Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Modulation in Sorption Dynamics of a pH-Sensitive Interpenetrating Polymer Network (IPN)

A. K. Bajpai[a]; J. Bajpai[a]; Sandeep Shukla[a]; R. A. Kulkarni[b]
[a] Department of Chemistry, Bose Memorial Research Laboratory, Government Autonomous Science College, Jabalpur, India [b] Polymer Chemistry Division, National Chemical Laboratory, Pune, India

To cite this Article Bajpai, A. K. , Bajpai, J. , Shukla, Sandeep and Kulkarni, R. A.(2004) 'Modulation in Sorption Dynamics of a pH-Sensitive Interpenetrating Polymer Network (IPN)', Journal of Macromolecular Science, Part A, 41: 2, 211 — 230
To link to this Article: DOI: 10.1081/MA-120027304
URL: http://dx.doi.org/10.1081/MA-120027304

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A41, No. 2, pp. 211–230, 2004

Modulation in Sorption Dynamics of a pH-Sensitive Interpenetrating Polymer Network (IPN)

A. K. Bajpai,[1,*] J. Bajpai,[1] Sandeep Shukla,[1] and R. A. Kulkarni[2]

[1]Department of Chemistry, Bose Memorial Research Laboratory, Government Autonomous Science College, Jabalpur, India
[2]Polymer Chemistry Division, National Chemical Laboratory, Pune, India

ABSTRACT

The water sorption dynamics of a binary interpenetrating polymer network (IPN) composed of polyvinyl alcohol (PVA) and poly(acrylamide-co-acrylic acid) was studied gravimetrically. The IPN was characterized by IR spectral analysis and various network parameters such as molecular weight between crosslinks (M_c), crosslink density (q) and number of elastically effective chains (V_e) were also evaluated. The effects of various parameters such as composition of the IPN, pH, and temperature of the swelling medium and addition of inorganic salts were investigated on the kinetics of the swelling process. The dynamic swelling parameters such as the swelling exponent, diffusion constants and penetration velocity were evaluated and the possible mechanisms of water sorption were evolved on the basis of the swelling exponent (n), diffusion constant (D), and penetration velocity (v). The enthalpy of mixing of the IPN and the solvent (water) was also calculated using the Gibbs–Helmholtz equation.

Key Words: Polyvinyl alcohol; Poly(acrylamide-co-acrylic acid); Swelling.

---

[*]Correspondence: A. K. Bajpai, Department of Chemistry, Bose Memorial Research Laboratory, Government Autonomous Science College, Jabalpur 482 001, India; Fax: 0761-325514; E-mail: akbmrl@yahoo.co.in.

DOI: 10.1081/MA-120027304
1060-1325 (Print); 1520-5738 (Online)

www.dekker.com

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

INTRODUCTION

Hydrogels are macromolecular systems designed to accommodate a large amount of water into their network structure.[1] The structure of a hydrogel is able to retain the solvent forming a swollen gel phase and, in a crosslinked state, they do not dissolve regardless of the solvent. The water imbibing property 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,[2] dialysis membranes,[3] artificial implants,[4] burn dressings,[5] drug-delivery systems,[6] etc. Hydrogels are indeed a novel class of materials.

One of the most significant applications of hydrogels has been in constructing pH-sensitive macromolecular systems which could be capable of selectively releasing the drug to the desirable part of the body.[7] For instance, a hydrogel targeted to deliver the drug to the low pH region of the stomach should be adequately swollen in the acidic pH range while the drug carrier vehicles aimed at delivering the drug to GI tract must exhibit a larger degree of swelling in the alkaline pH range.[8] Thus, pH-sensitive hydrogel systems constitute an active area of research in pharmaceuticals.[9]

Polyvinyl alcohol (PVA) hydrogels[10] have been widely used in preparing drug-carriers because of their inherent non-toxicity, non-carcinogenicity, good biocompatibility, and desirable physical properties such as rubbery or elastic nature, low fouling potential, long-term pH and temperature stability and good film forming quality.[11] The PVA hydrogels have also gained wide pharmaceutical applications as drug-delivery matrices[12] or in the form of powders added to a mixture of other excipients for tablet formation.[13] In spite of the above mentioned remarkable biophysical properties of PVA based hydrogels, they often suffer from lacking in high water sorption capacity which is essentially needed for many biomedical applications. For instance, to facilitate biodegradation of the hydrogels upon arrival in the colon, a high degree of equilibrium swelling is needed.[14] Thus, a modification in chemical architecture of PVA hydrogels deserves attention.

Among various techniques available to enhance water sorption capacity of hydrogels include copolymerization of hydrophilic monomers, formation of blends and composites, etc. For example, copolymers of vinyl acetate and acrylic acid have been prepared in solution via a free radical process, using azobisisobutyronitrile (AIBN) as an initiator.[15] The resulting P(VAC-co-AA) was then hydrolyzed with methanol to yield (VA-co-AA) copolymers that can form pH-sensitive hydrogels. The structure of such copolymers were characterized by Zhang et al.[16] used high resolution ^{13}C-NMR spectroscopy analyzed their possible phase separation and Liou et al.[17] who studied their swelling characteristics.

The possibility of preparing blends of PVA and (PAA) or composite membranes thereof has also been examined.[18] Composite membranes of PVA and PAA exhibit protein permeability that can be controlled by an electric field. Shiga et al.[19] showed that such gels have interesting electric properties and can be used as actuators.[20] Their swelling characteristics were studied under varying experimental conditions.[21]

An important route to modify the physico-chemical properties of a hydrogel is the preparation of interpenetrating polymer networks (IPNs) which are conventionally defined as intimate combination of two polymers, at least one of which is synthesized or crosslinked in the immediate presence of other.[22] Although a wide range of blends and composites have been studied, IPN hydrogels are less reported.

An IPN is normally prepared by polymerizing and crosslinking a monomer in the presence of a preformed polymer network. In most of the investigations both the preformed polymer and the polymerizing monomer(s) are crosslinked by two different crosslinkers and thus an IPN is obtained. We, however, in the present investigation are attempting to prepare an IPN in which the preformed polymer is covalently bonded to the crosslinked polymer (or copolymer) network thus resulting in the formation of a three dimensional covalent network. For the preparation of the IPN, PVA has been opted as a preformed polymer and acrylamide and acrylic acid as comonomers which will be polymerized in the presence of *N*,*N*′-methylene-*bis*-acrylamide (MBA), a crosslinker.

EXPERIMENTAL

Materials

Polyvinyl alcohol (hot processed, mol. wt. 40,000, degree of hydrolysis 98.6%) was obtained from the Burgoyne Burbidges & Co., Bombay, India, and used as received. Acrylamide (AM) (Research Lab, Poona, India) was crystallized twice in methanol and dried in vacuum over anhydrous silica for a week. Acrylic acid (AA) (Wilson Laboratories, Bombay, India) was freed from the inhibitor by washing it with 0.1 N NaOH, H_2SO_4, and distilled water, respectively and finally distilling it under vacuum. *N*,*N*′-methylene-*bis*-acrylamide (Central Drug House, Bombay, India) was used as a crosslinking agent and used as received. Potassium persulphate (KPS) (Loba Chemie, Bombay, India) was employed as a free radical initiator. All other reagents used were of analytical grade and bi-distilled water was used throughout the experiments.

