

Effect of Maleic Acid Content on Network Structure and Swelling Properties of Poly(*N*-isopropylacrylamide-*co*-maleic acid) Polyelectrolyte Hydrogels

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ABSTRACT: Hydrogels were prepared by γ -ray-induced polymerization in aqueous solution of *N*-isopropylacrylamide (NIPA) and of NIPA with three different charge densities, that is, maleic acid (MA) as a comonomer. The swelling behaviors of these hydrogels were analyzed in buffer solutions at various pH and temperature ranges. The equilibrium swelling ratios were relatively high and sensitive to pH and temperature. The polymer-solvent interaction parameter (χ) and the molecular weight between crosslinks (\bar{M}_c) of

P(NIPA/MA) polyelectrolyte hydrogels were calculated from swelling studies in buffer solutions at various pH values and related to MA content. A kinetic study of the absorption determined the transport mechanism as a non-Fickian type diffusion. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 763–769, 2004

Key words: hydrogels; swelling; crosslinking; radiation; polyelectrolytes

INTRODUCTION

Poly(*N*-isopropylacrylamide) [P(NIPA)] form swollen hydrogels of crosslinked species because of the presence of both hydrophilic amide groups and hydrophobic isopropyl groups in its side chains. The hydrophilicity of such hydrogels can be enhanced by incorporating ionizable functional groups such as carboxylic acid groups. Several studies have been reported on the properties of hydrogels as a function of their ionic group content.^{1–5} Increasing the number of ionic groups in the hydrogels is known to increase their swelling capacity. This is mainly attributed to the simultaneous increase of the number of counterions inside the hydrogel, which produces an additional osmotic pressure that swells the hydrogel.²

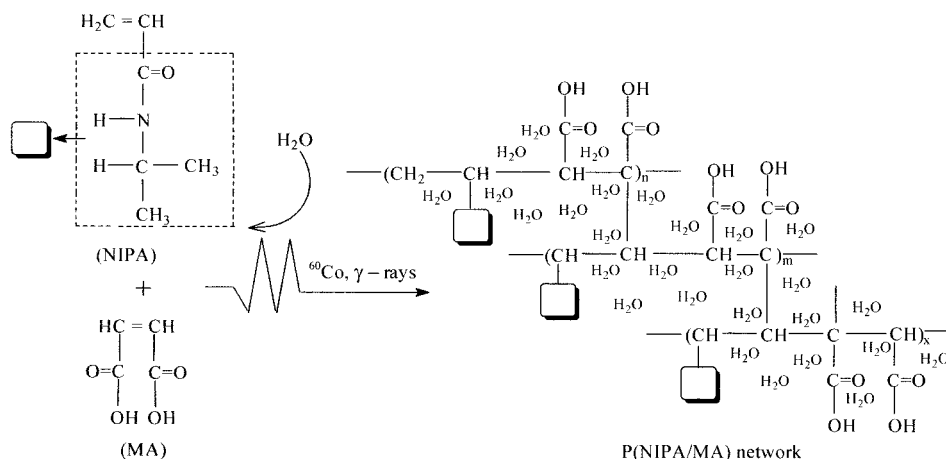
Copolymerization is also an important aspect for biomedical applications because the transition-temperature range can be modified by incorporating a more hydrophilic monomer to the hydrogel.^{6,7} PNIPA gels show a volume phase transition in water at about 34°C, going from a swollen to an unswollen state. This phenomenon could allow their use in intelligent systems for drug release,^{8–10} whose action would be triggered by the patient's temperature.

The swelling degree of a hydrogel is known to depend on its network structure.^{11,12} One of the basic parameters that describes the structure of electrolyte

and nonelectrolyte-type hydrogel networks is the molecular weight between crosslinks (\bar{M}_c) for highly swollen networks. This describes the average molecular weight of polymer chains between two consecutive junctions. These junctions may be chemical crosslinks, physical entanglements, crystalline regions, or even polymer complexes. Several theories have been proposed to calculate the \bar{M}_c values in polymeric networks. The earliest theory to describe the equilibrium swelling characteristics of networks was developed by Flory and Rehner^{2,13} for a crosslinked polymer system where the polymer chains are reacted in the solid state, and the macromolecular chains exhibit a Gaussian distribution. This theory deals with neutral polymer chains and tetrafunctional crosslinking within the polymer gel.

