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Buffer transport in hydroxyethyl methacrylate copolymer irradiated by γ-rays

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Abstract

The transport of buffer solutions (pH 4.1–7.2) in hydroxyethyl methacrylate copolymer (HEMA) is investigated. The diffusion coefficient of Case I transport, the velocity of Case II transport and the activation energy of the transport process in non-irradiated HEMA are determined. The buffer transport in HEMA copolymers irradiated by γ-rays in vacuum and in air is also studied. After irradiation, the data of mass gain at the short times and long times are designated as stages 1 and 2, respectively. The first stage is followed in Case I transport when the specimen is irradiated in vacuum and the anomalous transport when irradiated in air. The second stage, regardless of the irradiation atmosphere is followed in Case II transport. The equilibrium swelling ratio of irradiated specimens increases significantly when the pH value is greater than 5. A volume transition is observed at high γ-ray doses. The effect of γ-ray irradiation on the functional groups in the polymer is investigated using the infrared spectra. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Buffer; γ-Ray; Hydroxyethyl methacrylate

1. Introduction

The swelling behavior of hydrogels in a buffer solution is related to the transport of ions. Because of the electrostatic force, the ions in the buffer are fixed around the polymer chains to keep the charge neutral so that a Donnan potential is built-up. The swelling behavior of an ionizable polymer in a buffer has been studied extensively [1–4]. The extent of swelling of the polymers with an amino group increases with the decrease in pH value of solvent because the protonated amino group in an acid solution causes the destruction of the hydrogen bond between the polymer chains [5,6]. The swelling of the polymer with a carboxyl group increases with the pH value of the solvent [5,6]. The reason is that the production of the ionized carboxyl group in a basic solution corresponds to the reduction of hydrogen bond in the polymer network. Polymers containing both anions and cations collapse in a neutral pH solution and swell in either acidic or basic solution. Tanaka [7] analyzed the swelling behavior of hydrogels using the Flory theory [8], but his prediction was incorrect. The Donnan swelling theory introduced the electrostatic force to predict the relationship between the extent of swelling and pH value of the buffer [9–11].

The hydroxyethyl methacrylate copolymer (HEMA) is one of the most useful bio-materials because of the advantages of high water content and excellent bio-compatibility [12–15]. Chou et al. [16,17] showed that the water transport in an irradiated HEMA copolymer is in excellent agreement with the one-dimension model proposed by Harmon et al. [18,19]. The Harmon model accounts for Case I transport which is controlled by the Fickian diffusion, Case II transport due to the stress relaxation, and anomalous transport which is a mixture of Case I and Case II transport. It has been successfully applied to many solvent–polymer systems [20–22]. In this paper, we attempt to use this model to analyze the buffer transport in non-irradiated and irradiated HEMA.

The swelling equilibrium of hydrogel is determined by the balance of the chemical potential between the polymer and solvent, the net osmotic pressure resulting from the mobile counter-ions surrounding the fixed charge groups and the elastic force of the network [23,24]. The γ-ray irradiation induces the crosslinking or scission of polymer chains and the ionization of the functional groups [25,26]. It leads to a change in osmotic pressure between the buffer, at various pH values, and the polymer

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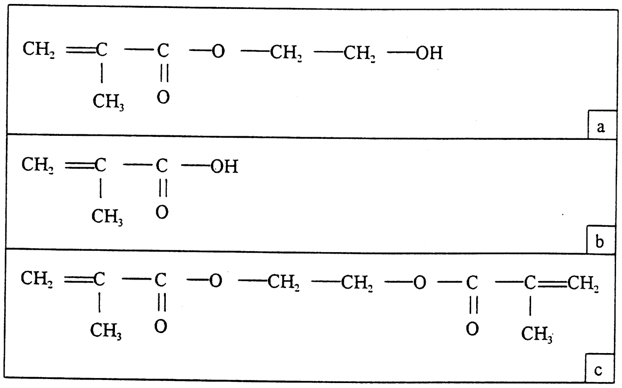

Fig. 1. The chemical structure of: (a) HEMA; (b) MAA; and (c) EDGMA.

and results in changes in the mass transport behavior. It prompted us to analyze the buffer transport in the irradiated HEMA copolymer.

2. Materials and methods

The soft contact lens blanks made of the HEMA copolymer were obtained from the Canadian Contact Lens Laboratories Ltd., Montreal, Quebec, Canada. The chemical compositions of HEMA copolymer as shown in Fig. 1 consist of HEMA, ethylene glycol dimethacrylate (EGDMA), and methacrylic acid (MAA). The blank was 12.8 mm in diameter and 6.0 mm in thickness. They were mounted on a bench lathe and thinned to 1.5 mm. The specimens were ground on 600 and 1200 grit emery papers and then polished with 1.0 and 0.05 μm aluminum slurries until the thickness reached 1.44 mm. They were annealed in vacuum for one week at 60°C and furnace cooled to 25°C. The purpose of annealing was to relax the residual stress in the specimen induced by machining.

