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Swelling behavior of acrylic acid hydrogels prepared by γ-radiation crosslinking of polyacrylic acid in aqueous solution

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Abstract

Swelling behavior of anionic acrylic acid polyelectrolyte hydrogel synthesized by γ-radiation crosslinking of polyacrylic acid in aqueous solution was investigated. Cross-linked polyacrylic acid (PAA) hydrogel was synthesized using a two-step method. First, uncrosslinked PAA was synthesized by free-radical precipitation polymerization of acrylic acid in benzene. In the second step, PAA was dissolved in aqueous solution, and it was crosslinked with γ-irradiation. The swelling behavior of the gels was studied as a function of the concentration of PAA in aqueous solution during γ-irradiation, radiation dose, and pH of the swelling medium. In a buffered solution of pH 4, the degree of swelling ranged from 30 to 300 for irradiation doses ranging from 5 to 25 kGy, and the swelling was Fickian. On the other hand, in a buffered solution of pH 7 the degree of swelling ranged from 80 to 500 depending on the irradiation dose and the swelling was non-Fickian.

Keywords: Hydrogels; Polyacrylic acid; γ-Irradiation; Crosslinking; Swelling

1. Introduction

Hydrogels are three-dimensional crosslinked polymeric structures which are able to swell in the aqueous environment [1,2]. Hydrogels are used extensively in medicine and pharmacy as drug delivery systems, contact lenses, catheters, wound dressings, and biosensors [3–6]. One of the most powerful applications of hydrogels is in controlled release systems for targeted delivery to specific areas of the body [7,8]. More specifically, ionic hydrogels are used to immobilize a drug delivery device on a specific site for targeted release and optimal drug delivery due to the intimacy and extended duration of contact [9–15]. After intimate contact is established, the rate and duration of drug release depends on the swelling behavior of the hydrogel [16,17]. Because of the presence of carboxylic acid side groups, the swelling behavior of the polyacrylic acid (PAA) hydrogel is highly dependent on the pH of the surrounding medium [18–23]. For example, since pK_a of acrylic acid is between 4.5 and 5.0, PAA hydrogels swell significantly above pH 5 which is the pH of the small intestine. However, they do not swell significantly below pH 4 which is the pH of the stomach [19]. Therefore, one of the major applications of acrylic acid gels is in sustained gastro-intestinal drug delivery systems [7,8].

Hydrogels can be prepared by simultaneous copolymerization and crosslinking of one or more monofunctional and one multifunctional monomer or by crosslinking of a homopolymer or copolymer in solution [24,25]. The latter involves two steps in which, in the first step, the linear polymer is synthesized in the absence of a crosslinking agent and in the second step, the synthesized polymer is crosslinked using either chemical reagents or irradiation. In recent years, considerable research has been done on the characterization and swelling behavior of hydrogels prepared by simultaneous free-radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent. For example, Peppas and coworkers have worked

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extensively on the characterization of anionic hydrogels synthesized by copolymerization of acrylic acid or methacrylic acid with hydroxyethyl methacrylate or chemically grafted with polyethylene glycol [16–23].

Hydrogels can also be synthesized by crosslinking with an electron beam or γ-irradiation [26,27]. However, little work is done on the characterization of hydrogels prepared by crosslinking of a homopolymer or copolymer in solution with γ-irradiation [28]. It is well known that the presence of an initiator and a crosslinking agent affects the macromolecular structure and phase behavior of hydrophilic polymers in solution and contributes to the inhomogeneity of the network structure [25,29]. It is argued that more homogeneous network structures can be synthesized, if crosslinking is accomplished with γ-irradiation in the absence of an initiator and a crosslinking agent. The structural homogeneity of the network affects the swelling behavior and mechanical properties of the hydrogel. The objective of this work was to investigate the swelling behavior of acrylic acid hydrogels synthesized by γ-irradiation crosslinking of uncrosslinked polyacrylic acid in aqueous solution. Uncrosslinked PAA was prepared by precipitation polymerization of acrylic acid in benzene.

2. Experimental

2.1. Materials

All reagents were obtained from the Merck Chemical Co., Germany. Acrylic acid monomer was distilled under a reduced pressure of 5 mmHg at 30°C to remove the inhibitor, hydroquinone mono-methyl ether. PAA was synthesized from the acrylic acid monomer by free-radical precipitation polymerization [30,31]. Benzene and 2,2′-azobis-2-methyl propionitrile (AIBN) were used as the solvent and initiator, respectively, without further purification.