Method

Preparation of Interpenetrating Polymer Network

The IPN was prepared by conventional free radical polymerization method as described in our other communications.[23] In brief, 10.5 mM of AM, 7.2 mM of AA, 0.5 g of PVA, 0.12 mM of MBA, and 0.073 mM of KPS were added into a petri dish (2 inch, corning), and the mixture was homogenized. The total volume of the feed mixture was maintained to 15 mL. The petri dish was then kept at 80°C for 30 min so that the entire mass was solidified, which indicated the formation of gel. The gel was placed at 60°C in an oven for 2 h, where it changed into a thin semi-transparent film. The dried gel (xerogel) was washed by equilibrating it in distilled water for 15 days. A constant weight of the swollen IPN was noticed after 7 days, which implies that the IPNs were stable. The swollen gels were dried at 60°C for 24 h and stored in air-tight containers.

Swelling Measurements

The progress of the swelling process was monitored gravimetrically as described by other workers.[24] In a typical swelling experiment, a pre-weighed circular piece of the IPN (0.04 g) was immersed into a definite volume of bi-distilled water, taken out at different

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

time intervals, and soaked in between two filter papers by pressing gently. The swollen piece was then weighed and the swelling ratio (SR) was calculated by the following equation:

$$\text{Swelling ratio } (Q) = \frac{\text{Weight of swollen gel}}{\text{Weight of dry gel}} \tag{1}$$

Swelling Kinetics

The SR of different hydrogels were determined at various time intervals and the following equations[25] were used in analyzing the kinetic data:

$$\frac{W_t}{W_\infty} = kt^n \tag{2}$$

where W_t is the amount of water imbibed at time t, W_∞ is the amount of water imbibed at equilibrium, k and n are constants depending on the nature of the gel and types of sorption process, respectively. For instance, when n is 0.5, the water sorption is Fickian in nature while $n > 0.5$ implies for a non-Fickian process. Also, when n is unity then it indicates a Case II transport.

Similarly, the diffusion contants D were also determined by the following equation,[26]

$$\frac{W_t}{W_\infty} = 4\left(\frac{D_t}{\pi \ell^2}\right)^{1/2} \tag{3}$$

where D is the diffusion constant and ℓ is thickness of the hydrogel.

Penetration Velocity

The dynamic swelling properties of a polymer includes a solvent sorption rate, the rate of approach to equilibrium swelling, the solvent front velocity, and the transport mechanism controlling sorption. The solvent sorption rate indicates the solvent uptake per unit time and is directly related to the equilibrium swelling. The solvent sorption rate is important in drug-delivery applications and this has been evaluated in terms of the penetration velocity (v). In the present study, the penetration velocity (v) of solvent in each IPN was determined by the weight-gain method as described elsewhere.[27] The penetration velocity was calculated from the slope of the initial portion of the water uptake curve by the following:

$$v = \frac{1}{\rho A}\frac{dw}{dt} \tag{4}$$

where dw/dt is the slope of the weight-gain vs. time curve, ρ is the density of the swelling solvent, A is the area of one face of the disc.

IR Spectral Analysis

IR spectral analysis of the IPN film (semi-transparent) was performed by a Backman Accu Lab-6 Spectrophotometer.

RESULT AND DISCUSSION

IR Analysis of the Interpenetrating Polymer Network

As stated earlier, the present study aims at preparing IPNs of PVA and poly(acrylamide-co-acrylic acid) in which preformed polymer PVA is covalently linked to copolymeric chains thus constructing a three dimensional network. For this purpose, the polymerization temperature was selected as 80°C so as to facilitate the ester formation between hydroxyls of PVA and carboxylics of PAA segments of the copolymer. Thus, the following hypothetical structural model of PVA could be assumed:

i. Copolymeric chains of acrylamide and acrylic acid are crosslinked to each other by the crosslinker MBA, and
ii. Hydroxyls of PVA are bonded to carboxylis of PAA via ester formation.

The proposed hypothetical structure of the IPN is shown in Fig. 1.

The IR spectra clearly shows the presence of alcoholic hydroxyls at 3583 cm^{-1} (O–H stretching), amide group at 3563 cm^{-1} (N–H stretching), and carboxylic groups at 1730 cm^{-1} (carbonyl stretching), respectively. The observed peaks confirm the presence of PVA, polyacrylamide (PAM) and PAA in the IPN. A significant consequence of the observed hydroxyls (OH) in the IPN is that it also rules out the possibility of grafting of copolymeric chains onto PVA as otherwise the OH groups would have been absent in the spectra because of their involvement in the grafting reaction.

The IR spectra also confirms the presence of ester group at 1748 cm^{-1} (C=O stretching) which further supports the proposed ester formation reaction as mentioned above (ii). Another important observation in the IR spectra is the presence of anhydride

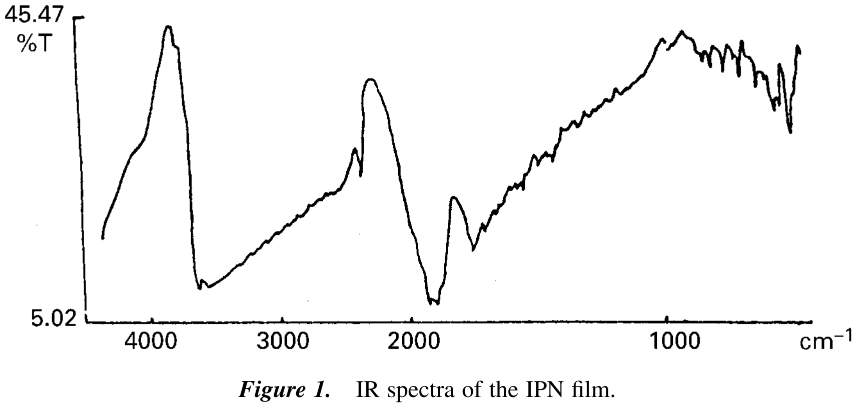

Figure 1. IR spectra of the IPN film.

group at 1921 and 1868 cm^{-1} (C=O stretching), which may be due to the possibility of a anhydride reaction between the two adjacent carboxylics of the PAA segments of the copolymer. It is worth mentioning here that the formation of ester and anhydride groups is also supported by the work of Arnat and coworkers,[28] who investigated the crosslinking reaction of PVA and PAA at high temperature and reported that whereas the anhydride formation was predominant crosslinking reaction, an ester formation was also detectable due to C=O and C–O–C vibrations, respectively.

Network Studies

One of the important parameters characterizing crosslinked polymers is M_c, the average molar mass between crosslinks, which is directly related to the crosslink density. The magnitude of M_c significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine M_c. Early research of Flory and Rehner laid the foundation for the analysis of equilibrium swelling. According to the theory of Flory and Rehner, for a perfect network:

$$M_c = -V_1 d_p \frac{V_s^{1/3} - V_s/2}{\ln(1 - V_s) + V_s + \chi V_s^2} \tag{5}$$

where M_c is the number average molar mass of the chain between crosslinks; V_l is the molar volume of water; d_p is the polymer density; V_s is the volume fraction polymer in the swollen gel; and χ is the Flory–Huggins interaction parameter between solvent and polymer.[29]

The SR (Q) is equal to $1/V_s$. Here, the crosslink density, q, is defined as the mole fraction of crosslinked units.

$$q = \frac{M_o}{M_c} \tag{6}$$

where M_o is the molar mass of the repeating unit.

Some authors define a crosslink density, V_e, as the number of elastically effective chains totally included in a perfect network, per unit volume, V_e is simply related to q since:

$$V_e = \frac{d_p N_A}{M_c} \tag{7}$$

where N_A is the Avogadro number. Then:

$$V_e = \frac{d_p N_A q}{M_c} \tag{8}$$

Since the hydrogel is a copolymeric structure, the molar mass of the polymer repeat unit, M_o, can be calculated using the following equation:

$$M_o = \frac{n_{AM} M_{AM} + n_{AA} M_{AA}}{n_{AM} + n_{AA}} \tag{9}$$

where n_{AM} and n_{AA} are the number of moles of acrylamide and acrylic acid, while M_{AM} and M_{AA} being the molar masses of the two monomers, respectively.