Two sets of specimens were irradiated in air and in vacuum, at 25°C by a 30,000 Ci cobalt-60 source at the Isotope Center of the National Tsing Hua University with a dose rate of 35.9 kGy/h. The specimens were exposed for different periods to reach doses of 100, 200, 300 and 400 kGy. The buffer solution was prepared by mixing the citric acid anhydrous obtained from Tedia Company, Ohio, USA, and sodium phosphate dibasic anhydrous obtained from the Showa Chemicals Inc., Tokyo, Japan, with water. Different contents of citric acid with sodium phosphate were used to produce the buffers of pH 4.1, 5.6, 6.5, 7.1. A Jenco Electronics digital pH meter was used to measure the pH values of the buffers.

For the absorption study, the specimen was pre-weighed and pre-heated to the elevated temperature in the buffer transport study. Then the specimen was immersed in a buffer-filled glass bottle in a thermostatted water bath kept at the same temperature. The specimen was removed from the water bath for measurement of its weight. Its surfaces were blotted and its mass was measured using an Ohaus Analytical Plus digital balance. After weighing, the specimen was immediately returned to the water bath for the next measurement. This process was repeated until the mass was saturated.

The infrared (IR) spectra of the non-irradiated and irradiated specimens were measured by a Bomen DA 8.3 FTIR spectrometer. The non-irradiated specimen and irradiated specimen with dose 400 kGy were ground and mixed with the KBr powder, and then punched into a disk for the IR spectrum test.

3. Results and discussion

3.1. Buffer transport in non-irradiated HEMA copolymer

The transport data of various buffer solutions in non-irradiated HEMA copolymer at 35–55°C are shown in Fig. 2(a)–(d). These data were analyzed by the one-dimensional Harmon model [18], which considers a specimen of half thickness ℓ immersed in a solvent bath. At the initial time, the specimen is solvent-free and the concentration of solvent is constant at all times on both the outer surfaces. The weight gain of solvent uptake at time t, M_t, based on the one-dimensional model is rewritten as [18]

$$\frac{M_t}{M_\infty} = 1 - 2\sum_{n=1}^{\infty} \frac{\lambda_n^2\left[1 - 2\cos\lambda_n \exp\left(-\frac{v\ell}{2D}\right)\right]}{\beta_n^4\left(1 - \frac{2D}{v\ell}\cos^2\lambda_n\right)} \times \exp\left(-\frac{\beta_n^2 Dt}{\ell^2}\right), \quad (1)$$

where

$$\beta_n^2 = \frac{v^2\ell^2}{4D^2} + \lambda_n^2, \quad (2)$$

$$\lambda_n = \frac{v\ell}{2D}\tan\lambda_n. \quad (3)$$

M_∞ is the final equilibrium-swelling ratio of solvent, D the diffusion coefficient of Case I transport, v the velocity of Case II transport, and ℓ the half thickness of the specimen. The roots of Eq. (3) (λ_n with $n = 1, 2, 3, \ldots,$) were used in Eqs. (1) and (2). If v is equal to zero, Eqs. (2) and (3) are reduced to $\beta_n = \lambda_n$ and $\lambda_n = (n + 1/2)$, respectively. Then Eq. (1) becomes

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=1}^{\infty} \frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2\pi^2 Dt}{4\ell^2}\right). \quad (4)$$

Eq. (4) is the pure Case I transport. On the other hand, when D is assumed to be zeroing, the weight gain of the