2.2. Precipitation polymerization

The following procedure was used for the precipitation polymerization. In a dry reaction flask, 233 ml of benzene (2.61 mol), 0.0638 g of AIBN (0.39 mmol), and 20 ml of acrylic acid (0.29 mol) were mixed. The molar ratio of the initiator to the monomer was 1:750. The mixture was allowed to react for 1 h at 70°C in a constant temperature bath until the mixture became opaque. Gaseous nitrogen was used to exclude oxygen during the course of the reaction. To reduce the probability of crosslinking reactions, the initial concentration of AA was kept below 10% by volume, and conversion was kept below 50%. It should be mentioned that precipitation polymerization was chosen in this study because this method substantially reduces the probability of crosslinking reactions.

Reichert and collaborators have investigated the precipitation polymerization of AA in toluene [32]. According to their results, in precipitation polymerization, after radicals are formed in the continuous phase, they precipitate and form the dispersed polymer particle phase such that the radical centers are oriented at the particle–solvent interface. As a result, the rate of polymerization is proportional to the concentration of radicals in the particle phase and concentration of the monomers in the solvent phase. Orientation of radicals at the particle–solvent interface significantly reduces the contact between radicals and polymer chains which reduces the rate of crosslinking reactions [33–35]. Therefore, AA can be polymerized to high conversions (greater than 60%) without significant crosslinking using precipitation polymerization in organic solvents. The reaction was stopped by reducing the temperature to 25°C, and the solvent was evaporated using a rotary evaporator. To remove the residual monomer and unreacted initiator, the polymer was dissolved in methanol and precipitated in diethyl ether twice. After purification, the PAA was dried in vacuo at 40°C for 12 h and stored in a desiccator.

2.3. Characterization

To test the purity of the synthesized PAA after purification, T_g of the sample was measured with a differential scanning calorimeter (TA Instruments). The T_g of the PAA was 105°C which was very close to the T_g value of 106°C reported for PAA in Ref. [36]. The intrinsic viscosity of the synthesized PAA in 1 M aqueous NaCl solution was measured with a capillary viscometer at a constant temperature of 25°C and the viscosity averaged molecular weight ($\overline{M}_v$) of the sample was determined using the Mark–Houwink–Sakurada (MHS) equation. The intrinsic viscosity of the synthesized PAA was 0.897. The constants K and a in the MHS equation were obtained from Ref. [37], and they were equal to 15.47×10^{-3} ml/g and 0.90, respectively. The $\overline{M}_v$ of the PAA sample was 1.6×10^5 g/mol.

2.4. γ-Irradiation

Two solutions of the synthesized PAA in deionized water with concentrations of 2.5 and 10.0 w/w PAA were prepared. Approximately 2 ml of each solution was poured in a 10 ml glass vial, purged with nitrogen, and the vial was sealed with a plastic top, and each vial was exposed to γ-radiation. However, the plastic top was not sealed to molecular oxygen. Each PAA solution was exposed to five different doses of radiation including 5, 10, 15, 20, and 25 kGy. The source of γ-radiation was cobalt ^{60}CO and the dose rate was 1.39 Gy/s. Therefore,

the duration of radiation for solutions exposed to doses of 5 and 25 kGy was 1 and 5 h, respectively. Gamma cell calibration was performed with the exposure time of the system based on dosimetry using a Fric chemical dosimeter. The irradiation experiments were performed at the γ-radiation center of Iran Atomic Energy Agency. It should be noted that the radiation doses chosen were in the range used for gamma sterilization in pharmaceutical and medical practice. After irradiation, the disk-shaped solid gel samples were washed twice with deionized water to remove uncrosslinked polymer, dried in vacuo at 40°C for 12 h and stored in a desiccator. Since the primary objective of this research was to study the swelling kinetics of γ-irradiated PAA gels, not the gelation kinetics, the sol and gel fractions of each sample were not measured.

