5}$) for HV5 gel swelled in water at different temperatures. D value estimated from these plots for different gels are tabulated in Table 3. The values indicated that D values increased with the temperature and therefore, the Arrhenius equation can be used to estimate the activation energy of diffusion for gels. The Arrhenius equation in modified form Equation (6) was applied to the experimental data to estimate the activation energy for the diffusion of water through hydrogel matrices as reported earlier (32).

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \tag{6}$$

where E_D is the apparent activation energy for the diffusion process.

Figure 6 represents the plot of ln (D) against the 1/T plot for different HEMA-co-VBT gels and the E_D values estimated for different gel are given in Table 3. It was found that the E_D value decreased with the increase in VBT content in the HEMA gel matrix. The interesting point here was that the E_D value for HV5 was the lowest one due to low crosslinking extent. It clearly indicates that the incorporation of ionic monomer into a non-ionic gel matrix facilitates its rate of swelling in aqueous medium.

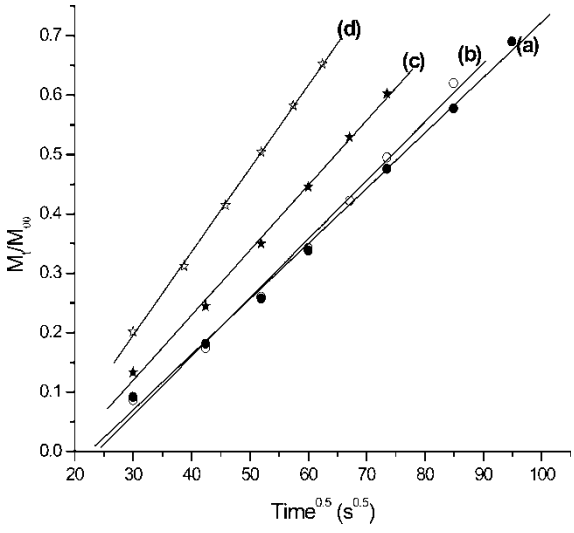

Figure 5. M_t/M_i vs. $t^{0.5}$ plot for HV5 gel at different swelling temperatures. (a) 28°C, (b) 37°C, (c) 50°C, (d) 60°C.

Effect of Electrolytes

To understand the swelling of polyelectrolyte hydrogels like PHEMA-co-VBT within the framework of the 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), deformation of network chains to a more elongated state(el), non-uniform distribution of mobile counter ions between the gel and the external solution(ion) and to osmotic swelling pressures caused due to changes in the electrostatic interactions (elect) of ionized

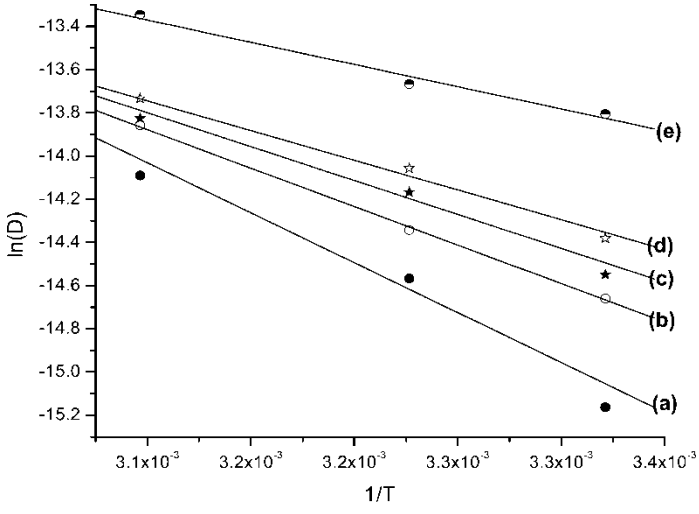

Figure 6. Plot of ln(D) against $1/T$ plot for different HEMA-co-VBT gels in double distilled water. (a) HV1, (b) HV2, (c) HV3, (d) HV4, (e) HV5.