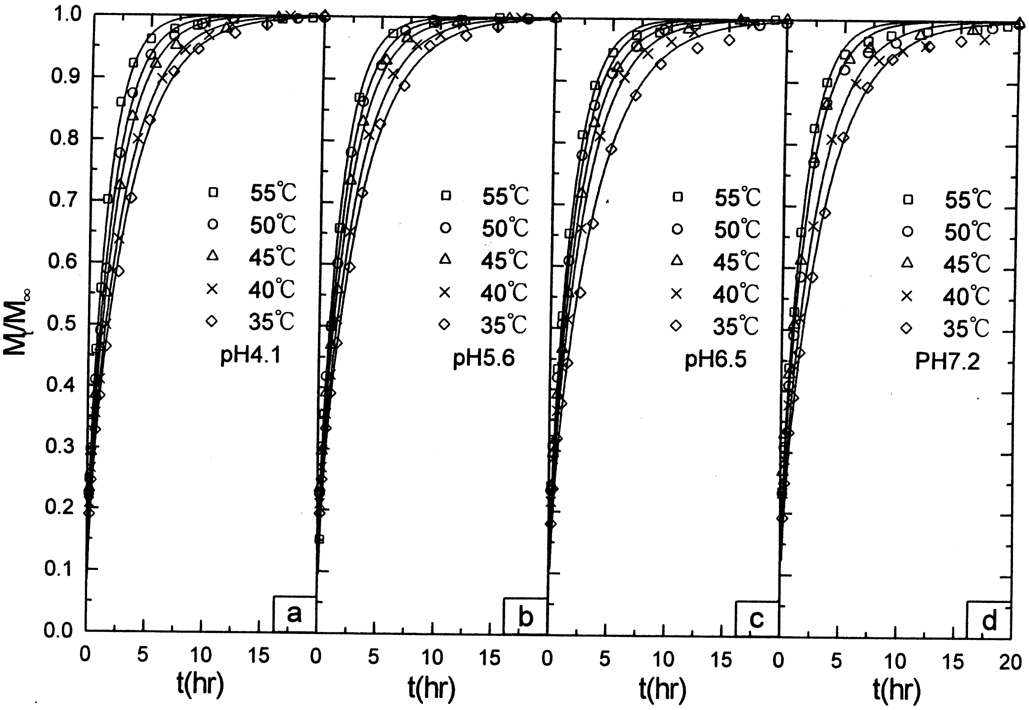

Fig. 2. Buffer sorption in the non-irradiated HEMA copolymer: (a) pH = 4.1; (b) pH = 5.6; (c) pH = 6.5; and (d) pH = 7.2.

solvent can be directly written from Eq. (1) as

$$\frac{M_t}{M_\infty} = \frac{|v|t}{\ell}, \tag{5}$$

in which t is less than $\ell/|v|$. Note that Eq. (5) can also be reduced from Eq. (1) with tedious calculation. Eq. (5) is the pure Case II transport.

The solid lines in Fig. 2 are curve-fitted based on Eq. (1). It is found that the experimental data are in excellent agreement with the theoretical model. The diffusion coefficient (D) of Case I transport and velocity (v) of Case II transport obtained from the curve fitting are listed in Table 1. The values of D and v increase with increasing temperature. The diffusion coefficient and velocity are found to satisfy the Arrhenius equation. Thus the activation energies of Case I (E_D) and Case II (E_v) transport were calculated for various buffer solutions and are tabulated in Table 2. The values of v and E_v decrease with increasing pH value. The values of D and E_D decrease to a minimum at pH 6.5 and then increase with increasing pH value. The pH effect on diffusion coefficient is caused by the change in the chemical potential difference between the solvent and HEMA copolymer, while the change of velocity is related to the swelling extent (or osmotic pressure).

The equilibrium swelling ratio (S) for the buffer absorbed by the specimen was determined by the weight ratio of saturated buffer content to the dry polymer. The value of S decreases with increasing temperature so that the transport process is exothermic. The heat of mixing (ΔH) was obtained by the van't Hoff plot and is listed in Table 2. The heat of mixing increases with increasing pH value of the buffer.

3.2. Buffer transport in HEMA copolymer irradiated in vacuum

The absorption study was operated at 40°C and the HEMA is irradiated in vacuum at room temperature. The data of the buffer transport in irradiated HEMA copolymer are shown in Fig. 3(a)–(c). When the dose is as high as 400 kGy, the specimen is subjected to serious damage and uptake is very hard to process. For pH = 4.1, the curves can be fitted using Eq. (4) where values of D are 2.55×10^{-7}, 2.65×10^{-7}, and 2.80×10^{-7} cm^2/s for $\phi = 100$, 200 and 300 kGy, respectively. That is, the mass transport is the pure Case I and diffusion coefficient increases with the increase of dose. However, most data (pH $\geq$ 5.6) in Fig. 3 are very complicated and difficult to analyze using Eq. (1) with single D and v. When the immersion period increases, the mass transport in specimen irradiated in vacuum changes from the pure Case I to pure Case II via anomalous transport. Therefore, we only analyze the data at the short times (stage 1) and long times (stage 2). From the curve fitting, we found that the first stage of the transport process matched with pure Case I transport (or fit with Eq. (4)), and the second stage was followed by pure Case II transport (or fit with Eq. (5)). The diffusion coefficient at stage 1 and the velocity at stage 2 are tabulated in Table 3. The diffusion coefficient at stage 1 decreases with increasing pH value for

Table 1
The diffusion coefficient of Case I transport (*D*), velocity of Case II transport (*v*) and equilibrium swelling ratio (*S*) of buffer in non-irradiated HEMA copolymer

