Preparation and Characterization of pH-Sensitive, Interpenetrating Networks of Poly(vinyl alcohol) and Poly(acrylic acid)

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SYNOPSIS

Hydrogels with varying cross-linking ratio and ionic content were prepared from interpenetrating networks of poly(vinyl alcohol) and poly(acrylic acid). Equilibrium swelling studies were conducted and the average molecular weight between cross-links, $\bar{M}_c$, and mesh size were determined. Hydrogels with large $\bar{M}_c$ values were found to swell to a greater extent than those with small $\bar{M}_c$ values. It was also observed that an increase in $\bar{M}_c$ yielded faster swelling and deswelling rates, as the rates for membranes with $\bar{M}_c$ = 18,000 were about twice as fast as were the rates for membranes with $\bar{M}_c$ = 34,000. Oscillatory swelling behavior was investigated in response to changes in the pH and ionic strength of the swelling medium. A change in pH from 3 to 6 caused an ionization of the hydrogels and an increase in the weight swelling ratio, with a greater increase exhibited by IPNs with a higher ionic content. Increase in pH also caused an increase in the average mesh size. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Membrane-separation processes require high permeant flux to maintain cost and energy consumption at reasonable levels, good mechanical strength for withstanding pressure and long use, and resistance to fouling by permeants. On the molecular level, the pores or network mesh within a membrane must be of sufficient size to allow the desired permeants to pass while rejecting others. In homogeneous, nonporous gel membranes, which exhibit a uniform structure throughout, transport occurs through the mesh of the network. Membranes containing pores with diameters in the 200–500 nm range are termed microporous,[1] whereas macroporous membranes contain pores of diameter greater than 500 nm.

Since hydrogels are hydrophilic, strong, and easily processed, they have been investigated for use in membrane processes, especially in bioseparations and medical applications. Ionizable, "environmentally sensitive," hydrogel networks are especially attractive because their permeability can be controlled not only by changing their molecular structure but also by adjusting external conditions. The desirable qualities of hydrogels have led to this work, which focuses on membranes of poly(acrylic acid)—an ionizable polymer—and poly(vinyl alcohol).

The hydrophilicity of such hydrogels can be enhanced by the incorporation of ionizable functional groups, such as carboxyl groups. 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. The equilibrium swelling ratio is also a function of the properties[2,3] of the swelling medium, including the pH and the ionic strength. An increase in the concentration of ions (ionic strength) in the swelling medium has been found[3] to decrease the equilibrium swelling ratio of an ionizable hydrogel.

The hydrogels investigated here for membrane applications were poly(vinyl alcohol) (PVA) and

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poly(acrylic acid) (PAA). PVA is of interest because of its strength, processability, low fouling potential, and long-term temperature and pH stability. PAA is anionic, containing carboxyl groups that become ionized[4] at pH values above the pK_a of 4.7. Membranes prepared from cross-linked PAA and from copolymers of AA with hydroxyethyl methacrylate (HEMA) exhibited higher equilibrium swelling ratios as pH and AA content (in the copolymers) were increased.[5]

Copolymers of vinyl acetate and acrylic acid have previously been prepared in solution via a free-radical process, using azobis-methylpropionitrile (AIBN) as an initiator.[6] The resulting P(VAc-co-AA) was then hydrolyzed with methanol to yield P(VA-co-AA) copolymers that can form pH-sensitive hydrogels. The structure of such copolymers has been well characterized by Zhang et al.[7] who used high-resolution ^{13}C-NMR spectroscopy to analyze their possible phase separation and Liou et al.[8] who studied their swelling characteristics.

The possibility of preparing blends of PVA and PAA or composite membranes thereof has also been examined.[9-13] Composite membranes of PVA and PAA[10] exhibit protein permeability that can be controlled by an electric field. Shiga et al.[11,12] showed that such gels have interesting electrical properties and can be used as actuators.[14,15] Their swelling characteristics have been studied under a variety of experimental conditions.[16-18]

Although a wide range of blends and composites of PVA and PAA has been prepared, interpenetrating polymer network (IPN) hydrogels have not been reported. A sequential IPN is prepared[19] by polymerizing and cross-linking a monomer in the presence of a preformed polymer network. A simultaneous IPN is synthesized by mixing two monomers, along with their respective initiators and cross-linking agents, to allow the formation of two interconnected networks simultaneously.

Interpenetrating network hydrogels of PVA and PAA will be investigated here because these two polymers are miscible with one another and can each be polymerized and cross-linked in aqueous solution. A combination of the two polymers should provide strength, hydrophilicity, and biocompatibility, in addition to environmental sensitivity.