In a similar way, the value of polymer–solvent interaction parameter will also be calculated, i.e.,

$$\chi = \frac{n_{AM}X_{AM} + n_{AA}X_{AA}}{n_{AM} + n_{AA}} \tag{10}$$

The value of V_1, X_{AM}, X_{AA} were taken from the literature.[30,31] The values of M_c, q and V_e calculated for the IPNs containing varying amounts of crosslinker have been summarized in Table 1, which implies that the average molecular weights between crosslinks varies inversely, with the crosslinker content in the hydrogels.

Dynamic Model of Water Sorption

The hydrogel in the present study could be considered as a IPN in which specific interactions (ester groups) are operative between the macromolecular chains of PVA and the crosslinked copolymer (PAMAA). Between these network chains will be present free volume patches into which the penetrant water molecules may be accommodated. Now, for visualizing the nature of the dynamic swelling process let us consider the case when the hydrogel contacts a still aqueous medium (Fig. 2). As the penetrant invades the hydrogel surface, a moving front is observed that clearly separates the unsolvated glassy polymer region ahead of the front from the swollen and rubbery gel phase behind it.[32] Just ahead of the front, the presence of solvent plasticizes the polymer and causes it to undergo a glass to rubber transition.[33] Now the following possibilities arise:

i. If the glass transition temperature of the polymer (T_g) is well below the experimental temperature, the polymer will be in the rubbery state and polymer chains will have a higher mobility that allows an easier penetration of the solvent.[34] This clearly results in a Fickian diffusion (Case I) which is characterized by a solvent diffusion rate; R_{diff}, slower than the polymer relaxation rate, R_{relax} ($R_{diff} \ll R_{relax}$). The whole mechanism is modelled in Fig. 3.
ii. If the experimental temperature is below T_g, the polymer chains are not sufficiently mobile to permit immediate penetration of the solvent in the polymer core. This gives rise to a non-Fickian diffusion process which indcludes Case II diffusion and anamalous diffusion depending on the relative rates of diffusion

Table 1. Network parameters of the semi-IPN containing varying amounts of the crosslinker (MBA) at fixed composition of PVA = 0.5 g, AM = 10.5 mM, AA = 7.2 mM, KPS = 0.073 mM.

MBA (mM)	M_c (mM)	$q \times 10^3$ (mM)	$V_e \times 10^{-18}$ (mM)
0.06	39,573	1.80	1.05
0.13	35,223	2.02	1.17
0.19	21,034	3.39	1.90
0.380	11,163	6.39	3.7

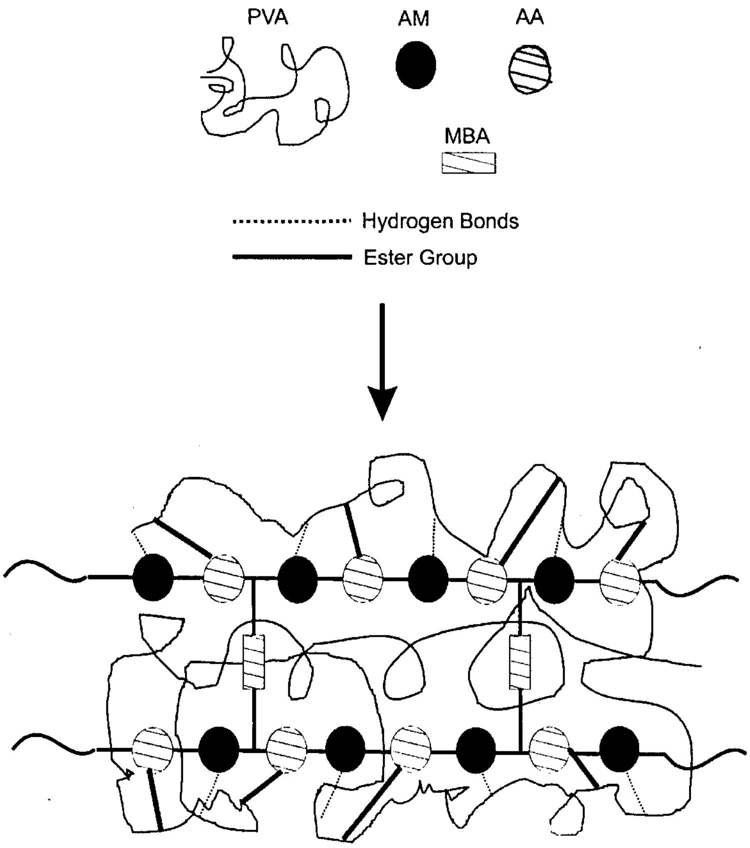

Figure 2. A schematic illustration showing the formation of the IPN.

and chain relaxation (for Case II, $R_{\mathrm{diff}} \gg R_{\mathrm{relax}}$ and for anamolous, $R_{\mathrm{diff}} \sim R_{\mathrm{relax}}$).

Both the possibilities of diffusion processes are depicted in Fig. 3(a) and (b), respectively.

Effect of Polyvinyl Alcohol Variation

The effect of PVA content of the IPN on its swelling ratio has been investigated by varying its concentration in the feed mixture in the range 0.5–1.0 g. The results are shown in Fig. 4, which indicate that with an increasing PVA content in the gel, the swelling ratio constantly decreases. The observed decrease in swelling ratio may be attributed to the fact that PVA is a hydrophilic polymer and will produce stronger interaction with the copolymer chains when present in increasing amounts in the IPN. This will consequently increase the compactness of the gel, and thus a smaller number of penetrant water molecules will be allowed to enter and swell the IPN. Obviously, this brings about a fall in

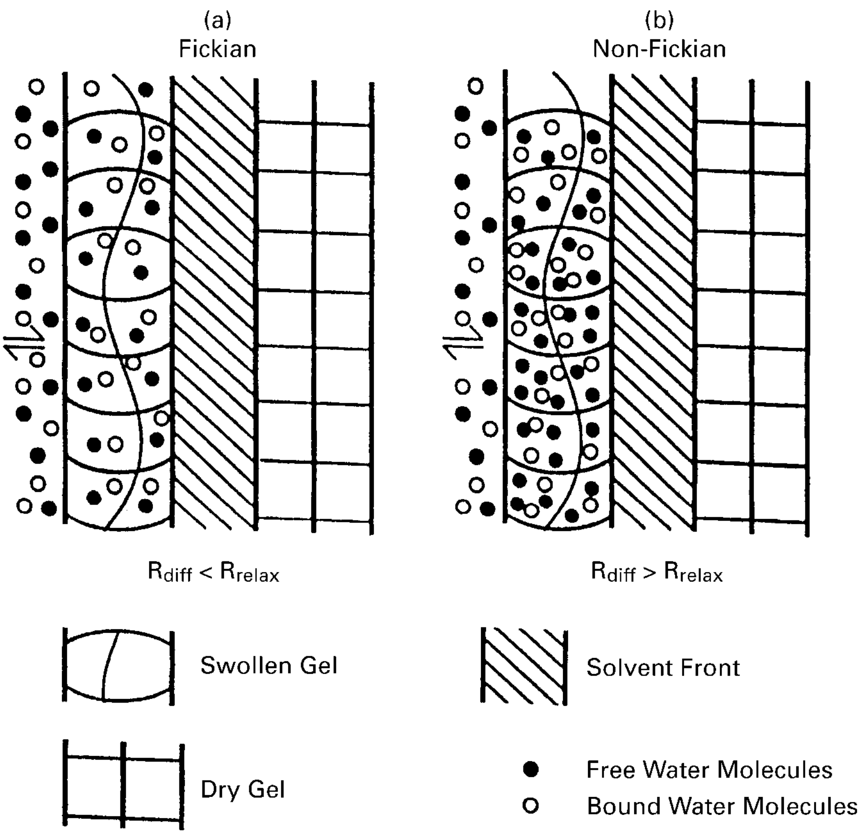

Figure 3. A hypothetical model depicting the dynamic water sorption process (a) Fickian and (b) non-Fickian.