T (K)	pH value	*D* (10^{-7} cm^2/s)	*v* (10^{-6} cm/s)	*S* (wt%)
328	4.1	2.70	2.90	47.90±0.20
	5.6	2.60	2.85	47.00±0.18
	6.5	2.50	2.72	46.06±0.19
	7.2	2.70	2.55	43.41±0.15
323	4.1	2.30	2.50	48.48±0.17
	5.6	2.25	2.45	47.57±0.19
	6.5	2.20	2.33	46.81±0.14
	7.2	2.35	2.20	44.44±0.17
318	4.1	1.90	2.10	49.03±0.18
	5.6	1.88	2.05	48.30±0.20
	6.5	1.85	2.00	47.35±0.17
	7.2	2.00	1.90	45.16±0.21
313	4.1	1.60	1.70	50.17±0.20
	5.6	1.60	1.70	49.05±0.21
	6.5	1.60	1.65	47.90±0.18
	7.2	1.63	1.55	45.58±0.16
308	4.1	1.38	1.43	50.75±0.18
	5.6	1.36	1.40	49.90±0.15
	6.5	1.34	1.35	49.08±0.17
	7.2	1.40	1.30	46.31±0.18

a given dose, and the velocity at stage 2 increases with increasing pH value and dose. The relationship between *D* and the irradiation dose for the buffer of pH 4.1 is different from that for the buffer of pH 5.6–7.2. The value of *D* increases with the increase of dose for the buffer of pH 4.1, but the trend is opposite for the buffer of pH 5.6–7.2. It implies that the interaction of the γ-ray with functional groups of HEMA raises the chemical potential difference between acidic buffer and polymer matrix. However, the basic component in the buffer of pH value 5.6–7.2 reacts with the fixed acidic group of the polymer and results in a reduction of the diffusion coefficient. This effect was enhanced with increasing dose.

Table 2
The activation energies of Case I transport (E_D), Case II transport (E_v) and the heat of mixing (ΔH) of buffer in non-irradiated HEMA copolymer

	Buffer			
	pH4.1	pH5.6	pH6.5	pH7.2
E_D (kcal/mol)	6.84±0.12	6.57±0.14	6.29±0.17	6.74±0.15
E_v (kcal/mol)	7.27±0.13	7.23±0.15	7.08±0.16	6.87±0.18
ΔH (kcal/mol)	0.61±0.08	0.61±0.06	0.61±0.07	0.62±0.06

3.3. Buffer transport in HEMA copolymer irradiated in air

The uptake measurement was made at 40°C and HEMA copolymer was irradiated in air at room temperature. The data of buffer transport in irradiated HEMA copolymer are shown in Fig. 4(a)–(d). The data for pH = 4.1 fit well with Eq. (1) with single *D* and *v*. That is, the mass transport is anomalous. When pH is greater than 5.6, the data are complicated and difficult to analyze using Eq. (1) with single *D* and *v*. The buffer transport in the specimen irradiated in air is changed from the anomalous transport to Case

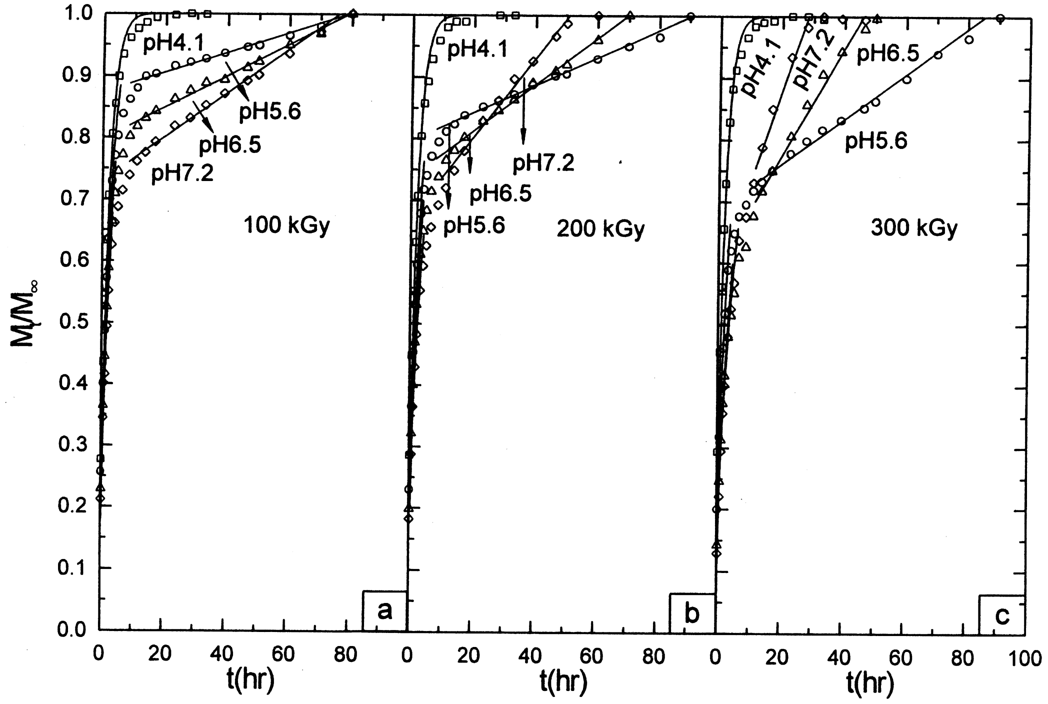

Fig. 3. Buffer sorption in HEMA copolymer irradiated by γ-ray in vacuum at 40°C: (a) $\phi = 100$ kGy; (b) 200 kGy; and (c) 300 kGy.