2.5. Swelling measurements

The swelling measurements were carried out in a buffered medium of pH 4 and 7 to simulate the pH of the gastric and enteric cavities, respectively. To prepare buffered pH 4, 50 ml of 0.1 M potassium hydrogen phthalate was mixed with 0.1 ml of 0.1 M hydrochloric acid, and the final volume was adjusted to 100 ml [38]. To prepare a buffered medium of pH 7, 50 ml of 0.1 M potassium dihydrogen phosphate was mixed with 29.1 ml of 0.1 M sodium hydroxide and the final volume of mixture was adjusted to 100 ml [38]. The p*K*a of the weak acids, hydrogen phthalate and dihydrogen phosphate were 6.7 [38] and 7.2 [39], respectively. The weight swelling ratio Q, defined as the difference between the weight of sample after swelling and the dry weight divided by the weight of the dry sample, was determined as a function of time. For each sample, three measurements of swelling were performed, and the average of the three values was reported.

3. Results and discussion

3.1. Mechanism of γ-radiation crosslinking

The mechanism of crosslinking of polymers in solution by γ-irradiation was studied by Chapiro [40,41], Saito [42–44] and others [45–47]. The subject is also reviewed by Peppas [25]. The mechanism is discussed here briefly for γ-irradiation of aqueous PAA solutions. First, the polymer, PAAH, and the solvent, HOH, absorb the γ-rays and go to the transient activated state of PAAH* and HOH*, respectively. In the activated state, the covalent bonds of the PAAH* and HOH* molecules dissociate, causing the formation of free radicals. If a C–H bond of the polymer breaks, then a polymer radical, PAA·, and a hydrogen radical, H·, are formed. Dissociation of the activated water molecule causes the formation of a hydroxyl radical, HO·, and a hydrogen radical, H·. Two hydrogen radicals can recombine causing the evolution of hydrogen gas. If the diffusion of the polymer radical is slow, such as γ-irradiation of polymers in the solid state, then the polymer radical, PAA·, recombines with a hydrogen radical, H·, to form the original polymer molecule, PAAH. The recombination reaction lowers the efficiency of crosslinking with γ-irradiation. The rate of the recombination reaction is minimum in dilute polymer solutions due to the high diffusivity of polymer radicals. Energy transfer reactions between inactivated molecules, PAAH or HOH, and activated molecules, PAAH* or HOH*, can occur during the irradiation of polymer solutions. Also, radical-transfer reactions between the PAA and water molecules with radicals, PAA·, H· or HO·, can occur in solution. In aqueous polymer solutions, due to high absorption of γ-radiation by water molecules, radical transfer reactions between polymer and hydroxy or hydrogen radicals dominate to form polymer radicals which increase the rate of crosslinking reactions. Therefore, the most important reactions in γ-radiation crosslinking of PAA in aqueous solution are as follows:

$$\mathrm{PAA}\cdot_m + \mathrm{HOH} \rightarrow \mathrm{PAA}_m + (\mathrm{H}\cdot \text{ or } \mathrm{HO}\cdot) \quad (1)$$

$$\mathrm{PAAH} + (\mathrm{H}\cdot \text{ or } \mathrm{HO}\cdot) \rightarrow \mathrm{PAA}\cdot + \mathrm{HOH} \quad (2)$$

$$\mathrm{PAA}\cdot_m + \mathrm{PAA}\cdot_n \rightarrow \mathrm{PAA}_m\text{–}\mathrm{PAA}_n \quad (3)$$

$$\mathrm{PAA}\cdot_{m+n} \rightarrow \mathrm{PAA}_m + \mathrm{PAA}\cdot_n \quad (4)$$

$$\mathrm{PAA}_{m+n}\cdot + \mathrm{O_2} \rightarrow \mathrm{PAA}_{m+n}\text{–}\mathrm{O_2}\cdot \rightarrow \mathrm{PAA}_m\text{–}\mathrm{C(O)H} + \mathrm{PAA}_n\text{–}\mathrm{O}\cdot \quad (5)$$