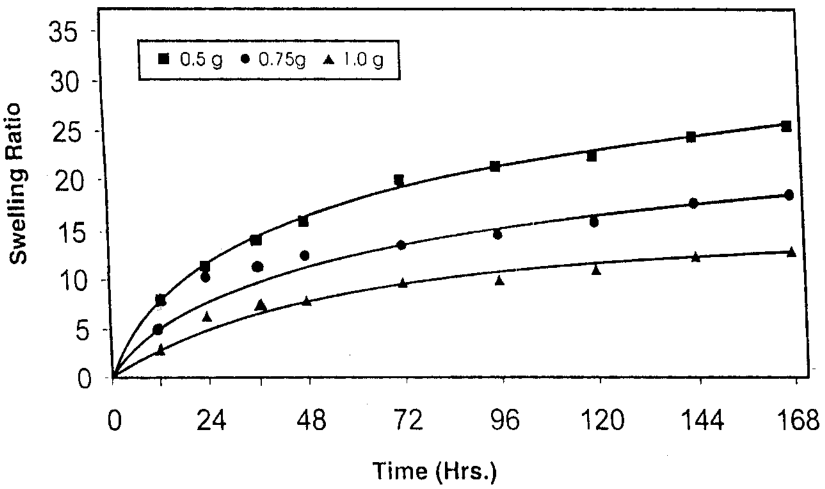

Figure 4. Effect of PVA variation in the feed mixture on the SR of the hydrogel.

the swelling ratio. A similar type of decrease in the swelling ratio has also been reported by Gravier et al.,[35] who synthesized hydrogels of PVA and sodium acrylate and noticed a fall in the swelling ratio when increasing number of molar ratios of PVA are present in the hydrogel samples.

Effect of Monomers Variation

When the concentration of AM, a hydrophilic, but non-ionic monomer increases in the concentration range 7.04–21.1 mM in the feed composition, the swelling ratio is found to decrease with increasing AM content. The observed fall in the swelling ratio is common as with increasing the proportion of PAM in the hydrogen, the network density increases which obviously brings about a decrease in the swelling ratio. It is also likely that an increased number of PAM chains in the IPN results in interchain hydrogen bonding between the amide group which produces a compact network. A similar type of observation has also been observed elsewhere.[36]

Another reason for the observed decrease in the swelling ratio with increasing AM content in the IPN may be that with greater amounts of AM in the feed mixture of the IPN, the polymer volume fraction increases in the IPN which directly reduces the mesh size.[9] The mesh size characterizes the space between macromolecular chains. Obviously, a decrease in mesh size will result in a penetration of a lesser number of water molecules into the IPN.

It is a common practice[37,38] to enhance the hydrophilicity of a hydrogel by the incorporation of ionizable functional groups, such as carboxyl groups into the network structure. When the functional groups are ionized, their fixed ions repel one another, and this repulsion leads to further swelling of the network. The extent to which the ionized hydrogel swells at equilibrium increases with an increase in the concentration of functional ionizable groups on the network. In the present study, a similar attempt has been made by copolymerizing AM with AA to produce a copolymer with ionizable polymer segments of PAA. The effect of increase in the concentration of AA on swelling ratio of the hydrogel has been investigated by varying the concentration of ionizable monomer in the feed mixture in the range 7.2–29.1 mM. The results are depicted in Fig. 5, which reveal that up to 14.5 mM the swelling ratio increases while beyond this concentration there is a fall in the swelling ratio. The results can be explained below.

The SR (Q) of a hydrogel can be best described by Flory's swelling theory as given below:

$$R^{5/3} = \frac{[(i/2V_{\mathrm{u}}S^{1/2}) + (1/2 - X_1)/V_1]^{1/2}}{(V_{\mathrm{e}}/V_{\mathrm{o}})} \tag{11}$$

where i/V_{u} is the concentration of fixed change referred to the unswollen network; S, the ionic concentration in the external solution; $(1/2 - X_1)/V_1$, the affinity of the hydrogel with water; and $V_{\mathrm{e}}/V_{\mathrm{o}}$, the crosslinked density of the hydrogel. Q has a relation to the ionic osmotic pressure, crosslinked density, and affinity of the hydrogel with water from the above equation. Now, with an increasing AA concentration, the number of carboxylate charged groups increase in the ionic polymer segment, which as a result of repulsions, widens the free volumes within the hydrogel, thereby increasing the water sorption rate.

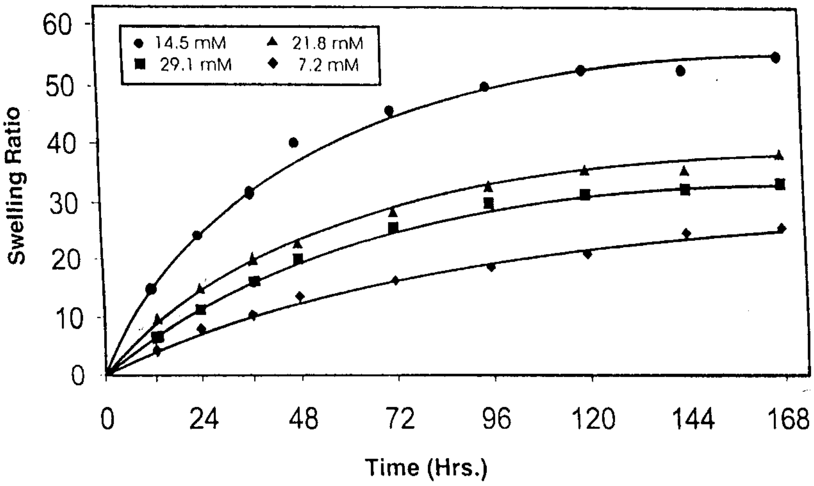

Figure 5. Variation in the SR of the hydrogel with varying amounts of AA in the feed mixture.

However, beyond an optimum concentration of AA in the hydrogel H-bonding forces become operative between the PVA chains and ionic segments of the copolymer. This clearly enhances the network density of the hydrogel which results in a decreased swelling ratio.