The Flory-Rehner² and Peppas and Merrill¹⁴ models describe the \bar{M}_c values for neutral polymer networks, although hydrogels may be neutral or ionic in nature. If the polymer chains making up the network contain ionizable groups, the forces influencing swelling may be greatly increased because of the localization of charges within the hydrogel. The equilibrium swelling ratios attained are often an order of magnitude larger than those of neutral networks, given that intermolecular interactions such as coulombic, hydrogen bonding, and polar forces are present. Peppas and Merrill's equation can be applied to systems that have solvent present during the crosslinking process of the macromolecular chains. It also introduces an additional term to represent the polymer volume fraction in the relaxed state. This equation has also been used in poly(vinyl alcohol)/poly(acrylic acid) interpen-

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Scheme 1

trating networks,¹⁵ although modified swelling equations have been developed more recently by Brannon-Peppas and Peppas¹⁶ in an attempt to predict the swelling behavior of hydrogels with monoprotic acid moieties. However, these equations are based on an affine network model and can be used only for the polymeric networks prepared by crosslinking reaction from the homopolymers that have previously known number-average molecular weight (\bar{M}_n). On the other hand, the χ parameter had to be determined previously for the application of these equations to calculate \bar{M}_c values.

In the present work, by considering a combined evaluation of the approaches of Brannon-Peppas and Peppas and the James-Guth phantom network model,¹⁷ the equation is accordingly derived for simultaneous determination of the \bar{M}_c and the χ parameters of hydrogels based on *N*-isopropylacrylamide (NIPAA) and maleic acid (MA) prepared by radiation-induced simultaneous polymerization and crosslinking reactions of the monomers. The effect of external stimuli such as the pH and temperature on the equilibrium swelling ratios of these hydrogels was investigated and the transport mechanism was also determined by a kinetic study of the absorption.

EXPERIMENTAL

Materials

The two monomers used in this study, *N*-isopropylacrylamide (NIPAA) and maleic acid (MA), were supplied from Merck (Darmstadt, Germany). Glacial CH_3COOH , H_3PO_4 (85%), H_3BO_3 , and standardized NaOH were used to prepare Britton-Robinson (B-R) buffers. B-R buffer solution was prepared in such a way that 2.3 mL glacial acetic acid, 2.7 mL phosphoric acid, and 2.4720 g boric acid dissolved by dilution triple-distilled water to 1.0 L; 50 mL portions of this

solution were taken and the pH was adjusted between 2.0 and 9.0 by addition of an appropriate amount of 2.0M NaOH.

Preparation of hydrogels

The P(NIPAA/MA) hydrogels were prepared by radiation-induced simultaneous process of polymerization and crosslinking of NIPAA and MA in aqueous solutions without the use of any crosslinker by the following procedure (see Scheme 1).

Aqueous solutions of monomers were prepared in 4 mL of pure water in different compositions (NIPAA/MA mole ratios: 91.9/8.1, 89.5/10.5, 68.2/31.8). These solutions were placed in poly(vinylchloride) (PVC) straws of 4 mm diameter and irradiated to 80 kGy in air at ambient temperature in a ^{60}Co γ -irradiator at fixed dose rate of 2.8 kGy/h. Hydrogels obtained were dried in a vacuum oven at 315 K to constant weight and subjected to Soxhlet extraction with water to remove the uncrosslinked polymer and unreacted MA from copolymers. The extracted gels were dried again in vacuum oven at 315 K to constant weight. When the aqueous extract was titrated by using NaOH (0.05M), endpoint detection was not observed because there was no unreacted MA. The weight swelling ratio of hydrogels after preparation q_F was calculated as

$$q_F = \frac{\text{mass hydrogel after preparation}}{\text{mass dry hydrogel}} \quad (1)$$

The volume fraction of polymer network after preparation v_{2r} was calculated from q_F values as

$$v_{2r} = \left[1 + \frac{(q_F - 1)\rho_2}{\rho_1} \right]^{-1} \quad (2)$$

where ρ_2 and ρ_1 are densities of polymer network and solvent, respectively. The values ρ_2 and ρ_1 used were 1.35 and 1 g/mL, respectively. The density of polymer network was determined by a pycnometer using acetone as nonsolvent.