Table 3
The diffusion coefficient of Case I transport (*D*) and velocity of Case II transport (*v*) of buffer in HEMA irradiated in vacuum copolymer at 40°C. Note that ϕ denotes dose

ϕ (kGy)	pH	Stage	*D* (10^{-7} cm^2/s)	*v* (10^{-7} cm/s)
100	4.1	1	2.55	0
	5.6	1	1.98	0
		2	0	0.31
	6.5	1	1.75	0
		2	0	0.49
	7.2	1	1.4	0
		2	0	0.71
200	4.1	1	2.65	0
	5.6	1	1.70	0
		2	0	0.45
	6.5	1	1.45	0
		2	0	0.75
	7.2	1	1.10	0
		2	0	1.22
300	4.1	1	2.80	0
	5.6	1	1.35	0
		2	0	0.69
	6.5	1	0.85	0
		2	0	1.70
	7.2	1	0.83	0
		2	0	2.95

II transport while the immersion duration increases. Therefore, we only analyze those data at the short times (stage 1) and long times (stage 2). During stage 1, the buffer transport in the specimen irradiated in air is the anomalous transport (fit with Eq. (1)) which is similar to that in the non-irradiated specimen, but it is towards Case I transport (fit with Eq. (4)) at a high dose and high pH value which occurs in the specimen irradiated in air. Because the oxygen exists in air but not in vacuum, the chain session due to γ-ray irradiation is more serious in vacuum than in air [16,17]. Compared to the transport of the specimens irradiated in vacuum, the diffusion coefficient for the specimen irradiated in air was smaller. This effect is pronounced for low pH values and low irradiation doses. During stage 2, the transport behavior switched to Case II transport (fit with Eq. (5)). The data of *D* and *v* for each stage obtained from curve fitting are listed in Table 4. The effect of pH value on *D* and *v* of specimens irradiated in air is different from that in vacuum because of the oxidation of free radicals and ionic groups in air. The further swelling at stage 2 is induced by the transfer and exchange of ions caused by the electrostatic potential and the attractive force between ions in the buffer and the ionic groups in the specimen. The relaxation of polymer chains was limited to this interaction so that the transport process shows the Case II behavior at the second stage.

3.4. Interaction between γ-ray irradiation and polymer

The IR of non-irradiated and irradiated specimens are shown in Fig. 5. After irradiation, most of the bands are reduced in intensity by the γ-rays. The absorbed bands at 1641 cm^{-1} and 2500–2750 cm^{-1} are broadened and their absorption intensities are increased. These wavenumbers correspond to the absorption bands of the carboxyl group.