groups upon swelling (33).

$$\pi = \pi_{\text{mix}} + \pi_{\text{el}} + \pi_{\text{ion}} + \pi_{\text{elect}} \tag{7}$$

For a non-ionic gel like PHEMA in equilibrium with the solvent, π_{ion} and π_{elect} component of pressure do not contribute. However, for polyelectrolyte hydrogels, the two-pressure terms π_{ion} and π_{elect} contribute significantly and control the swelling of the gels to a greater extent. The Donnan equilibrium theory evaluates the osmotic pressure π_{ion} of the hydrogel system by the following Equation (8) (34, 35):

$$\pi_{\text{ion}} = RT \sum_i (C_i^g - C_i^s) \tag{8}$$

where, C_i is the mobile ion concentration of species i, g, and s represent the gel and solution, respectively. This equation indicates that the greater the difference between the ionic concentration inside the gel and in the external solution, the larger the swelling. The concentration inside the gel is typically much higher than the external solution, so π_{ions} is quite high. As a result, water flows into the gel to dilute the ion concentration, causing the gel to swell. As the contribution due to π_{ions} is significant in the extent of swelling of polyelectrolyte gels, the volume of such gels can change sharply with a change in the pH or ionic strength of the surroundings. Figure 7 shows swelling kinetics of HV5 gel in NaCl solution of different concentrations at 28°C.

The swelling extent of gel decreased with the increase in the NaCl concentration. In the absence of NaCl electrolyte in the aqueous medium, π_{ion} is much higher due the a large difference in the ion concentration inside the gel and external solution. When NaCl is added to the swelling medium, the ionic concentration in the medium C_i^s increases, which decreases the ionic concentration gradient ($C_i^g - C_i^s$) and eventually decreases the π_{ions} pressure term, resulting in lower swelling ratios. Also, the salt ions in the swelling medium cause the screening of the repulsive electrostatic interactions between ionized groups on the polymer chains and reduces the π_{elect} pressure term, resulting in

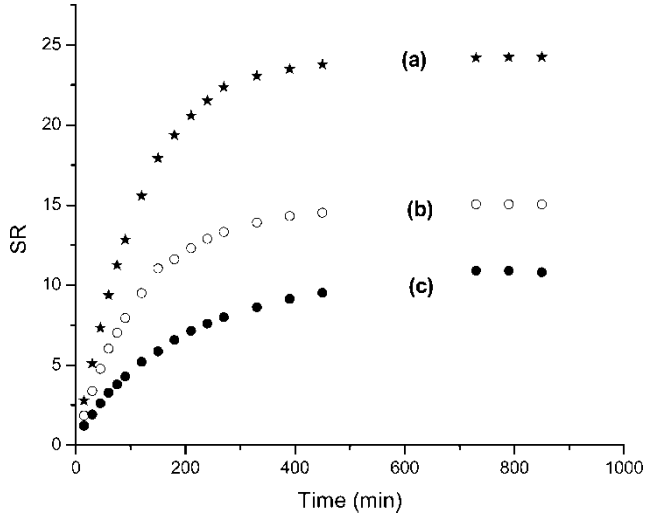

Figure 7. Swelling kinetics of HEMA-co-VBT gel (HV5) in aqueous medium with different NaCl concentration (a) 0.01 M, (b) 0.05 M, (c) 0.1 M.