Determination of equilibrium swelling ratio

The swelling study was conducted on the hydrogels to observe the behavior as functions of pH and temperature of swelling medium. The weight swelling ratios of hydrogels q_w were calculated using the following equation:

$$q_w = \frac{\text{mass hydrogel in solution}}{\text{mass dry hydrogel}} \quad (3)$$

To measure the swelling ratio, preweighed dry samples were immersed in water. After wiping off the excessive water on the samples' surface using moistened filter paper, the weight of the swollen samples was measured in the pH range 2–9 and in the temperature range from 4 to 65°C.

The equilibrium swelling ratio of hydrogels q_v was calculated as

$$q_v = 1 + \frac{(q_w - 1)\rho_2}{\rho_1} \quad (4)$$

The volume fraction of the polymer network v_{2m} was calculated as

$$v_{2m} = 1/q_v \quad (5)$$

Theory of swelling equilibrium

The pH-responsive swelling behavior of the hydrogels was analyzed within the framework of the Flory–Rehner theory of swelling, according to which the osmotic pressure π of a hydrogel during swelling is given as the sum of the pressures attributed to (1) polymer–solvent mixing (mix), (2) deformation of network chains to a more elongated state (el), and (3) the nonuniform distribution of mobile counterions between the hydrogel and the external solution (ion)²:

$$\pi = \pi_{\text{mix}} + \pi_{\text{el}} + \pi_{\text{ion}} \quad (6)$$

The mixing term is satisfactorily represented by a Flory–Huggins-type expression of the form²

$$\pi_{\text{mix}} = -\frac{RT}{V_1} [\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2] \quad (7)$$

where R is the gas constant and T is temperature. To describe the elastic contribution π_{el} to the swelling

pressure, we will use here the James–Guth phantom network model¹⁷ to describe the behavior of our hydrogels:

$$\pi_{\text{el}} = -RT \left[\frac{(1 - 2/\phi)\rho_2 v_{2r}^{2/3} v_{2m}^{1/3}}{\bar{M}_c} \right] \quad (8)$$

The ionic contribution π_{ion} to the swelling pressure is caused by the concentration difference of counterions between the hydrogel and the outer solution. The ideal Donnan theory gives π_{ion} as the pressure difference of mobile ions inside and outside the hydrogel²:

$$\pi_{\text{ion}} = RT \left(\frac{i^2 c_2^2}{4I} \right) \quad (9)$$

In the above equation, i is the degree of ionization, I is the ionic strength of the swelling medium, and c_2 is the concentration of the ionizable polymer (mol cm⁻³). c_2 can be written in terms of polymer structural parameters for copolymeric hydrogels as

$$c_2 = \frac{f_i}{\bar{V}_r} v_{2m} \quad (10)$$

where f_i is the mole fraction of the ionic unit in the gel system and \bar{V}_r is the average molar volume of polymer repeat units. \bar{V}_r can be calculated as

$$\bar{V}_r = \frac{M_n(1 - f_i) + M_i f_i}{\rho_2} \quad (11)$$

where M_n is the molecular weight of the neutral unit and M_i is the molecular weight of the ionic unit in the gel system.

The degree of ionization i can be expressed in terms of other analytical variables of the polymer–solvent system. For hydrogels with diprotic acid moieties, the ionization i is defined as¹⁸

$$i = \frac{2K_{a1}K_{a2} + 10^{-\text{pH}}K_{a1}}{2[(10^{-\text{pH}})^2 + 10^{-\text{pH}}K_{a1} + K_{a1}K_{a2}]} \quad (12)$$

By substituting eqs. (10) and (12) into eq. (9) and, because the swelling pressure of diprotic polymeric networks equals zero at swelling equilibrium, one obtains the final equation:

$$\left[\frac{2K_{a1}K_{a2} + 10^{-\text{pH}}K_{a1}}{2[(10^{-\text{pH}})^2 + 10^{-\text{pH}}K_{a1} + K_{a1}K_{a2}]} \right]^2 \frac{V_1 f_i^2}{4I v_r^2} - v_{2m}^{-2} \ln(1 - v_{2m}) - v_{2m}^{-1} = \chi + \frac{(1 - 2/\phi)V_1 \rho_2 v_{2r}^{2/3} v_{2m}^{-5/3}}{\bar{M}_c} \quad (13)$$