EXPERIMENTAL

Synthesis of IPN Hydrogels

Poly(vinyl alcohol) (PVA; Elvanol® 90-50, E.I. duPont de Nemours and Co., Wilmington, DE) was added to deionized water and heated at 85–90°C for 4–5 h to make a solution containing 10% PVA by weight. The number-average and weight-average molecular weights of the PVA were $\bar{M}_n$ = 35,420 and $\bar{M}_w$ = 79,200, respectively, and the degree of hydrolysis was 99.6%. Acrylic acid (AA; Aldrich Chemical Co., Milwaukee, WI) was combined with AIBN (0.5–1% by weight). The two solutions were then combined to yield PVA–AA molar ratios of 50 : 50, 60 : 40, or 67 : 33.

Glutaraldehyde and ethylene glycol dimethacrylate (EGDMA) (Aldrich) were used as cross-linking agents. The procedure involved the addition of EGDMA (0.5–1% by weight) to the AA–AIBN mixture, which was then combined with the PVA solution. The resulting mixture was poured into Petri dishes to form films 2–4 mm thick. The dishes were tightly covered with Saran Wrap® and placed in an oven at 62°C for 20 h to induce polymerization and cross-linking. The glutaraldehyde mixture was then added at a cross-linking ratio, X, of 0.02 mol glutaraldehyde/mol PVA repeating unit, and the mixture was heated at 73 ± 1°C for 40 min. The quantities of reactants used to prepare these IPN hydrogels are summarized in Table I.

In addition to the PAA/PVA hydrogels, hydrogels of the PVA homopolymer were prepared by combining the glutaraldehyde mixture (X = 0.019 mol/mol) with the 10% aqueous PVA solution and heating at 73°C for 40 min.

Swelling Studies

Investigation of the cross-linked structure of the prepared hydrogels was done by the method of Meadows and Peppas.[1] Squares of approximately 1 cm^2 were cut from each sample following polymerization. Sample weights were measured in air and in a nonsolvent (n-heptane). The latter weight was obtained by placing the sample in a stainless-steel mesh basket suspended in heptane. The samples were then placed in deionized water, allowed to swell to equilibrium, and again weighed in air (after being blotted with a tissue to remove surface moisture) and in n-heptane. Finally, the samples were dried at ambient conditions and under vacuum, and their weights in air were measured. The five weights thus determined for each sample were used for calculation of the polymer volume fraction in the relaxed (before swelling) and swollen states.

In the equilibrium swelling studies, dried samples were placed in a solution of the desired pH (3–8), ionic strength (0, 0.01, or 0.1M), and temperature (25 or 37°C). The pH was adjusted by addition of hydrochloric acid or sodium acetate (Mallinckrodt, Paris, KY) to water. Every 3–5 days, each sample

Table I Quantities of Reactants and Corresponding Cross-linking Ratios in the Preparation of PVA/PAA IPN Hydrogels[a]

Sample Code No.	PAA Content (Mol %)	Mass of AA (g)	Mass of EGDMA (g)	Volume of 25% Aqueous Glutaraldehyde (mL)	Nominal Cross-linking Ratio, X (mol/mol)
I4b'	50	1.6	0.010	0.13	0.009
I5	50	1.6	0.010	0.15	0.010
I1e	50	1.6	0.010	0.17	0.011
I4B	50	1.6	0.010	0.22	0.014
I1d	50	1.6	0.010	0.22	0.014
I4	50	1.6	0.010	0.22	0.014
L4	60	2.5	0.063	0.05	0.008
L4'	60	2.5	0.063	0.12	0.011
L2b'	60	2.5	0.063	0.15	0.012
L2b	60	2.5	0.063	0.20	0.015
L2	60	2.5	0.063	0.22	0.016
L3	60	2.5	0.063	0.22	0.016

[a] Each membrane was prepared using 10 g 10% aqueous PVA in addition to the reactants listed above.

was removed from the solution, blotted, and weighed. Measurements were continued until a constant weight was reached for each sample. This weight was used to calculate the equilibrium weight swelling ratio.

For investigation of the oscillatory swelling behavior, PAA/PVA IPN hydrogel samples were first equilibrated in a solution of pH 3, then alternated between solutions of pH 6 and 3, immersed for several hours in each solution. Weights were measured at time intervals of between 5 and 30 min.

RESULTS AND DISCUSSION

Synthesis

The preparation of hydrogels from PAA/PVA IPNs was investigated. The IPN hydrogels were subsequently used in swelling studies for determination of their cross-linked structure and evaluation of their response to changes in external pH, ionic strength, and temperature.