Table 4
Dynamic swelling parameters of HEMA-co-VBT gel (HV5) in different presence of solutes and dyes

Solutes	n	MST (h)	D (cm^2s^{-1}) $\times 10^7$
NaCl (0.01 N)	0.86	1.41	9.7
NaCl (0.05 N)	0.79	1.47	9.2
NaCl (0.1 N)	0.69	2.43	4.7
Glucose (0.5M)	0.80	2.27	4.9
Triton-X (0.1%)	0.82	2.21	5.0
Urea (0.2M)	0.85	1.41	8.7
DOCA (0.1%)	0.87	1.04	11.9
		Dyes	
AB25 (500 ppm)	0.57	4.73	1.9
CR (500 ppm)	0.78	2.35	5.9
AY99 (500 ppm)	0.73	1.92	6.4

coiling of the polymer chains reflected as a decrease in swelling of the gel. Table 4 gives the n, MST, and D values calculated from experimental data on swelling in the NaCl solution. The n and D values decreased from 0.86 to 0.69 and 9.7×10^{-7} to $4.7 \times 10^{-7}\,cm^2s^{-1}$, respectively and the MST values increased from 1.42 to 2.43 h with an increase in concentration of NaCl. The decrease in n value suggests that the transport mechanism tends to shift from anomalous to Fickian with an increase in NaCl concentration. This may be attributed to the fact that the presence of NaCl screens the repulsive forces between the ionic groups on VBT, which causes comparatively less swelling of the gel and allows the gel to behave like non-ionic gel {like pure poly(HEMA), $n = 0.5$}. The slow diffusion through the gel, which is not so highly swelled, may be due to its closed pores in a shrunken state through which water diffusion into the gel matrix is comparatively difficult. Same explanation can be extended for reduction in D values and increase in MST values.

Figure 8 shows the swelling–deswelling of the gel HV5 when it was allowed to undergo cyclic swelling-shrinking by transferring to water and 0.1 N NaCl solution. It was found that the swelling of gel in water was slower as compared to shrinking in the 0.1 N NaCl solution. The slow swelling may be due to closed pores of the gel in shrunken state through which water diffusion into the gel matrix is comparatively difficult, whereas in the swelled state the pores are wide open through which water can flow out easily. Also, it has to be mentioned that the changes in the swelling ratio here were not rapid in terms of time, they are only abrupt in the sense that they could be provoked in the presence of NaCl in the medium. Thus, the overall swelling-deswelling cycle for gels becomes slow, but for practical application, the swelling-deswelling cycle should be sufficiently fast.

Since our studies revealed that swelling rates of gels increased with temperature, therefore, to decrease the time for swelling-deswelling cycle, the swelling was carried out at elevated temperature (60°C) and deswelling in 0.1 M NaCl at 28°C. Figure 9 shows swelling-deswelling cycle of HV5 gel in water-NaCl solution, when the swelling was carried out at different temperatures and deswelling at the same temperature in the presence of NaCl in the medium. It is clear from the figure that time for swelling cycle could be halved when swelling was carried out at 60°C instead of 28°C.

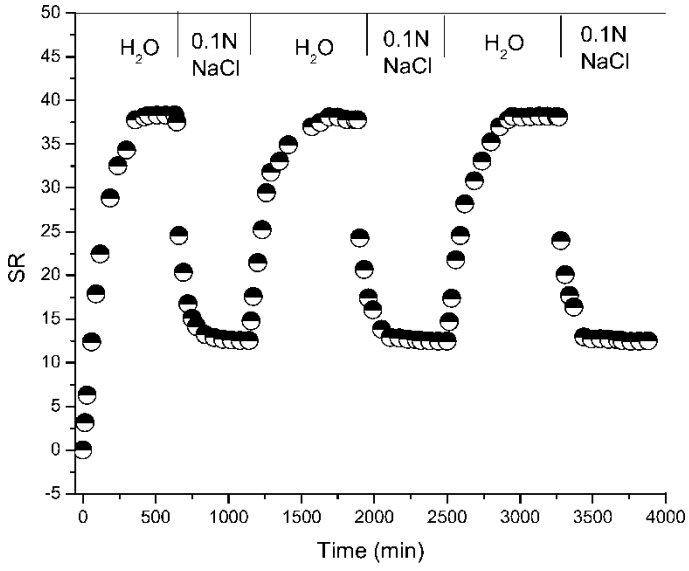

Figure 8. Cyclic swelling-deswelling of hydrogel HV5 in water-NaCl solution.