Effect of Crosslinker Variation

The swelling characteristics of a hydrogel could be desirably modified through the manipulation of the concentrations of the hydrogel components including polymer(s), monomer(s), crosslinking agent, and experimental protocol. It has been frequently observed[39] that increasing the percentage of crosslinker in the hydrogel, reduces the degree of swelling while affecting the swelling kinetics in a complex way. In the present study, the concentration of crosslinker MBA has been varied in the feed mixture in the range 0.06–0.38 mM. The results are displayed in Fig. 6, which imply that with increasing concentration of MBA, the swelling ratio and swelling rate decrease significantly. One more remarkable point is that at higher amounts of MBA, the equilibrium swelling is attained quite earlier as shown in the swelling ratio–time curves in Fig. 6. The observed decrease in degree of swelling with increasing MBA may be attributed to a subsequent decrease in solvent diffusivity and the relaxation rate of the polymer chains. Also, the increasing number of crosslinks reduce the average molecular weight (M_c) between crosslinks (Table 1), which, in turn, decreases the mesh sizes of the free volumes in the IPN. This obviously slows down the swelling rate and the swelling ratio. The reason for the early arrival of equilibrium swelling is that at a greater crosslink density in the IPN, the penetration of invading water molecules is much more difficult and this obviously makes the IPN as a "water-saturated hydrogel" at premature times. A similar type of findings have also been reported by other workers.[40]

Another reason, as noticed by some other workers,[41] may be that an increase in the crosslinked density of the IPN results in an increase in glass transition temperature (T_g) of

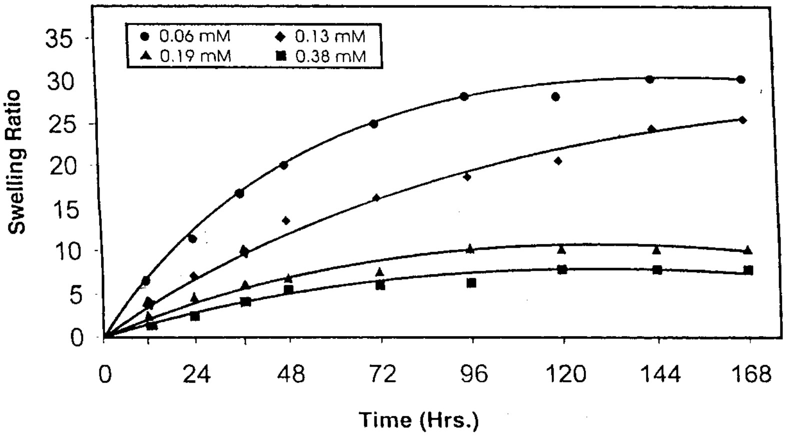

Figure 6. Effect of crosslinker on the SR of the hydrogel.

the polymer which because of glassy nature of the matrix does not permit loosening of the macromolecular chains and, therefore, results in a lower water sorption.

Effect of pH

The role of pH in affecting the swelling characteristics of hydrogel is of great practical significance, particularly when the hydrogel incorporates ionic polymer segments.[42] In the present study since the hydrogel contains copolymeric chains of AM and AA, the hydrogel is expected to exhibit a high pH-dependent swelling. The effect of pH on the swelling ratio of the hydrogel has been investigated by varying the pH of the swelling medium in the range 2.0–11.0. The results are depicted in Fig. 7, which clearly imply that

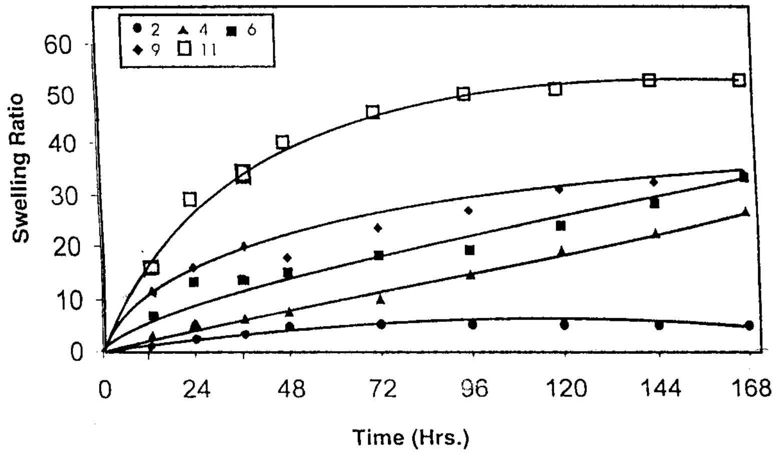

Figure 7. Variation in the SR of the hydrogel with varying pH of the swelling medium.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

the swelling ratio increases substantially with increasing pH of the medium. It also reveals from the figure that the swelling ratio rises markedly above pH 4.0 only and it becomes optimum at pH 11.0.

The results can be explained by the fact that the p*K*a value of PAA is 4.7[43] and, therefore, above pH 4.7 the carboxylic group (unesterified and produced by hydrolysis of ester) of the polymer will be present in the carboxylate ion form, thus producing repulsive forces among the ionic polymer segments. Due to this repulsion, the macromolecular chains of the hydrogel will stretch and the free volumes in the hydrogel widen. This clearly results in a larger swelling ratio. Similar larger water sorption at higher pH has also been reported by other workers.[44]

It has also been found that at pH 2.0 the swelling is substantially reduced which may be due to the compact arrangement of hydrogel chains resulting from the strong interaction between the PVA and PAMAA polymeric segments. This will also result in reluctancy of network chains towards relaxation and, therefore, an equilibrium swelling is attained at a much earlier time. However, at pH 11.0, where the swelling is much greater, an equilibrium swelling is also noticed at later time period which may be because of the reason that at later times the hydrogel chains might have relaxed so much that there is no further scope for more relaxation and as a consequence, an equilibrium swelling is attained.

Effect of Temperature

The temperature of the swelling medium is an important parameter that also affects the swelling pattern of the hydrogel. In the present work, the effect of temperature on the swelling ratio of the hydrogel has been investigated by varying it in the range 5°C–45°C. The results are depicted in Fig. 8, which clearly indicate that both the swelling rate and the swelling ratio increase with an increase in temperature. However, at 45°C, the swelling ratio decreases. The results are quite expected one as with rising temperature, the

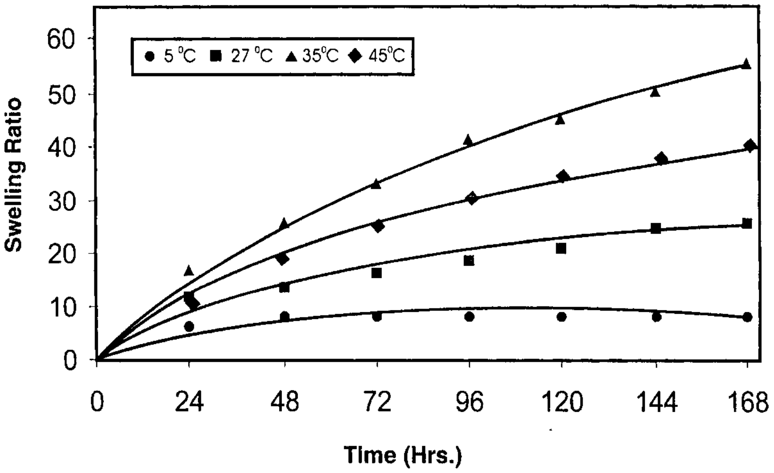

Figure 8. Effect of temperature of the swelling medium on the SR of the hydrogel.

segmental mobility of the hydrogel network also increases which consequently widens the free volume in the hydrogel which is accessible to penetrant water molecules. This clearly explains the increased swelling of the hydrogel.

A notable observation that can be realized in Fig. 8 is that in the higher temperature range, i.e., at 35°C and 45°C the swelling vs. time curves are not much different from each other. We also noted a similar type of trend in sorption study of another hydrogel composed of PVA and poly(acrylamide-co-styrene).[45] Such a result could be attributed to the fact that at a higher temperature the water molecules may detach themselves from the macromolecular chains and thus the net degree of swelling may decrease or remain nearly unchanged.