Reaction (1) involves the transfer of radicals from polymer to water molecules which reduces the efficiency and extent of crosslinking. Reaction (2) involves the transfer of radical from water to polymer which increases the concentration of PAA radicals and increases the rate of crosslinking and gelation. In reaction (3), two polymer radicals, PAA·, with m and n repeat units combine to form a crosslinked point. In reaction (4), a polymer radical, PAA·, with $m + n$ repeat units degrades to from a polymer with m repeat units, PAA_m, and a polymer radical with n repeat units, $\mathrm{PAA}\cdot_n$. In reaction (5), molecular oxygen present in the γ-irradiation chamber reacts with a polymer radical, PAA·, with $m + n$ repeat units and forms a polymer radical–oxygen adduct, $\mathrm{PAA}_{m+n}\text{–}\mathrm{O_2}\cdot$. This radical–oxygen adduct is unstable and decomposes to an aldehyde terminated polymer with m repeat units, $\mathrm{PAA}_m\text{–}\mathrm{C(O)H}$, and a relatively unreactive polymer radical with n repeat units, $\mathrm{PAA}_n\text{–}\mathrm{O}\cdot$ [48,49]. Reactions (4) and (5) degrade the polymer chains and decrease the efficiency of gelation. As the concentration of the polymer in the aqueous

solution increases, the rate of degradation reaction increases. Therefore, the concentration of polymer significantly affects the minimum dose required for gelation. It should be mentioned that solid gels were obtained for all the samples radiated in the range 5–25 kGy. Therefore, the presence of oxygen in the γ-radiation chamber did not inhibit gel formation but, like reaction (4), it lowered the efficiency of gelation.

3.2. Kinetics of swelling

Figs. 1 and 2 show the weight swelling ratio as a function of time for 2.5% w/w PAA in aqueous solution crosslinked with radiation doses ranging from 5 to 25 kGy in which the swelling measurements were performed in buffered pH 4 and 7, respectively. Figs. 3 and 4 show the same results for 10% w/w PAA in aqueous solution crosslinked with radiation doses ranging from 5 to 25 kGy. As the pH was increased from 4 to 7, the rate of swelling increased for all radiation doses and for 2.5% and 10% PAA solutions. As the radiation dose was increased from 5 to 25, the rate of swelling decreased drastically. As the concentration of PAA increased from 2.5% to 10%, the rate of swelling decreased. Therefore, according to Figs. 1–4, the swelling behavior of γ-radiation crosslinked samples depended on the concentration of polymer and dose of irradiation.

3.3. Equilibrium swelling

Fig. 5 shows the equilibrium weight swelling of 2.5% and 10% PAA solutions as a function of the irradiation dose measured in buffered pH 4. In pH 4, the equilibrium swelling was relatively independent of the irradiation dose for 2.5% PAA in solution, and the values ranged from 110 to 70 corresponding to radiation doses of 10 and 15 kGy, respectively. However, at the same pH, for the 10% PAA solution, the equilibrium swelling decreased significantly when the irradiation dose was increased from 5 to 25 kGy, and the swelling values ranged from 140 to 40, corresponding to radiation doses

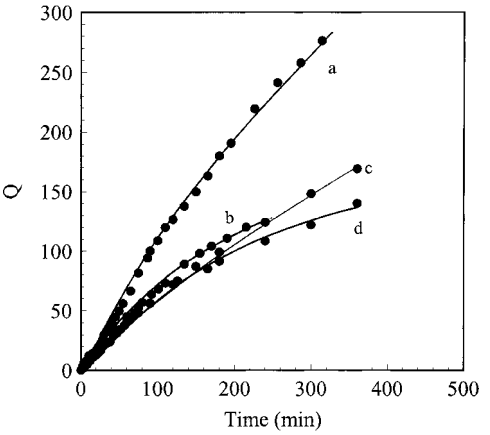

Fig. 2. Weight-swelling ratio as a function of time for 2.5% w/w PAA in aqueous solution during γ-irradiation crosslinked with radiation doses of (a) 5, (b) 10, (c) 15, and (d) 25 kGy in which the swelling measurements were performed in a medium of pH 7.