Effect of Co-solutes

The swelling behavior of hydrogels like PHEMA, HEMA-co-AA(17), HEMA-co-SSS (18), HEMA-co-NVP(27), and polyampholytic SSS-co-VBT gels (36) are known to be affected by the presence of solutes of biological interest viz. NaCl, urea and glucose.

For practical applications, equilibrium swelling and swelling kinetics of hydrogel has to be investigated in different swelling mediums. The equilibrium swelling study of

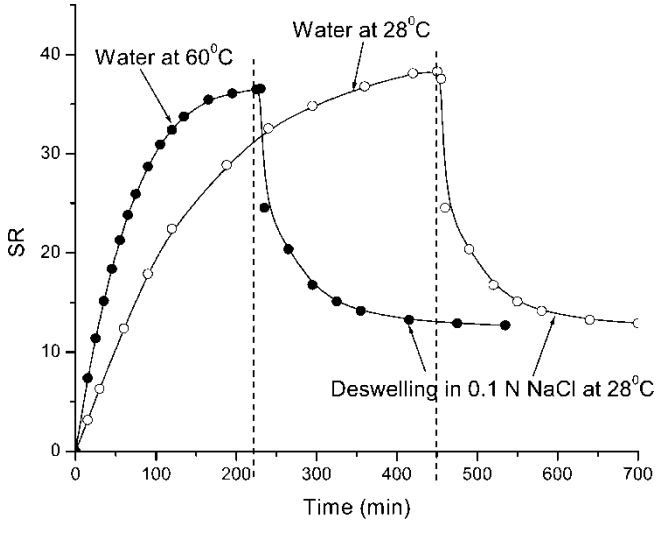

Figure 9. Effect of swelling temperature on the time of swelling-deswelling cycle of hydrogel HV5 in a water NaCl solution.

HEMA-co-VBT gels in different swelling environments has already been reported in an earlier part of our work (22). Therefore, the effect of some of the biologically important additives (glucose, urea) and other additives like Triton-X and 7-Deoxycholic acid on the swelling kinetics and swelling mechanism of HEMA-co-VBT gels was investigated. The swelling kinetics of HV5 gel in the presence of various solutes is shown in Figure 10.

Comparing the swelling kinetics profile clearly indicates that the rate of swelling of the gel is slowest in the presence of glucose in the swelling medium. When other kinetic parameters (given in Table 4) were estimated for these gels from dynamic swelling data obtained, it was also found that n values indicated anomalous diffusion in the presence of these solutes. The D values were found to follow the order DOCA > Water > Urea > Triton-X > Glucose indicating diffusion increased only in the presence of DOCA. We reported that the swelling extent (22) is in order Triton-X > Water > Glucose > Urea > DOCA due to charge neutralization of VBT of the gels. It seems though the charge neutralization causes a decrease in the extent of swelling, the adsorption of DOCA on gel matrix results in a more porous rigid structure through which the diffusion is much faster.

Swelling in Dye Solutions

Polyelectrolyte gels of VBT, due to their anion exchange capability, can act as an effective anion exchange vehicle for the anionic dyes. As pure VBT gels, because of their very high water uptake capacity, have poor strength and dimensional stability, HEMA-co-VBT gels with good swelling ratio and physical strength, were investigated for swelling kinetics in anionic dye solutions namely, AB25, AY99, and CR. In order to investigate the swelling kinetics of HV5 gel in different dye solutions, the pre-weighed gel sample was immersed in definite volume of dye solution of 500 ppm concentration and allowed to swell. Figure 11 shows the swelling kinetics of gels in dye solutions. Although the swelling