In order to have a more realistic insight into the temperature effect, the Gibbs–Helmholtz equation can be applied.[46]

$$\frac{d\ln(W_\infty)}{d(1/T)} = \frac{-\Delta H_\mathrm{m}}{\mathrm{R}} \tag{12}$$

where R is a gas constant and ΔH_m is the enthalpy of mixing between the dry polymer and an infinite amount of water. When W_∞ is plotted against equal swelling temperature $(1/T)$, a straight line with a negative slope is obtained (Fig. 9) which means an exothermic process. The value of ΔH_m has been calculated to be $-2.86\,\mathrm{kJ/mol}$.

Effect of Electrolyte

A hydrogel immersed in an aqueous solution changes its dimensions due to water sorption which is basically regulated by the balance between the osmotic pressure and the polymer elasticity of the gel.[47] The Donnan equilibrium theory evaluates the osmotic pressure (π_ion) of a hydrogel system by the following equation:

$$\pi_\mathrm{ion} = \mathrm{RT}\sum_i (c_i^{\,g} - c_i^{\,s}) \tag{13}$$

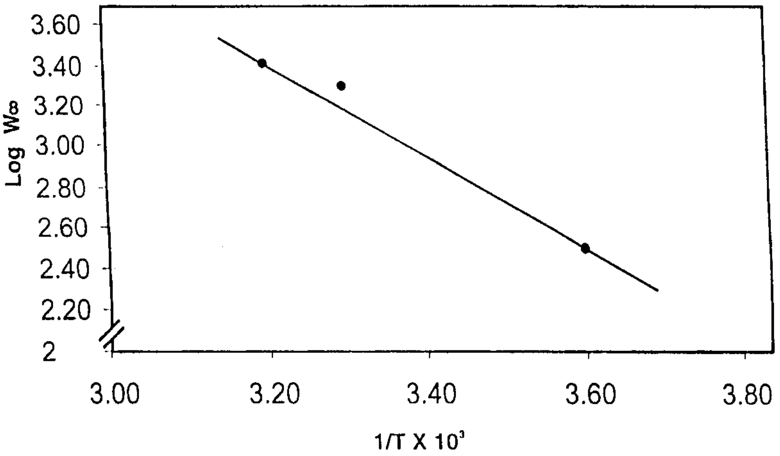

Figure 9. A plot drawn between $1/T$ and $\ln W_\infty$ for evaluating enthalpy of mixture ΔH_m.

where C is the mobile ion concentration of species i, and g and s represent gel and solution phases, respectively. It is clearly implied by the above equation that the greater the difference between the ionic concentrations of the hydrogel and the external solution, the larger the swelling. In the present work, the effect of ionic concentration on the SR of the hydrogel has been studied by adding NaCl to the bathing medium in the concentration range 0.01–0.1 M. The results are presented in Fig. 10, which reveal that up to 0.01 M concentration of added salt the SR, as well as the swelling rate decreases, while beyond the 0.01 M concentration, a fall in the degree of swelling is observed. The observed results may be explained as below.

On adding NaCl to the external swelling medium, the concentration of ions in the solution phase (C_i^s) increases which result in a decrease in the ionic osmotic pressure in Eq. (13) and therefore, the SR, but it is most likely that some of the added chloride ions diffuse into the network and produce repulsion with the carboxylate ions of the copolymeric segments. This, obviously results in a widening of the network chains, and as a consequence, the SR increases. However, beyond 0.01 M concentration of added salt, the term C_i^s increases greatly in Eq. (13), whereas the Cl^- ion entered into the network may not produce much loosening of the network chains due to limited elasticity of the IPN. This obviously results in a fall in the SR. Similar types of results have also been produced by other workers.[48]

Analysis of Dynamic Sorption Data

The water sorption process, as discussed previously, results mainly from the diffusion of the penetrant water molecules and segmental mobility of the macromolecular chains of the hydrogel. The two processes are quantitatively evaluated by Eqs. (3) and (2), respectively and their numerical values provide insight into the dynamics of the swelling process. Although the water uptake by the hydrogel is contributed by many factors, such as the elasticity of the network, solvent polymer interaction, polymer–polymer interaction,

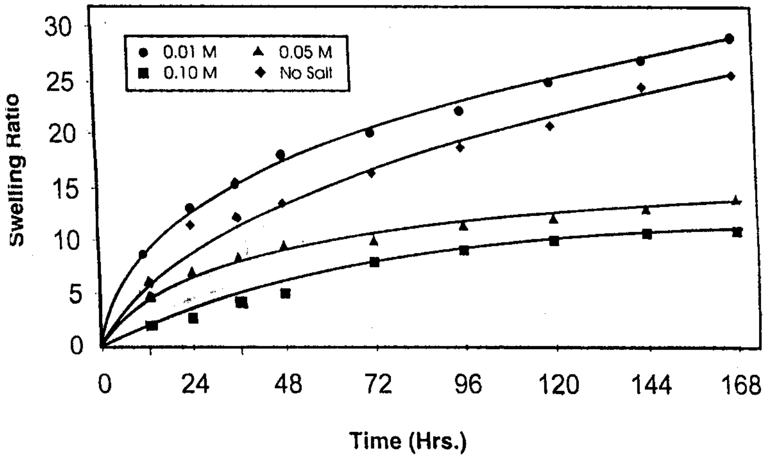

Figure 10. Variation in the SR of the hydrogel with varying ionic strength of the swelling medium caused by NaCl.

etc., however, the swelling exponent "*n*" given by Eq. (2) is a significant parameter in predicting the relative contributions of the diffusion and chain relaxation processes towards the swelling phenomenon. The values of *n* and *D* calculated from Eqs. (2) and (3) under varying experimental conditions have been summarized in Table 2. Now, the kinetic data could be analyzed to focus the following facts.

When the PVA content increases in the feed mixture of the IPN the SR is found to decrease. It is implied from Table 1 that the value of *n* is almost constant and is near to 0.5 which suggests for the Fickian nature of the process, i.e., a diffusion controlled swelling process where $R_{\text{diff}} > R_{\text{diff}}$. The reason for such a type of behavior is that PVA chains do not produce a highly compact network because of their hydrophilic nature and thus the diffusion becomes rate limiting. Nearly identical values of *D* also support the idea of independent behavior. The results are further supported by decreasing values of penetration velocity (v), which suggest that water molecules diffuse slowly into the IPN matrix.

In the case of AM variation, the values of *n* are near Fickian value and are not much different from each other thus suggesting that the sorption process is still diffusion controlled. This also implies from the data that the values of the corresponding diffusion constants are nearly constants.

On increasing the content of the ionic comonomer (AA) in the IPN, it is found that the swelling exponent *n* increases in the anamolous range, thus showing a deviation from Fickian diffusion. The observed non-Fickian swelling could be attributed to the greater water sorption by the IPN because of increasing chain relaxation due to existing repulsive forces. It has been noticed in several sorption investigations that the transport mechanism is strongly related to the SR, i.e., the larger the SR for a hydrogel, the more the transport mechanism tends towards non-Fickian behavior.[49]

When the concentration of crosslinker (MBA) increases in the feed mixture, the value of *n* decrease below the Fickian value, thus suggesting a decreasing Fickian process. The reason for

Table 2. Data showing the values of swelling exponent (*n*), diffusion constant (*D*) and penetration velocity (*v*) at varying compositions of the hydrogel.