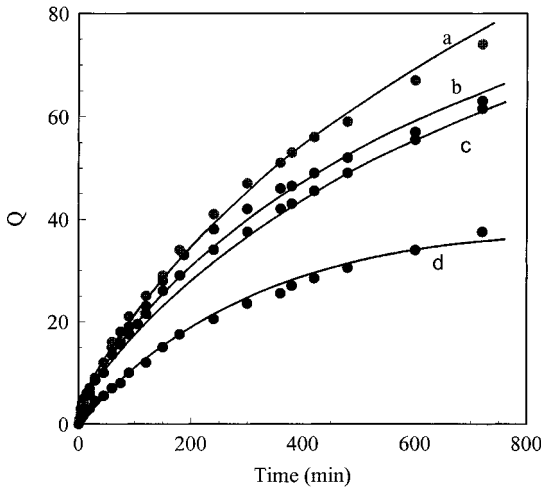

Fig. 1. Weight-swelling ratio as a function of time for 2.5% w/w PAA in aqueous solution during γ-irradiation crosslinked with radiation doses of (a) 5, (b) 10, (c) 15, and (d) 25 kGy in which the swelling measurements were performed in a medium of pH 4.

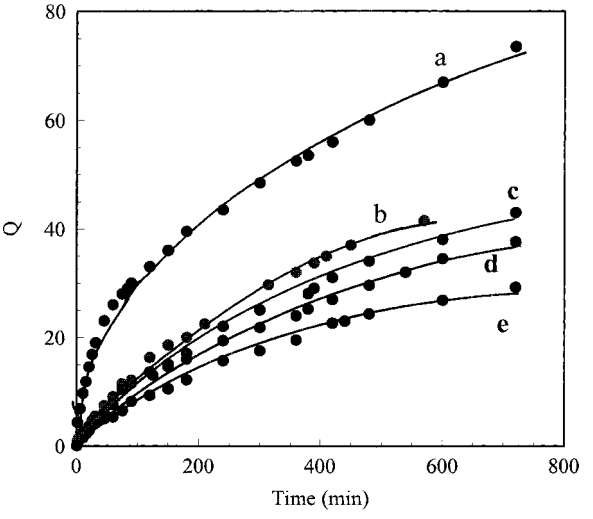

Fig. 3. Weight-swelling ratio as a function of time for 10.0% w/w PAA in aqueous solution during γ-irradiation crosslinked with radiation doses of (a) 5, (b) 10, (c) 15, (d) 20, and (e) 25 kGy in which the swelling measurements were performed in a medium of pH 4.

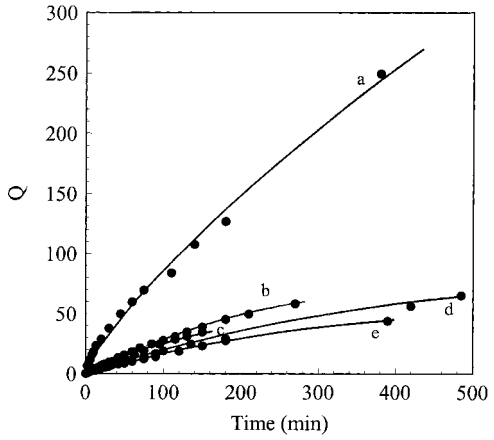

Fig. 4. Weight-swelling ratio as a function of time for 10.0% w/w PAA in aqueous solution during γ-irradiation crosslinked with radiation doses of (a) 5, (b) 10, (c) 15, (d) 20, and (e) 25 kGy in which the swelling measurements were performed in a medium of pH 10.

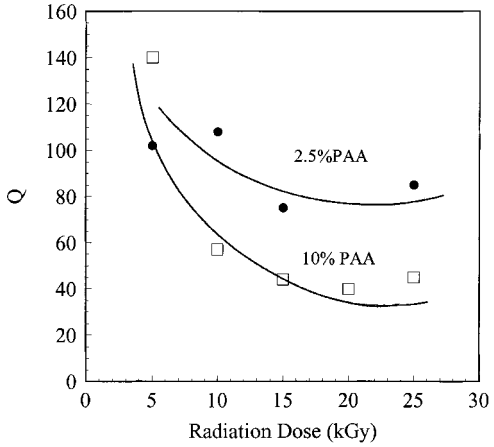

Fig. 5. Equilibrium weight-swelling ratio as a function of γ-irradiation dose for 2.5% and 10.0% w/w PAA in aqueous solution during irradiation in which the swelling measurements were performed in a buffered medium of pH 4.

of 5 and 20 kGy, respectively. Fig. 6 shows the equilibrium swelling of the same samples at pH 7. At pH 7, the final swelling decreased significantly as the radiation dose increased for 2.5% and 10% PAA solutions. For the 2.5% solution at pH 7, the maximum and minimum swelling was 500 and 300 corresponding to radiation doses of 5 and 25 kGy, respectively. For 10% solution at pH 7, the maximum and minimum swelling was 550 and 100 corresponding to radiation doses of 5 and 25 kGy, respectively. For all the radiation crosslinked PAA samples, the final swelling leveled-off for radiation doses greater than 15 which indicated that the degradation of