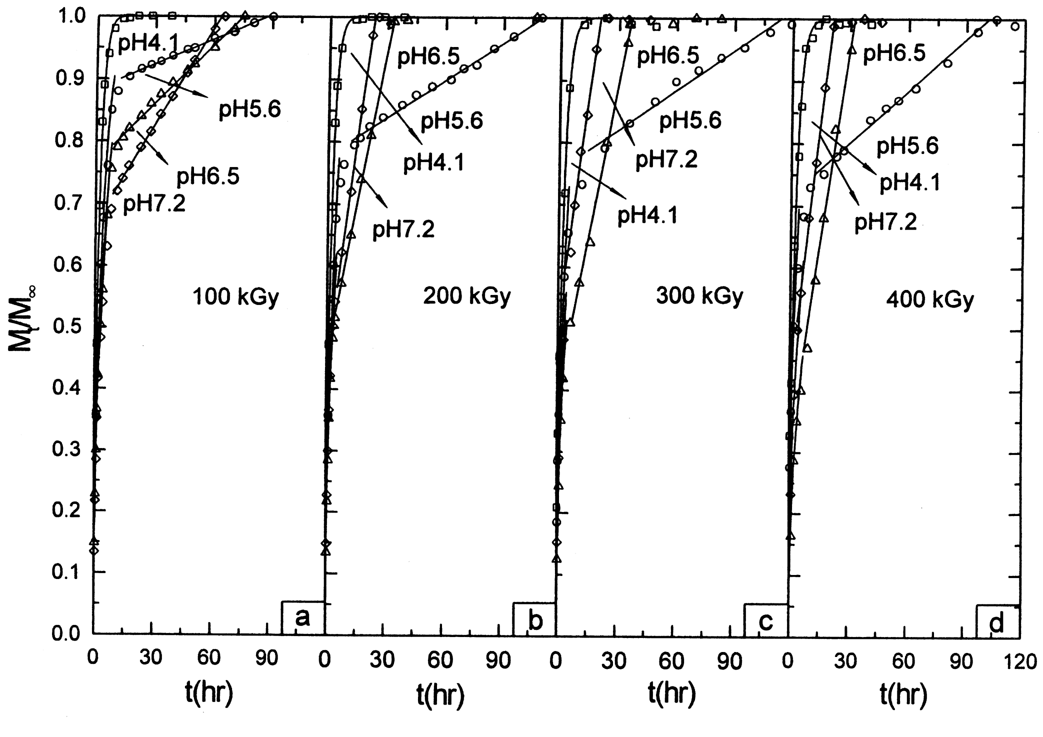

Fig. 4. Buffer sorption in HEMA copolymer irradiated by γ-ray in air at 40°C: (a) $\phi = 100$ kGy; (b) 200 kGy; (c) 300 kGy; and (d) 400 kGy.

Table 4
The diffusion coefficient of Case I transport (D) and velocity of Case II transport (v) of buffer in HEMA copolymer irradiated in air (ϕ is the irradiation dose)

ϕ (kGy)	pH	Stage	D (10^{-7} cm^2/s)	v (10^{-7} cm/s)
100	4.1	1	1.6	1.65
	5.6	1	1.55	1.60
		2	0	0.25
	6.5	1	1.45	1.50
		2	0	0.61
	7.2	1	1.45	1.35
		2	0	1.01
200	4.1	1	1.60	1.60
	5.6	1	1.00	0.50
		2	0	0.35
	6.5	1	0.64	0
		2	0	2.69
	7.2	1	0.70	0
		2	0	3.95
300	4.1	1	1.55	1.50
	5.6	1	0.90	0
		2	0	0.35
	6.5	1	0.50	0
		2	0	2.9
	7.2	1	0.60	0
		2	0	4.05
400	4.1	1	1.48	1.45
	5.6	1	0.90	0
		2	0	0.45
	6.5	1	0.26	0
		2	0	3.55
	7.2	1	0.50	0
		2	0	4.80

The number of carboxyl groups is greater in air than in vacuum. On the other hand, the raise in transmittance at 3400–3500 cm^{-1} corresponds to the decreasing number of hydroxyl group. The number of hydroxyl groups in the specimen is more in vacuum than in air. The result shows that the γ-ray irradiation induces the destruction of the pendent hydroxyl ethyl group and the production of the carboxyl group. In summary, the γ-ray causes greater acidification of the specimen irradiated in air than in vacuum.

3.5. Irradiation effect on equilibrium swelling ratio

Section 3.1 discussed that equilibrium swelling ratio of non-irradiated specimen decreases monotonically with increasing pH value. This trend was not observed in the irradiated specimen. The change of equilibrium swelling ratio with pH value for various irradiation doses is shown in Fig. 6. The value of equilibrium swelling ratio, S, increases rapidly in the range of pH 5.5–6.5. For the buffer with pH $<$ 5, the sequence of equilibrium swelling ratios from large to small is as follows: non-irradiated specimen, specimen irradiated in vacuum, and specimen irradiated in air. However, for the buffer of pH $\geq$ 5.5, the sequence was reversed. The chain session was more serious for HEMA irradiated in vacuum than in air. Thus the data of equilibrium swelling ratio for $\phi = 400$ kGy is available for HEMA irradiated in air, but not for HEMA irradiated in vacuum. The equilibrium swelling ratio (S) of various buffers in irradiated HEMA copolymer showed a volume transition at pH 5.5–6.5. The transition of equilibrium

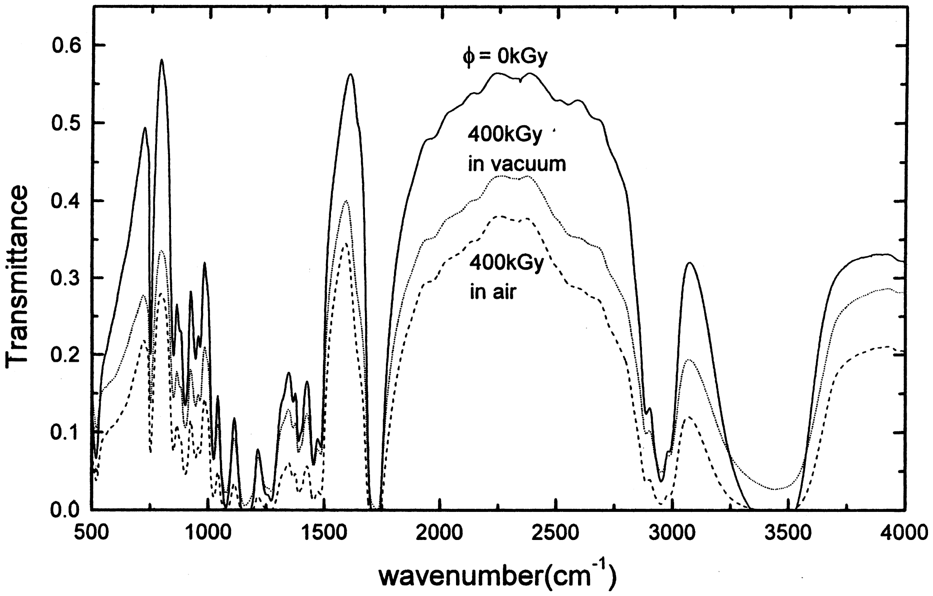

Fig. 5. The FTIR spectrum of non-irradiated and irradiated HEMA copolymers.