The technique used to prepare IPNs was successful in providing the desired cross-linked hydrogels. Experimental parameters that were varied during the IPN preparation were the amount of glutaraldehyde used, the heating (reaction) time, and the PAA–PVA ratio. Their effects on swelling of the samples will be discussed below.

Characterization of the cross-linked structure of the PVA/PAA IPN hydrogel samples was achieved by equilibrium swelling studies in water at 25°C as

described by Meadows and Peppas[1] and Peppas and Barr-Howell.[20] The polymer volume fraction in the gels immediately after preparation (relaxed state), $v_{2,r}$, and the polymer volume fraction of the swollen gels (swollen state), $v_{2,s}$, were determined using eqs. (1) and (2):

$$v_{2,r} = \frac{V_p}{V_{g,r}} \quad (1)$$

$$v_{2,s} = \frac{V_p}{V_{g,s}} \quad (2)$$

Here, V_p is the volume of the dry polymer sample, and $V_{g,r}$ and $V_{g,s}$, the gel sample volumes before and after equilibrium swelling, respectively. These volumes were determined from the weight of the dry polymer, W_d; the weights in air, $W_{a,r}$, and in n-heptane, $W_{h,r}$, before swelling; and the weights in air, $W_{a,s}$, and in n-heptane, $W_{h,s}$, after swelling. They were calculated using eqs. (3) and (4), where ρ_d and ρ_h are the densities of the polymer and n-heptane, respectively:

$$V_p = \frac{W_p}{\rho_p} \quad (3)$$

$$V_{g,r} = \frac{W_{a,r} - W_{h,r}}{\rho_h} \quad (4)$$

$$V_{g,s} = \frac{W_{a,s} - W_{h,s}}{\rho_h} \quad (5)$$

The equilibrium polymer volume fractions in equilibrium swollen IPN gels are presented in Table II for hydrogels of varying cross-linking ratio, X (mol cross-linking agent/mol PVA repeating unit), and varying PAA content. The data show that an increase of the cross-linking ratio led to an increase of the polymer volume fraction, as denser networks could not swell appreciably. Therefore, adjusting the amount of cross-linking agent used in the synthesis process is an effective means of *controlling the cross-linked structure* of the IPN hydrogels prepared.

Molecular Weight Between Cross-links

The equilibrium swelling data were used to evaluate the cross-linked structure of the IPN samples. Typically, the number-average molecular weight between cross-links, $\bar{M}_c$, was calculated. This parameter is an indication of the cross-linked nature of the IPN hydrogels as high values of $\bar{M}_c$ imply loosely cross-linked hydrogels.

First, the theoretical values of $\bar{M}_{c,t}$ were calculated from eq. (6) using the nominal cross-linking ratio, X:

$$\bar{M}_{c,t} = \frac{M_r}{2X} \qquad (6)$$

Here, M_r is the molecular weight of the IPN repeating unit that was calculated as the average of the repeating units of PVA ($M_r = 44$) and PAA ($M_r = 72$), based on the molar ratios of the polymers in the IPN samples.

Experimental values of $\bar{M}_{c,e}$ were calculated using an expression developed by Peppas and Merrill[21] for swollen networks produced by cross-linking in solution:

$$\frac{1}{\bar{M}_{c,e}} = \frac{2}{\bar{M}_n} - \frac{\frac{\bar{v}}{\bar{V}_1}[\ln(1 - v_{2,s}) + v_{2,s} + \chi v_{2,s}^2]}{v_{2,r}\left[\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_{2,s}}{v_{2,r}}\right)\right]} \qquad (7)$$

Here, $\bar{V}_1$ is the molar volume of water (18.1 cm^3/mol); $\bar{M}_n$, the number-average molecular weight of the polymer before cross-linking; and $\bar{v}$, the specific volume of the polymer (approximated as 0.788 cm^3/g, the specific volume of PVA). The value of $\bar{M}_n$ of 100,000 is the weighted average of the value of the molecular weight of uncross-linked PAA (400,000) and the PVA used here. The Flory polymer–solvent interaction parameter, χ, was calculated as a weighted average of the values for PVA ($\chi = 0.494$) and PAA ($\chi = 0.50$) in water.[22]

Experimental and theoretical values of $\bar{M}_c$ are listed in Table III for samples of varying cross-linking ratio. The experimental values of $\bar{M}_c$ increased with a decreasing nominal cross-linking ratio, X, in PVA/PAA IPN hydrogels. The experimental values of $\bar{M}_c$ were much smaller than those predicted by theory. This difference may have arisen from entanglements of the polymer chains that served as additional physical cross-links, thus leading to a larger number of junctions per unit volume, or to a smaller $\bar{M}_c$.