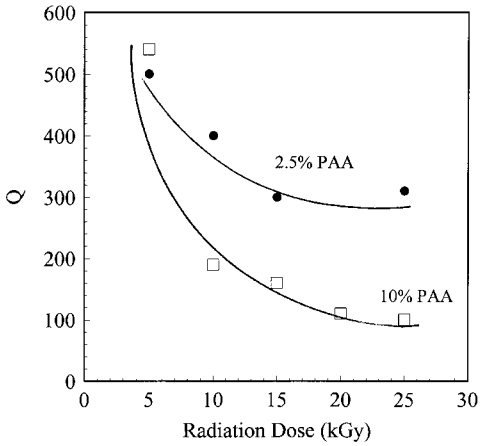

Fig. 6. Equilibrium weight-swelling ratio as a function of γ-irradiation dose for 2.5% and 10.0% w/w PAA in aqueous solution during irradiation in which the swelling measurements were performed in a buffered medium of pH 7.

the polymer during γ-irradiation became more significant as the irradiation dose increased.

3.4. Determination of molecular weight between crosslinks

The molecular weight between crosslinks, $\overline{M}_c$, was determined from the swelling data using the following equation proposed by Brannon-Peppas and Peppas [16] for equilibrium swelling of anionic polyelectrolyte gels:

$$\left(\frac{V_w}{4I}\right)\left(\frac{f'\phi_{p,s}}{\upsilon_{mp,d}}\right)^2\left[\frac{K_a}{(10^{-pH}+K_a)}\right]^2 = \left(\ln(1-\phi_{p,s})+\phi_{p,s}+\chi_{pw}\phi_{p,s}^2\right) + \left(\frac{V_w}{\upsilon_{p,d}\overline{M}_c}\right)\left(1-\frac{2\overline{M}_c}{\overline{M}_n}\right)\phi_{p,s} \times\left[\left(\frac{\phi_{p,s}}{\phi_{p,r}}\right)^{1/3}-\frac{1}{2}\left(\frac{\phi_{p,s}}{\phi_{p,r}}\right)\right]. \quad (6)$$

In the above equation, V_w is the molar volume of the swelling agent, water, I is the ionic strength of the aqueous solution, f' is the ionizable fraction of the monomers in the hydrogel, $\phi_{p,s}$ is the volume fraction of polymer in the swollen state, $\upsilon_{mp,d}$ is the molar volume of the polymerized monomer in the dry state, K_a is the dissociation constant of the ionic COOH group of PAA, χ_{pw} is the PAA–water interaction parameter, $\upsilon_{p,d}$ is the specific volume of polymer in dry state, $\overline{M}_c$ is the average molecular weight between crosslinks, $\overline{M}_n$ is the number average molecular weight of polymer before γ-irradiation, and $\phi_{p,r}$ is the volume fraction of the polymer in the relaxed state after crosslinking but before swelling.

The volume fraction of polymer in the swollen state, $\phi_{p,s}$, was calculated from the weight swelling ratio, Q, by the following equation:

$$\phi_{p,s} = \frac{1}{\left[1 + Q\left(\frac{\rho_p}{\rho_w}\right)\right]}. \quad (7)$$

In the above equation, ρ_p and ρ_w are the densities of polymer and water, respectively.