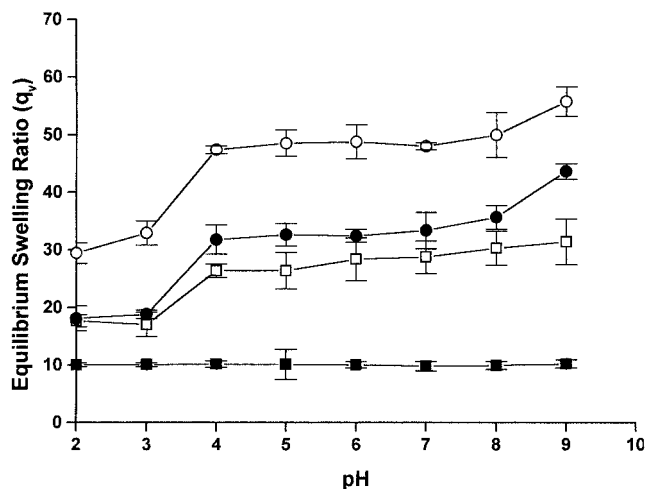


Figure 1 Effect of pH on the equilibrium swelling ratio q_v of hydrogels: (■) PNIPA; (□) P(NIPA/MA)-1; (●) P(NIPA/MA)-2; (○) P(NIPA/MA)-3. The curves show the trend of the data.

RESULTS AND DISCUSSION

Synthesis of hydrogels

P(NIPA/MA) hydrogels were synthesized by radiation-induced simultaneous polymerization and crosslinking of an aqueous solution of the monomers without any additive. When an aqueous solution of NIPA and MA monomers is irradiated, monomeric radicals are generated by both the direct effect of radiation and the indirect effect based on the reaction of the products of water radiolysis with the monomers.¹⁹ The radiolysis products of water, especially hydroxyl free radicals, are very effective in attacking the monomer and already formed polymer chain. At low dose, the network consists of polymer chains united through multifunctional junctions with no or very few closed cycles (effective crosslinks), thus forming giant molecules with branches and entanglements. When the radiation dose was increased beyond a certain value, polymer chains crosslinked and a gel was then obtained. γ -Ray-induced copolymerization of NIPA and MA is a free-radical process (**Scheme 1**).

The MA content in P(NIPA/MA) hydrogels was determined by titration of the uncrosslinked MA against NaOH (0.05 mol/L) to the phenolphthalein endpoint. It was found that the hydrogel composition was about the same as that of the mixture of comonomers in the feed, in accordance with yields of the reaction of polymerization close to 100%. The same results were found for similar hydrogels.^{20,21}

pH dependency of equilibrium swelling ratio

The equilibrium swelling behaviors of P(NIPA/MA) hydrogels were investigated as a function of pH (2–9)

at fixed ionic strength ($I = 1 \times 10^{-4}$ mol cm⁻³) and temperature ($T = 25^\circ\text{C}$). The equilibrium swelling studies were performed on three samples of each hydrogel at different pH values. Figure 1 shows the swelling behavior of P(NIPA/MA) hydrogels containing various mole ratios of MA with changing pH values. The equilibrium swelling ratios of nonionic PNIPA hydrogels at different pH values are also included in Figure 2 for comparison. For the PNIPA (without MA), the equilibrium swelling ratio was independent of the pH value because there is no ionizable group in this type of hydrogel. However, the equilibrium swelling ratio of the P(NIPA/MA) hydrogels increased with an increment of maleic acid content because of the increase in the carboxyl number and showed distinct swelling transitions between pH 3 and 4. Also notable is the fact that the addition of only a slight amount of MA comonomer (2.4 mol %) radically changed the swelling behavior of the hydrogel P(NIPA/MA)-1 (mole ratio 91.9./8.1) over that of P(NIPA/MA)-2 (mole ratio 89.5./10.5).