Experimentally determined values of $\bar{M}_c$ are plotted in Figure 1 as a function of the polymer volume fraction for IPN hydrogel samples containing

Table II Physicochemical Characteristics of Equilibrium Swollen PVA/PAA IPN Hydrogels Swollen to Equilibrium at 25°C

Sample Code No.	PAA Content (Mol %)	Nominal Cross-linking Ratio, X (mol/mol)	Equilibrium Polymer Vol Fraction $v_{2,s}$
I1e	50	0.015	0.171
I1d	50	0.014	0.166
I4	50	0.014	0.164
I4b	50	0.014	0.082
I5′	50	0.010	0.053
I4b′	50	0.009	0.059
L2	60	0.015	0.190
L3	60	0.015	0.179
L2b	60	0.015	0.175
L2b′	60	0.012	0.160
L4	60	0.011	0.125
L4′	60	0.008	0.103

Table III   Cross-linked Structure of Water-swollen PVA/PAA Hydrogels at 25°C

Sample Code No.	Nominal Cross-linking Ratio, X (mol/mol)	Theoretical Molecular Weight Between Cross-links $\bar{M}_{c,t}$ (g/mol)	Experimental Molecular Weight Between Cross-links $\bar{M}_{c,e}$ (g/mol)	Mesh Size ξ (Å)
I1e	0.015	1900	2,700	18
I4b	0.014	2000	2,800	25
I5'	0.010	2800	16,000	38
I4b'	0.009	3200	22,000	43
L2b	0.015	2100	1,200	15
L2b'	0.012	2500	1,700	17
L4	0.011	2900	2,400	19
L4'	0.008	3900	5,400	26

50 and 60 mol % PAA. The average molecular weight between cross-links decreased for both systems as the volume fraction of the polymer increased and the network structure became denser.

Cross-linking Density and Mesh Size

For further analysis of the cross-linked structure of the hydrogels, the cross-linking density, ρ_x, was calculated by eq. (8):

$$\rho_x = \frac{1}{\bar{v}\bar{M}_c} \qquad (8)$$

The cross-linking density of the PAA/PVA IPN samples was found to increase with an increase in cross-linking ratio, as indicated by the data in Table IV and Figure 2.

The network mesh size, ξ, was next calculated using eq. (9):

$$\xi = v_{2,s}^{-1/3}\left[C_n\left(\frac{2\bar{M}_c}{M_r}\right)\right]^{1/2} l \qquad (9)$$

The mesh size characterizes the space between macromolecular chains. In this expression, C_n is the Flory characteristic ratio ($C_{n,\mathrm{PVA}} = 8.3$ and $C_{n,\mathrm{PAA}} = 6.7$), and l is the carbon–carbon bond length (1.54 Å).

Figure 3 shows that the mesh size in IPN hydrogels decreased with increasing polymer volume frac-
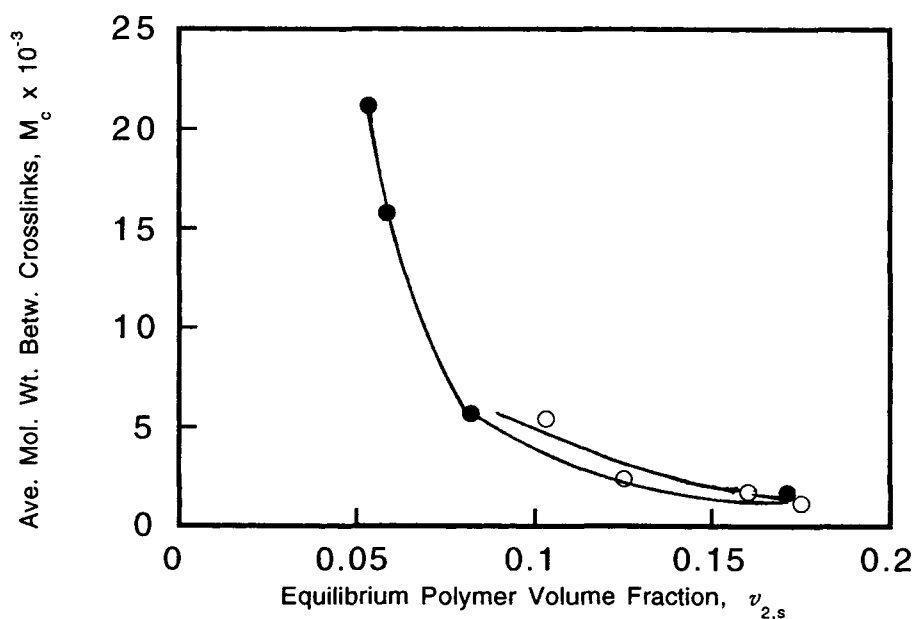