The value of 0.45 for the compatibility parameter between PAA and water, χ_{pw}, from Ref. [50] was used. The value of 4.5 was used for the pK_a of the acid group of PAA from Ref. [51] and it was assumed that the pK_a was independent of pH. The experimental temperature was 25°C and the value of 1.2 g/cm^3 was used for the density of PAA at this temperature [52]. f' was equal to one because only the AA monomer was used for gel preparation. $\upsilon_{mp,d}$ can be shown to be equal to the molecular weight of the AA monomer divided by the density of PAA. Therefore, the value of 60 cm^3/mol was used for $\upsilon_{mp,d}$. In buffered pH 4, mobile ions hydrogen, chlorine, potassium, hydrogen phthalate, and phthalate were present. Assuming complete dissociation of hydrogen chloride to hydrogen and chlorine ions and complete dissociation of potassium hydrogen phthalate to potassium and hydrogen phthalate ions and knowing the pK_a of hydrogen phthalate and PAA and using the Henderson–Hasselbach equation [39], the ionic strength of the buffered pH 4 solution was determined to be equal to 10.05×10^{-2} mol/l. In buffered pH 7, mobile ions hydrogen, sodium, potassium, dihydrogen phosphate, and hydrogen phosphate were present. Assuming the complete dissociation of sodium hydroxide to hydroxyl and sodium ions and the complete dissociation of potassium dihydrogen phosphate to potassium and dihydrogen phosphate ions and knowing the pK_a of dihydrogen phosphate and PAA, the ionic strength of the buffered pH 7 solution was determined to be equal to 13.1×10^{-2} mol/l. The number–average molecular weight of the PAA sample before crosslinking, $\overline{M}_n$, was approximated by the $\overline{M}_v$ of the sample which was equal to 1.6×10^5 g/mol. Maximum uncertainty in the calculated value of $\overline{M}_c$ due to the use of $\overline{M}_v$ in place of $\overline{M}_n$ in Eq. (6) was 27% for the sample with the highest calculated $\overline{M}_c$ value of 34 600 g/mol. For other samples, the uncertainty in the $\overline{M}_c$ values was in the range of 5–15%. This range of uncertainties did not affect the conclusions made, based on the trends shown in Fig. 7. The $\overline{M}_c$ of crosslinked samples as a function of the irradiation dose is given in Fig. 7 for aqueous solutions containing 2.5% and 10% PAA. For 2.5% PAA solution, the $\overline{M}_c$ values for irradiation doses of 5, 10, 15, and 25 were 12 600, 12 300, 6000, and 8100 g/mol, respectively. For 10% PAA solution, the $\overline{M}_c$ values for the irradiation doses of 5, 10, 15, 20, 25 were 34 600, 10 300, 9600, 5200, and 5700 g/mol, respectively. These results indicated that the extent of crosslinking was almost independent of the irradiation dose for 2.5% PAA solution. At low concentrations of PAA, the distance between the chains was longer and the rate of radical transfer from polymer to water (reaction (1)) was higher compared to the rate of crosslinking reaction (reaction (4)). Therefore, no significant change in $\overline{M}_c$ was observed when the irradiation dose was increased. On the other hand, at high concentrations of PAA, the distance between the chains was shorter, and the rate of radical transfer from polymer to water was lower compared to the rate of crosslinking reaction. Therefore, $\overline{M}_c$ decreased significantly as the irradiation dose was increased. For a 10% solution, the $\overline{M}_c$ leveled off for irradiation doses of 20 and 25 kGy due to the increased rate of degradation of polymer by reactions (4) and (5).

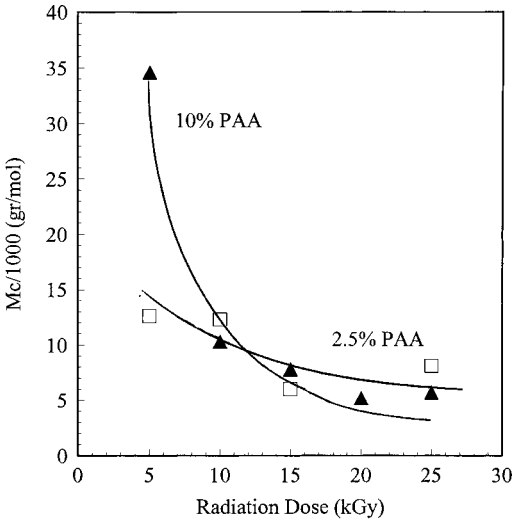

Fig. 7. Average molecular weight between crosslinks, $\overline{M}_c$, as a function of γ-irradiation dose for 2.5% and 10.0% w/w PAA in aqueous solution during irradiation. The reported $\overline{M}_c$ values are the average values obtained from swelling measurements in a buffered medium of pH 4 and 7.