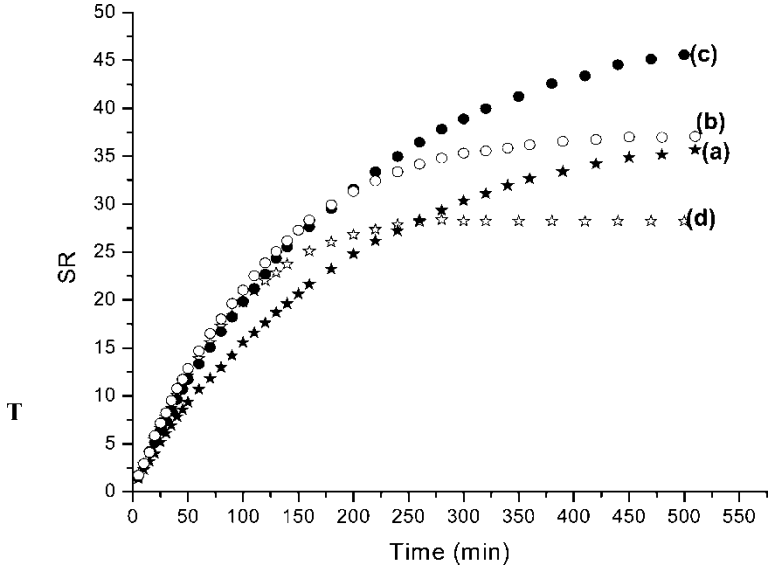

Figure 10. Swelling kinetics of HEMA-co-VBT gel (HV5) in aqueous medium containing different additives (a) Glucose, (b) Urea, (c) Triton-X, (d) 7-Deoxycholic acid.

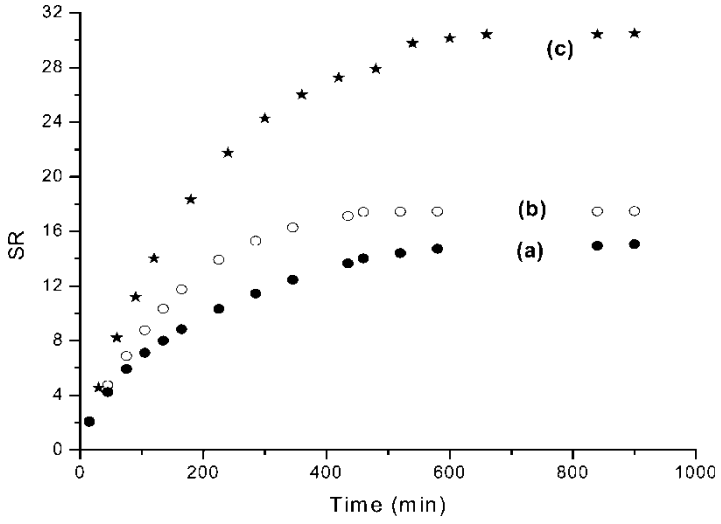

Figure 11. Swelling kinetics of HEMA-co-VBT gel (HV5) in aqueous medium containing different mono-valent anionic dyes (a) AB25, (b) AY99, (c) CR.

extent of gel in dye solutions are in the order CR > AY99 > AB25, the D values were found to follow the order AY99> CR > AB25. Dynamic swelling kinetic parameters for these gels are tabulated in Table 4.

Conclusions

High energy gamma radiation can be effectively used to synthesize HEMA-co-VBT hydrogels of good swelling extent and mechanical strength. Dynamic swelling studies and SEM studies confirm that introduction of VBT increases the rate of diffusion of water into the medium. The increase in k_d leads to k_d becoming comparable to k_r, as a result, the diffusion mechanism for pure poly(HEMA) matrix shifts from Fickian to anomalous for HEMA-co-VBT gels. The swelling kinetics of HEMA-co-VBT gels was a function of gel composition, temperature of swelling medium, type and concentration of solute in swelling medium. A combination of higher temperature and suitable solute was demonstrated to reduce the time of swelling-deswelling cycle. It was found that the higher the extent of swelling of gels, the greater the possibility of swelling being anomalous.

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