Determination of \bar{M}_c and χ parameters

The change in the equilibrium swelling ratio with pH was also evaluated for determination of the average molecular weight between crosslinks (\bar{M}_c) and polymer–solvent interaction parameter (χ). The left-hand side of eq. (13) is designated (A), whereas the coefficient of $1/\bar{M}_c$ is designated (B). (A) plotted against (B), a linear relation, must be obtained with χ and \bar{M}_c values as the intercept and inverse slope, respectively, expressed by

$$A = \chi + B/\bar{M}_c \quad (14)$$

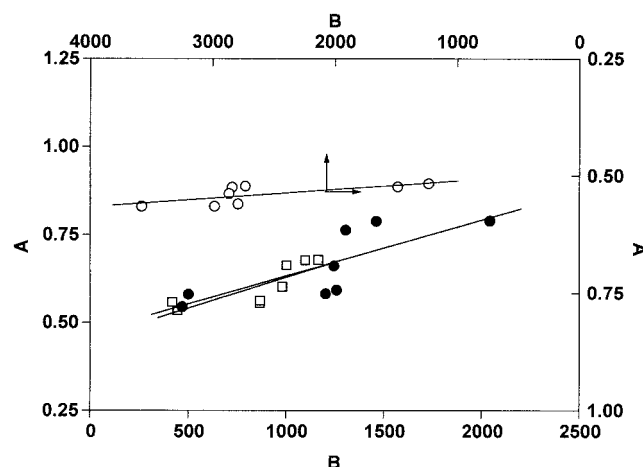


Figure 2 Determination of χ and \bar{M}_c values of hydrogels from swelling data. See the text for the explanation of A and B: (□) P(NIPA/MA)-1 ($r^2 = 0.815$); (●) P(NIPA/MA)-2 ($r^2 = 0.789$); (○) P(NIPA/MA)-3 ($r^2 = 0.703$).

TABLE I
 χ and \bar{M}_c Values of P(NIPA/MA) Hydrogels

Gel name	χ	\bar{M}_c
P(NIPA/MA)-1	0.45 ± 0.04	5700 ± 800
P(NIPA/MA)-2	0.47 ± 0.07	6300 ± 900
P(NIPA/MA)-3	0.49 ± 0.02	$54,000 \pm 3800$

The relevant experimental parameters to be used with eq. (13) are as follows: ionic strength $I = 1 \times 10^{-4}$ mol cm^{-3} ; molar volume of the solvent $V_1 = 18 \text{ cm}^3 \text{ mol}^{-1}$; the number of branches originating from a crosslinking site $\phi = 4$; $K_{a1} = 1.48 \times 10^{-3}$ and $K_{a2} = 8.51 \times 10^{-7}$ for the MA unit; $f_i = 0.081, 0.105$, and 0.318 ; and $\bar{V}_r = 83.8, 83.9$, and $114.0 \text{ cm}^3 \text{ mol}^{-1}$ for P(NIPA/MA)-1, P(NIPA/MA)-2, and P(NIPA/MA)-3 hydrogels, respectively.

In the preparation of hydrogels, no crosslinking agents were used in this work. Crosslinking agents were obtained by high-energy radiation. It was determined and definitively established that the radiation-induced crosslinking product has a functionality $\phi \geq 3$.²² In any case there are four branches originating from a crosslinking site. The reference state for ν_{2r} is, properly, that in which polymer chains have random walk configurations, although it is usually identified¹⁴ with the state of network just after synthesis. In this case, $\nu_{2r} = 0.168, 0.172$, and 0.215 for P(NIPA/MA)-1, P(NIPA/MA)-2, and P(NIPA/MA)-3 hydrogels, respectively. By using the experimentally measured polymer volume fraction ν_{2m} of the gels in their equilibrium-swollen state and the above-mentioned data, it is possible to establish the corresponding linear relationships as shown in Figure 2. The respective \bar{M}_c and χ values were determined by linear regression analysis of the lines given in Figure 2, which are listed in Table I. When the \bar{M}_c values listed in Table I are compared with the equilibrium swelling ratios shown in Figure 1, the hydrogels containing higher MA moieties swell more than the others at all given pH values. In other words, the \bar{M}_c values show an increase with increasing MA content in the gels. The former effect indicates that MA does not act as a crosslinking agent. Ionic content dependency of elastic behavior originates from the variation of the extent of cyclization reactions depending on the charge density of the polymer coil.²³ According to this approach, as the ionic content of the polymer increases, the growing chains in the pregel regime will assume an extended conformation. This will result in a decrease of cyclization reactions because of the thermodynamic excluded volume effect and therefore will increase the \bar{M}_c values of the final hydrogel. A similar behavior was observed during the swelling studies reported for poly(*N*-vinyl-2-pyrrolidone/itaconic acid) and poly(acrylamide/maleic acid) hydrogel systems.²⁰