3.5. Determination of swelling power

The swelling mechanism of the γ-crosslinked samples was determined using the following equation:

$$\frac{(M_t - M_0)}{M_0} = Kt^n. \quad (8)$$

In the above equation, M_t and M_0 are the weight of the swollen and dry sample at time t, respectively, t is the time, K is the swelling constant, and n is the swelling exponent. For disk-shaped samples, n is 0.5 if the swelling is by Fickian diffusion of water, n is between 0.5

Table 1
Calculated values of the swelling power, n, as a function of percent PAA in the aqueous solution during γ-irradiation, irradiation dose, and pH of the swelling medium

% PAA	Irradiation dose (kGy)	Swelling power (n), pH = 4	Swelling power (n), pH = 7
2.5	5	0.63	1.00
2.5	10	0.63	0.94
2.5	15	0.59	0.75
2.5	25	0.57	0.77
10	5	0.43	0.76
10	10	0.59	0.76
10	15	0.58	0.76
10	20	0.53	0.64
10	25	0.59	0.70

and 1.0 for non-Fickian or anomalous diffusion, n is 1.0 for case II diffusion, and n is greater than 1 for super-case-II diffusion. The swelling data versus time were fitted to the above equation using the linear least squares method, and the swelling power, n, was determined. The values of n are shown in Table 1 as a function of the concentration of PAA in solution, irradiation dose, and the pH of the swelling medium. For 10% PAA solutions swollen at pH 4, the mechanism of swelling was Fickian as the average swelling power was 0.54 for radiation doses between 5 and 25 kGy which indicated that chain relaxation had little effect on the rate of swelling. For 2.5% PAA solutions swollen at pH 4, the mechanism of swelling was a combination of Fickian and anomalous diffusion as the average n value was 0.61 indicating that chain relaxation contributed to the rate of swelling. For 10% PAA solutions at pH 7, the mechanism of swelling was anomalous diffusion as the average n value was 0.73, and the chain relaxation had a major contribution on the rate of swelling. For 2.5% PAA solutions swollen in pH 7, the swelling mechanism was between anomalous and case-II as the average n value was 0.87 indicating that chain relaxation was the rate limiting step. Super-case-II diffusion was not observed in the swelling of γ-radiation crosslinked PAA solutions. The range of n values observed can have great implications for applications in drug delivery systems. As the n value approaches 1, the rate of swelling and the rate of release of the bioactive agent from the hydrogel becomes constant. Therefore, it is possible to synthesize hydrogels with zero order release rate by crosslinking polyacrylic acid in solution with γ-irradiation. Due to differences in the experimental procedure, a direct comparison between our results and previous works is not possible. However, the results of this work, especially the effect of concentration, radiation dose, and pH on swelling behavior of γ-radiation crosslinked PAA gels are in accord with published research on γ-radiation crosslinking of polymers in solution [16,17,28,53].

4. Conclusion

PAA, synthesized by precipitation polymerization of AA in benzene, was successfully crosslinked in solution with γ-irradiation with doses ranging from 5 to 25 kGy. Kinetics of swelling and equilibrium swelling of these gels were measured as a function of concentration of PAA in aqueous solution during γ-radiation, radiation dose, and pH of the swelling medium. At equilibrium, the highest and lowest swelling ratio were 140 and 40 at pH 4 and 540 and 100 at pH 7, respectively. From the equilibrium swelling data, the average molecular weight between crosslinks was determined using the swelling equation for anionic polyelectrolyte gels in buffered solution. The average molecular weight between crosslinks ranged from 12 600 to 6000 g/mol depending on irradiation dose for solutions containing 2.5% PAA and 34 600 to 5200 g/mol for solutions containing 10% PAA, respectively. The mechanism of swelling depended on the pH of the swelling medium and concentration of PAA in solution during γ-irradiation. For 10% PAA solutions swollen at pH 4, the average swelling power was 0.54 and the mechanism of swelling was Fickian. For 2.5% PAA solutions swollen at pH 4, the average swelling power was 0.61 and the mechanism of swelling was a combination of Fickian and anomalous diffusion. For 10% PAA solutions at pH 7, the average swelling power was 0.73, and the mechanism of swelling was anomalous diffusion and chain relaxation had a major contribution on the rate of swelling. For 2.5% PAA solutions swollen in pH 7, the average swelling power was 0.87, and the swelling mechanism was between anomalous and case-II indicating that chain relaxation was the rate-limiting step in the swelling of the hydrogel.

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