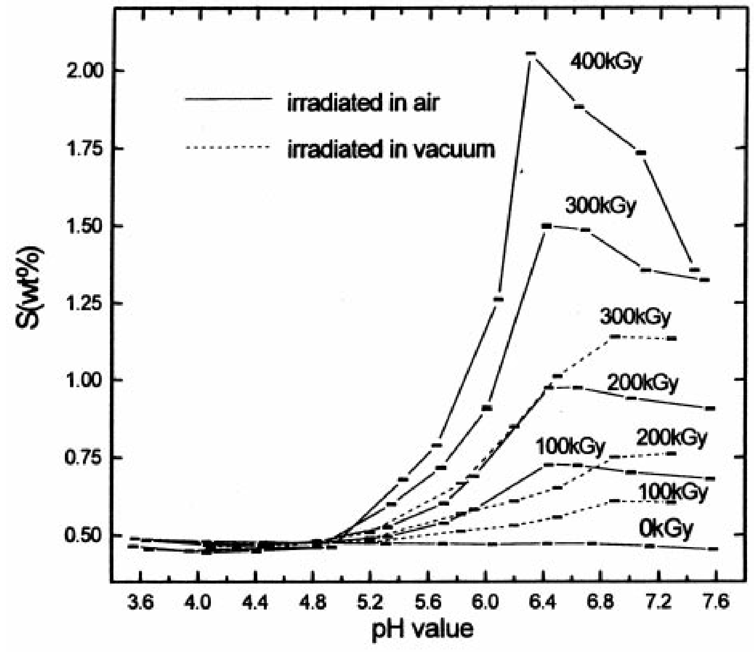

Fig. 6. Plots of equilibrium-swelling ratio (*S*) versus pH value of buffer in non-irradiated and irradiated HEMA copolymers.

swelling ratio in this region became pronounced at high doses. A volume transition of an irradiated specimen was induced by the production of the carboxyl group in the irradiated specimen [5,6]. The carboxyl group enhanced the absorption of the basic buffer because it decreases the hydrogen bonds and increases the osmotic pressure. The presence of oxygen during irradiation promoted the formation of carboxyl group so that the transition phenomenon was more significant for specimen irradiated in air than in vacuum.

3.6. Discussion

The glass transition temperatures of specimens irradiated in air and in vacuum were studied by Chou et al. [16,17]. They found that glass transition temperature before solvent treatment maintains a constant value if the dose is less than 327 kGy for the specimen irradiated in vacuum or 397 kGy for the specimen irradiated in air. The glass transition temperatures after solvent treatment decreases significantly for both irradiation environments. For a given dose, the glass transition temperature after solvent treatment is greater for the specimen irradiated in air than for the specimen irradiated in vacuum. This implies that the chain scission of the specimen irradiated in vacuum is more than that in air. The oxygen atmosphere prevents the chain scission due to γ-ray irradiation. The glass transition temperature is proportional to the molecular weight of the polymer. The molecular weight of HEMA irradiated in vacuum after solvent treatment is lower than that in air. The sequence of molecular weight from high to low is followed as non-irradiated specimen, specimen irradiated in air and specimen irradiated in vacuum. Case I transport is influenced by molecular weight so that the behavior of transport at stage 1 in specimen irradiated in air is between non-irradiated specimen (anomalous transport at low dose) and specimen irradiated in vacuum (pure Case I transport at high dose).

Case II transport is attributed to the stress relaxation of the polymer chain. It implies that Case II transport is controlled by swelling. The oxygen during irradiation enhances the formation of the carboxyl group and prevents the formation of the hydroxyl group so that the swelling is more for the specimen irradiated in air than that in vacuum. The more the number of carboxyl groups, the greater is the swelling [5,6]. The swelling of specimen irradiated in air is greater than that in vacuum. Therefore, the velocity at stage 2 is greater for the specimen irradiated in air than for that in vacuum (see Tables 3 and 4).