By applying the Flory–Rehner theory, Erbil et al.²⁴ determined the χ and \bar{M}_c values for poly(*N*-isopropylacrylamide) and poly(*N*-isopropylacrylamide/itaconic acid) hydrogels prepared under different experimental conditions. These investigators found χ values of 0.53 and 0.51 for PNIPA homopolymer and the copolymer, respectively. These values are quite similar to those that we found from swelling measurements, 0.45 ± 0.05 and 0.49 ± 0.02 , for P(NIPA/MA) hydrogels.

Swelling dynamics of P(NIPA/MA) hydrogels

When a dry gel is immersed in solution, it penetrates into the gel in the form of a front, which shifts from the surface to the core. The rate of translation of the solvent front depends on both the shape²⁵ and the history of the polymer sample.²⁶ The swelling ratio (S_w) of P(NIPA/MA) hydrogels was calculated from the following equation:

$$S_w = \frac{W_s - W_d}{W_d} \quad (15)$$

where W_s is the weight of swollen hydrogel and W_d is the weight of dried hydrogel. Figure 3 shows a typical time dependency of swelling, observed for the pure PNIPA and P(NIPA/MA) hydrogels in pH 9 solution. As usual, swelling ratios of these hydrogels increase at short times and level off to a maximum swelling ratio at longer times. For the largest MA content, $S_w = 26$ and above, the maximum swelling ratio is reached instantly and from then on S_w is almost constant with time. This is a general trend in ionizable hydrogels. To determine the transport mechanism, initial swelling data were fitted to the following exponential equation²⁷:

$$F = kt^n \quad (16)$$

where F denotes the amount of solvent fraction at time t , k is a characteristic constant of the hydrogel, and n is a characteristic exponent of the mode of transport of the penetrate. The constants n and k were calculated from the slopes and intercepts of the graph of $\log F$ against $\log t$. For a hydrogel, a value of $n = 0.5$ indicates Fickian diffusion, a value $0.5 < n < 1$ indicates non-Fickian or anomalous transport, and $n = 1$ implies case II (relaxation-controlled transport). For the Fickian mechanism the sorption curve as a function of the square root of time is linear in the initial stage, and above the linear portion the absorption curve is concave to the abscissa.²⁸ From data shown in Figure 3 values of n were 0.58, 0.70, 0.74, and 0.85 for the pure PNIPA, P(NIPA/MA)-1, P(NIPA/MA)-2, and P(NIPA/MA)-3 hydrogels, respectively. These re-

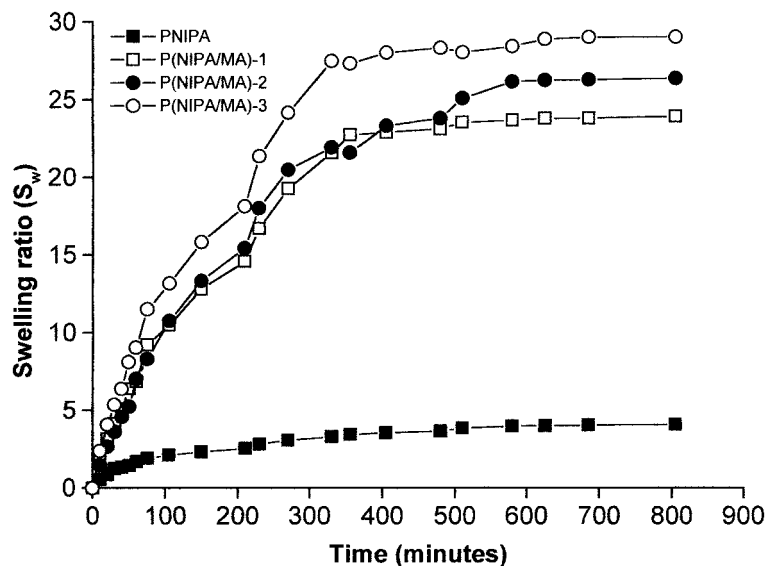


Figure 3 Time dependency of swelling in pH 9 solution of PNIPA and P(NIPA/MA) hydrogels. The curves show the trend of the data.

sults indicate that the swelling transport mechanism is of the non-Fickian type.