PVA (g)	AM (mM)	AA (mM)	MBA (mM)	$D \times 10^9$ (cm^2/s)	*n*	$v \times 10^3$ (cm/s)
0.50	10.5	7.2	0.13	3.31	0.47	11.0
0.75	10.5	7.2	0.13	2.37	0.48	6.6
1.0	10.5	7.2	0.13	2.83	0.47	5.4
0.50	7.04	7.2	0.13	6.35	0.50	51.9
0.50	14.0	7.2	0.13	7.08	0.56	25.2
0.50	21.1	7.2	0.13	5.94	0.50	13.3
0.50	10.5	14.5	0.13	4.77	0.63	76.0
0.50	10.5	21.8	0.13	2.12	0.81	32.0
0.50	10.5	29.1	0.13	4.41	0.85	25.0
0.50	10.5	7.2	0.06	2.46	0.37	24.0
0.50	10.5	7.2	0.19	2.46	0.25	6.2
0.50	10.5	7.2	0.38	5.94	0.20	2.8

Note: PVA = Polyvinyl alcohol, AM = acrylamide, AA = acrylic acid, MBA = *N*,*N*′-methylene-*bis*-acrylamide.

the observed behavior is that a greater number of crosslinking chains in the hydrogel reduce the rate of chain relaxation on the one hand, while they also greatly slow down the water penetration rate which ultimately results in decreasing diffusivity of the water molecules. Thus, the occurrence of values lower than 0.5 are attributed to poor water sorption. This logic is further supported by decreasing diffusion constants and penetration velocity values.

Table 3 provides a very convincing logic on the effect of pH on *n* and *D* values. It is clear from the data that at pH 2.0 the process is far from being Fickian in nature. This is also true as being due to undissociated carboxylic groups in the IPN, the network is compact and diffusion of water is rather difficult. This is evident from very low values of the diffusion constant. However, at pH 4.0 (which is near p*K*a) the diffusion constant increases due to widening of the free volumes in the hydrogel and a Case II transport mechanism is obtained. An increase in the diffusion constant at pH close to p*K*a of acrylic acid may be due to an increased contribution of sorption coming from ionization in the Flory equation. Upon further increasing the pH of the external medium, the water transport tends to approach a Fickian value of 0.52, thus indicating an increasing tendency of chain relaxation which is expected also, as greater ionic repulsion at higher pH will give rise to faster chain relaxation.

CONCLUSION

The semi IPN prepared of PVA and poly(acrylamide-co-acrylic acid) display high swelling behavior which spreads over a period of seven days. The swelling rate decreases with increasing PVA content and follows the Fickian controlled kinetics. With an increase in the non-ionic monomer (AM) content in the feed mixture of the semi IPN the SR decreases, but yet the water sorption process remains almost Fickian in nature. When the proportion of ionic monomer (AA) increases in the hydrogel, the SR initially increases, while beyond an optimum concentration (14.5 mM) it further decreases. The swelling process is found to be diffusion controlled, i.e., Fickian in nature. The crosslinking density adversely affects the SR and the swelling process tends to move away from the Fickian nature with an increasing concentration of crosslinker (MBA) in the feed mixture. The penetration velocity also decreases with increasing MBA. The SR of the hydrogel is quite sensitive to the pH of the external medium and above p*K*a of AA (4.7) the SR substantially increases. It is seen that whereas at pH 4.0 the swelling is non-Fickian in nature (Case II transport), it gradually shifts towards a Fickian type of transport mechanism with an

Table 3. Variation in the swelling exponent (*n*), diffusion constant (*D*) and penetration velocity (*v*) at varying pH of the swelling medium for a fixed gel, PVA = 0.50 g, AM = 10.5 mM, AA = 7.2 mM, MBA = 0.13 mM, KPS = 0.73 mM.

pH	$D \times 10^9$ (cm^2/s)	*n*	$v \times 10^3$ (cm/s)
2.0	0.57	0.14	10.0
4.0	6.64	1.05	13.0
6.0	17.66	0.85	13.0
9.0	4.77	0.52	17.0
11.0	0.57	0.42	38.0

increase in pH. The temperature also affects the SR and with an increasing temperature of the bathing medium, the SR also increases. The presence of an electrolyte, such as NaCl, also affects the SR of the IPN and a decrease in degree of swelling is observed with increasing ionic strength of the swelling medium.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial assistance rendered to them by the Department of Science and Technology (New Delhi) in the form of a major research project (No. SP/S1/G-11/2001). The authors also acknowledge the Central Drug Research Institute (C.D.R.I.) Lucknow (India) for recording the IPN spectra.

REFERENCES

1. Tokita, M.; Tanaka, T.J. Friction coefficient of polymer networks of gels. J. Chem. Phys. **1991**, *95*, 4613.
2. Clayton, A.B.; Chirila, T.V. Hydrophilic sponges based on 2-hydroxy ethylmethacrylate. V. Effect of crosslinking agent reactivity on mechanical properties. Lou, X., Polym. Int. **1997**, *44*, 201.
3. Paul, W.; Sharma, C.P. Polyacrylanitrile-reinforced poly (vinyl alcohol) membrane: mechanical and dialysis performance. J. Appl. Polym. Sci. **1995**, *57*, 1447.
4. Willium, D.F. *Concise Encyclopedia of Medical and Dental Materials*; Pergamon Press: Oxford, England, 1990.
5. Rosiak, J.M.; Ulanski, P.; Pajewski, L.A.; Yoshii, F.; Makuuchi, K. Radiation formation of hydrogel for biomedical purposes: some remarks and comments. Radiat. Phys. Chem. **1995**, *46* (2), 161.
6. Dumitriu, M. Polymeric drug carriers. In *Polymeric Biomaterials*; Dumitriu, S., Ed.; Marcel Dekker: New York, 1994.
7. Friend, D.R. *Oral Colon-Specific Drug Delivery*; Friend, D.R., Ed.; CRC Press: Boca Raton, FL, 1992.
8. Akala, E.O.; Kopeckova, P.; Kopecek. Novel pH sensitive hydrogel with adjustable swelling kinetics. V. J. Biomaterials **1998**, *19*, 1037.
9. Risbud, M.V.; Hadikar, A.A.; Bhat, S.V.; Bhonde, R.R. pH sensitive free dried chitosen-polyvinyl pyrrolidone hydrogels as controlled release system for antibiotic delivery. J. Contr. Rel. **2000**, *68*, 23.
10. Hyon, S.H.; Cha, W.I.; Ikada, Y.; Kita, M.; Ogura, Y.; Honda, Y. J. Biomater. Sci. Polym. Ed. **1994**, *5*, 397.
11. Masuda, M. *Polyvinyl Alcohol*; Finch, C.A., Ed.; John Wiley and Sons Ltd, 1992.
12. Urushizaki, F.; Yamaguchi, H.; Nakamura, K.; Namagiri, S.; Sugibayashi, K.; Morrimonto, Y. Swelling and mechanical properties of poly(vinyl alcohol) hydrogels. Int. J. Pharm. **1990**, *58*, 135.
13. Peppas, N.A. Hydrogels of poly(vinyl alcohol) and its copolymers. In *Hydrogel in Medicine and Pharmacy. Vol. II, Polymers*; Peppas, N.A., Ed.; CRC Press: Boca Raton, Florida, 1987; 1.