4. Conclusions

In this paper, the buffer transport in non-irradiated HEMA copolymers is studied. The experimental data are in excellent agreement with the Harmon model. The transport behavior is anomalous. The diffusion coefficient and activation energy of Case I transport of the acidic buffer decrease with increasing pH value, but the trend of the basic buffer is opposite. The velocity and activation energy of Case II transport decrease monotonically with increasing pH value. Equilibrium swelling ratio decreases with increasing pH value, but the heat of mixing is independent of the acidity of the buffer solution.

For the irradiated specimen, the chain scission reduces the molecular weight of polymer and ionization affects the osmotic pressure of the polymer–buffer solution system. When pH = 4.1, the buffer transport is anomalous in the specimen irradiated in air and Case I in the specimen irradiated in vacuum. When pH ≥ 5.6, the buffer transport in irradiated HEMA copolymer is complicated and it is difficult to analyze the whole data with simple equations. We analyzed the data at the short times and long times only and they are assigned as stages 1 and 2, respectively. It is found that for specimens irradiated in vacuum, stage 1 belongs to the Case I transport, while for specimens irradiated in air, it is anomalous transport at low pH value (or low dose) and pure Case I transport at high pH value (or high dose). This is due to the chain scission of the irradiated specimen immersed in buffer solution. The molecular weight of the specimen from small to large is according to the sequence: specimen irradiated in air, specimen irradiated in vacuum and non-irradiated specimen. The oxygen during irradiation prevents the chain scission. The second stage of the transport process is pure Case II transport for both the irradiation environments. This arises from an increase in carboxyl groups when the irradiated specimen is immersed in the buffer solution. The carboxyl group increases with swelling and swelling controls Case II transport. The effect of pH values on Case II transport behavior of the specimen irradiated in air is more pronounced than that of the specimen irradiated in vacuum. The data of equilibrium swelling ratio of irradiated specimen versus pH value shows a volume transition in the range of pH 5.5–6.5. From the analysis of IR spectra, the γ-ray irradiation destroys the hydroxyl ethyl group and creates the carboxyl group. The existence of oxygen during irradiation effectively enhances these reactions.

References

[1] Firestone BA, Siegel RA. J Biomater Sci Polym Ed 1994;5:433.

[2] Baker JP, Blanch HW, Pransnitz JM. J Appl Polym Sci 1994; 52:783.

[3] Guan YL, Shao L, Liu J, Yao KD. J Appl Polym Sci 1996;62:1253.

[4] Siegel RA, Firestone BA. Macromolecules 1988;21:3254.

[5] Peng T, Yao KD, Yuan C, Goosen MFA. J Polym Sci, Part A: Polym Chem 1994;32:591.

[6] Yao KD, Peng T, Xu MX, Yuan C, Goosen MFA, Zhang QQ, Ren L Polym Int 1994;34:213.

[7] Tanaka T. Sci Am 1981;244:124.

[8] Flory PJ. Principles of polymer chemistry. New York: Cornell University Press, 1953 (chap. 13).

[9] Ricka J, Tanaka T. Macromolecules 1984;17:2916.

[10] Matsuo ES, Tanaka T. J Chem Phys 1988;89:1695.

[11] Donnan FG. Chem Rev 1925;1:73.

[12] Refojo MF. Encyclopedia of polymer science and technology. New York: Wiley, 1976 (p. 195–219).

[13] Ratner BD, Miller IF. J Biomed Mater Res 1973;7:353.

[14] Tollar M, Stol M, Kliment K. J Biomed Mater Res 1969;3:305.

[15] Lazarus SM, LaGuerre JN, Kay H, Weinberg SR, Levowitz BS. J Biomed Mater Res 1971;5:129.

[16] Chou KF, Han CC, Lee S. J Polym Sci, Part B: Polym Phys 2000; 38:659.

[17] Chou KF, Han CC, Lee S. Polym Engng Sci 2000;40:1004.

[18] Harmon JP, Lee S, Li JCM. J Polym Sci, A: Polym Chem Ed 1987;25:3215.

[19] Harmon JP, Lee S, Li JCM. Polymer 1988;29:1221.

[20] Lin CB, Lee S, Liu KS. Polym Engng Sci 1990;30:1399.

[21] Wu T, Lee S, Chen WC. Macromolecules 1995;28:575.

[22] Ouyang H, Chen CC, Lee S, Yang HJ. J Polym Sci, Part B: Polym Phys 1998;36:163.

[23] Tanaka T, Sun ST, Hirokawa Y, Katayama S, Kucera J, Hirose Y, et al. Nature 1987;325:796.

[24] Ohmine I, Tanaka T. J Chem Phys 1982;77:5725.

[25] Saito O. In: Dole M, editor. The radiation chemistry of macromolecules, vol. 1. New York: Academic Press, 1972. p. 223.

[26] Reichmanis E, Frank CW, O'Donnell JH, Hill DJT. In: Reichmanis E, O'Donnell JH, editors. Irradiation of polymeric materials. Washington, DC: American Chemical Society, 1993 (chap. 1).