Temperature dependency of equilibrium swelling ratio

In an aqueous system, the temperature dependency of the swelling of a polymeric hydrogel is closely related to the temperature dependency of polymer–water and polymer–polymer interactions. When the hydrogel is cold, the swollen state is thermodynamically stable, but as the hydrogel warms, interaction of the molecular chains stabilizes the shrunken state instead. Much of the

fundamental swelling behavior of hydrogels was previously investigated by Tanaka²⁹ for PNIPA derivatives.

Figure 4 shows the temperature-dependent swelling of the hydrogels when the temperature of aqueous media increased from 4 to 65°C. The phase-transition temperature of PNIPA was around 32°C in water. However, P(NIPA/MA) hydrogels showed a slightly higher phase-transition temperature ($\sim 36^\circ\text{C}$) than that of PNIPA with the increase of MA content, and P(NIPA/MA)-3 did not exhibit the phase-transition temperature range between 20 and 65°C. By incorporation of hydrophilic comonomers, the phase-transi-

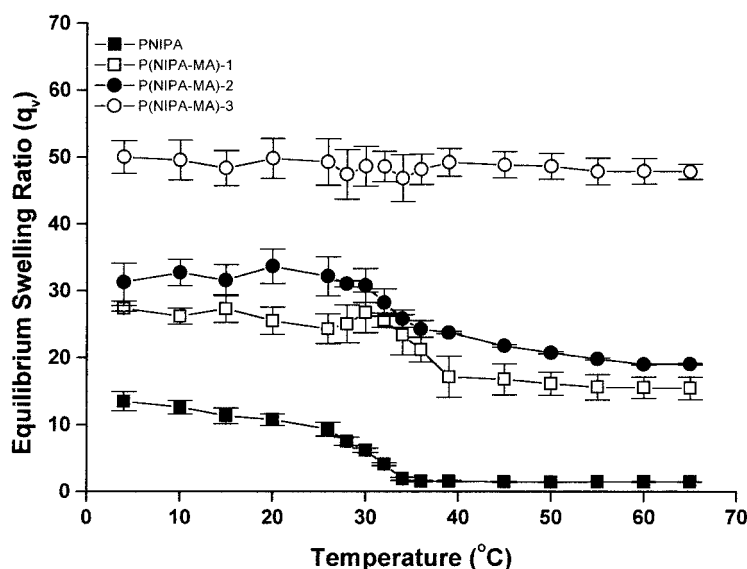


Figure 4 Effect of temperature on the equilibrium swelling ratio q_v of hydrogels. The curves show the trend of the data.

tion temperature shifted to higher temperature. Acrylic acid,³⁰ acrylamide,³¹ and *N,N*-dimethylacrylamide³² copolymers with NIPA are known to show higher phase-transition temperature. In the case of random copolymeric hydrogels, the hydrogels do not demonstrate a sharp phase transition at phase-transition temperature, which is attributed to a decrease of the hydrophobic aggregation of PNIPA sequences. Hydrophilic MA units in the copolymer chain disrupt the PNIPA sequences, resulting in the decreased aggregation force of dehydrated PNIPA chains at higher temperature.

CONCLUSIONS

In this study, ionic hydrogels were prepared by γ -ray-induced crosslinking copolymerization of NIPA and MA monomers. The swelling capacities of the hydrogels were measured in buffer solutions over a pH range of 2 to 9 and a temperature range of 4 to 65°C. The swelling studies show that pH and temperature are basic parameters affecting the equilibrium swelling ratios of P(NIPA/MA) hydrogels. Also notable is the fact that incorporation of only a few percent MA comonomer radically changes the swelling behavior of PNIPA, which becomes a completely responsive hydrogel by this modification. The equilibrium swelling values at each pH value were used to determine \bar{M}_c and χ parameters. On the other hand, from the dynamic swelling curves at pH 9, the mechanism of water transport through these hydrogels was determined as a non-Fickian type.

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