14. Yeh, P-Y.; Kopeckova, P.; Kopecek, J. Degradability of hydrogels containing azoarmatics crosslinks. Macromol. Chem. Phys. **1995**, *196*, 2183.
15. Klee, D.; Hocker, H. Polymers for biomedical applications: improvement of interface compatibility. Adv. Polym. Sci. **2000**, *149*, 1.
16. Zhang, X.; Takegochi, K.; Hikichi, K. Phase separation and thermal degradation of poly(vinyl alcohol)/poly(methylacrylic acid) and poly(vinyl alcohol)/poly(acrylic acid) systems by ^{13}C c.p./m.a.s.n.m.r. Polymer **1992**, *33*, 718.
17. Liou, F.J.; Niu, G.C.C.; Wang, Y.J. Preparation and characterization of two HEMA/PVA copolymers: poly[HEMA-co (PVA-AA)] and poly[HEMA-co-(PVA-MA)]. Appl. Polym. Sci. **1992**, *46*, 1967.
18. Rhim, J.W.; Sohn, M.Y.; Lee, K.H. Pervaporation separation of binary organic aqueous liquid mixtures using crossinked PVA membranes, II. Phenol–water mixtures. J. Appl. Polym. Sci. **1994**, *52*, 1217.
19. Shiga, T.; Fukumori, K.; Hirose, Y.; Okada, A.; Kurauchi, T. Pulsed MMR study of the structure of poly(vinyl alcohol)–poly(sodium acrylate) composite hydrogels. J. Polym. Sci. Polym. Phys. **1994**, *32*, 85.
20. Park, J.B. *Biomaterials Science and Engineering*; Plenum Press: New York, 1984.
21. Hukim, D.W.L.; Leahy, C.J.; Mathias, K.J. Biomaterials defining the mechanical properties of natural tissues and selection of replacement materials. J. Mater. Chem. **1990**, *9*, 629.
22. Sperling, L.H. *Source Based Nomenclature of Polymer Blends*; IPN's and Related Materials, Division of Polymer Chemistry Nomenclature Committee Document, 1994.
23. Bajpai, A.K.; Shrivastava, M. Dynamics swelling behavior of polyacrylamide based three component hydrogels. J. Macromol. Sci. Pure & Appl. Chem. **2000**, *A37* (9), 1069.
24. Peppas, N.A.; Wright, S.L. Solute diffusion poly(vinyl alcohol)/poly(acrylic acid) interpenetrating networks. Macromolecules **1996**, *29*, 8798.
25. Walker, C.M.; Peppas, N.A. Solute and penetrant diffusion in swellable polymer: V. Swelling of multi-ethylene glycol dimethylacrylate copolymers. J. Appl. Polym. Sci. **1990**, *39*, 2043.
26. Knop, K. Influence of buffer solution composition on drug release from pellets coated with neutral and quaternary acrylic polymers and on swelling of free polymers films. Eur. J. Pharm. Sci. **1996**, *4*, 293.
27. Lee, W.F.; Yeh, P-L. Thermoreversible hydrogels. IV. Effect of some factors on the swelling behavior of *N*-tetra hydrofurfurylacrylamide. J. Appl. Polym. Sci. **1998**, *68*, 1597.
28. Arndt, K.F.; Richter, A.; Ludwig, S.; Zimmerman, J.; Kressler, J.; Kuckling, D.; Adler, H.J. Poly(vinyl alcohol)/poly(acrylic acid) hydrogels: FTIR spectroscopic characterization and work at transition point. Acta Polymerica **1999**, *50* (11–12), 383.
29. Ding, Z.Y.; Akinois, J.J.; Saloyev, R. Model filled polymer. VI. Determination of crosslinking density of polymeric beads by swelling. J. Polym. Sci. Poly. Phys. **1991**, *29*, 1035.
30. Baker, J.P.; Hong, L.H.; Blanch, H.W.; Prausnitz, J.M. Swelling equilibria for positively ionized polyacrylamide hydrogels. Macromolecular **1990**, *23*, 1096.
31. Gudeman, L.F.; Peppas, N.A. Preparation and characterization of pH sensitive interpenetrating networks of poly(vinyl alcohol) and poly(acrylic acid). J. Appl. Polym. Sci. **1995**, *55*, 919.
32. Alfrey, T.; Gurnee, E.F.; Lloyd, W.G. Solute and penetrate diffusion in swellable polymers. II. Verification of theoretical models. J. Polym. Sci. **1966**, *C12*, 249.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

33. Thomas, N.L.; Windle, A.H. A deformation model for case II diffusion. Polymer **1980**, *21*, 613.
34. Grinsted, R.A.; Clark, L.; Koenig, J.L. Study of cyclic sorption–desorption into poly(methyl methacrylate) rods using NMR imaging. Macromolecules **1992**, *25*, 1235.
35. Graiver, D.; Hyon, S-H.; Ikada, Y. Poly (vinyl alcohol)–poly(sodium acrylate) composite hydrogel. I. Kinetic of swelling and dehydration. J. Appl. Polym. Sci. **1995**, *57*, 1299.
36. Firestone, B.A.; Siegel, R.A. Kinetics and mechanisms of water sorption in hydrophobic, ionizable copolymers gels. J. Appl. Polym. Sci. **1991**, *43*, 901.
37. Hariharan, D.; Peppas, N.A. Swelling of ionic and natural polymers networks in ionic solutions. J. Membr. Sci. **1993**, *78*, 1.
38. Peppas, N.A.; Khare, A. Preparation, structure and diffusional behavior hodrogels in controlled release. Adv. Drug. Deliv. Rev. **1993**, *11*, 1.
39. Robert, C.R.; Buri, P.A.; Peppas, N.A. Effect of degree of crosslinking on water transport in polymer microparticles. J. Appl. Polym. Sci. **1985**, *30*, 301.
40. Urdahl, K.G.; Peppas, N.A. Anamalous penetrate transport in glossy polymers V. Cyclohexane transport in polystyrene. J. Appl. Polym. Sci. **1987**, *33*, 2669.
41. Ramaraj, B.; Radhakrishnan, G. Modification of dynamic swelling behavior of poly(2-hydroxyethylmethylacrylate) hydrogels in water through interpenetrating polymer networks (IPNs). Polymer **1994**, *35* (10), 2167.
42. Shin, H.S.; Kim, S.Y.; Lee, Y.M.; Lee, K.H.; Kim, S.J.; Rogers, C.E. Permeation of solutes through interpenetrating polymer network hydrogels composed of poly(vinyl alcohol) and poly(acrylic acid). J. Appl. Polym. Sci. **1998**, *69*, 479.
43. Greenwald, H.L.; Luskin, L.S. *Handbook of Water Soluble Gums and Resins*; Davidson, R.L., Ed.; McGraw Hill: New York, 1980.
44. Byun, J.I.; Lee, Y.M.; Cho, C.S. Swelling of thermosensitive interpenetrating polymers networks composed of poly(vinyl alcohol) and poly(acrylic acid). J. Appl. Polym. Sci. **1996**, *61*, 697.
45. Bajpai, A.K.; Bajpai, J.; Shukla, S. Water sorption through a semi-interpenetrating polymer network (IPN) with hydrophilic and hydrophobic chains. React. Funct. Polym. **2001**, *50*, 9.
46. Korsmeyer, R.W.; Merrwal, E.W.; Peppas, N.A. Solute and penetrate diffusion in swellable polymers. III. Verification of theoreticals model. J. Polym. Sci. Polym. Phys. Ed. **1986**, *24*, 409.
47. Flory, P.J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
48. Baker, J.P.; Blanch, H.W.; Prausnitz, J.M. Swelling properties of acrylamide-based ampholytic hydrogels: comparison of experiments with theory. Polymer **1995**, *36*, 1061.
49. Lee, W.F.; Yeh, P.L. Thermoreversible hydrogels. IV. Effect of some factors on the swelling behavior of *N*-tetrahydrofurfuralacrylamide. J. Appl. Polym. Sci. **1997**, *65*, 909.

Received February 2003
Accepted July 2003