Figure 1   Effect of equilibrium polymer volume fraction, $v_{2,s}$, on the molecular weight between cross-links, $\bar{M}_c$, for PVA/PAA IPN hydrogels cross-linked by EGDMA and glutaraldehyde and containing of (●) 50 mol % and (○) 60 mol % PAA.

Table IV   Cross-linking Density, ρ_x, of PAA/PVA Hydrogels with Varying PAA Content and Cross-linking Ratio

Sample Code No.	PAA Content (Mol %)	Nominal Cross-linking Ratio, X (mol/mol)	Cross-linking Density, $\rho_x \times 10^4$ (mol/cm^3)
I4b′	50	0.009	0.6
I5′	50	0.010	0.8
I4b	50	0.014	2.8
Ile	50	0.015	7.6
L4′	60	0.008	2.3
L4	60	0.011	5.3
L2b′	60	0.012	7.6
L2b	60	0.015	10.8

tion. The mesh sizes of the networks varied between 15 and 700 Å, implying that permeation of molecules with a wide range of sizes would be possible.

Equilibrium Swelling Behavior

The equilibrium weight swelling ratio of an IPN laminate or membrane was defined as the ratio of the weight of the swollen polymer to that of the dry polymer:

$$q = \frac{W_{a,s}}{W_p} \tag{10}$$

For characterization of the response of the laminates and membranes to external conditions, sam-

ples were allowed to swell to equilibrium in aqueous buffers of varying pH (3, 6, and 8), ionic strength, I (0, 0.01, and 0.01N), and temperature (25 and 37°C) in order to determine the weight swelling ratio. The two temperatures were selected to simulate biological and environmental (waste water) conditions, respectively. The pH values were selected to allow comparison of swelling behavior in both the ionized (pH > 4.7) and nonionized (pH < 4.7) states.

The results in Table V demonstrate the influence of temperature and pH on the equilibrium weight swelling ratio of hydrogel samples of varying polymer volume fraction. The data indicate that swelling increased with increasing pH and temperature. A comparison of the swelling behavior of IPN samples
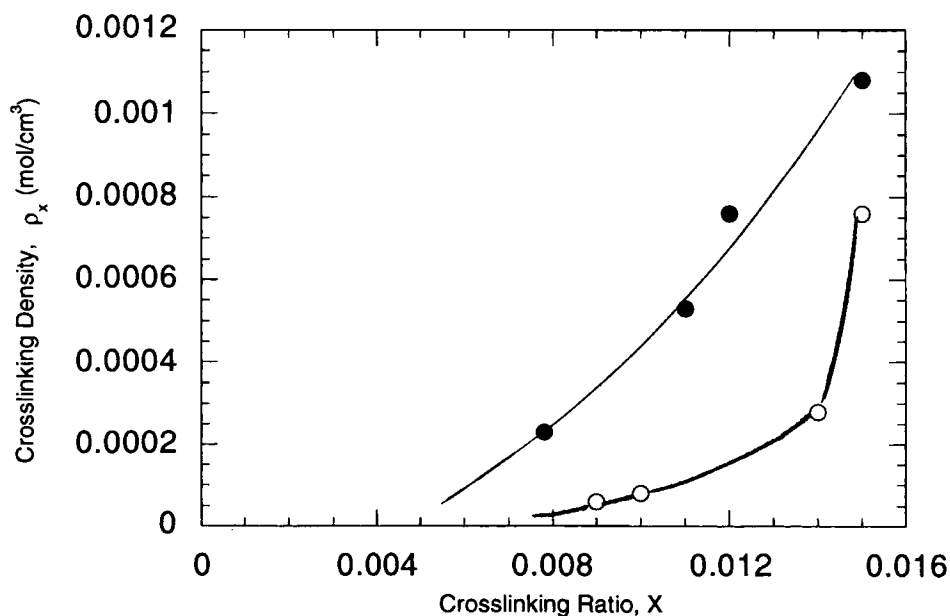
Figure 2   Effect of nominal cross-linking ratio, X, on cross-linking density, ρ_x, of IPN hydrogels containing (○) 50 mol % or (●) 60 mol % PAA.
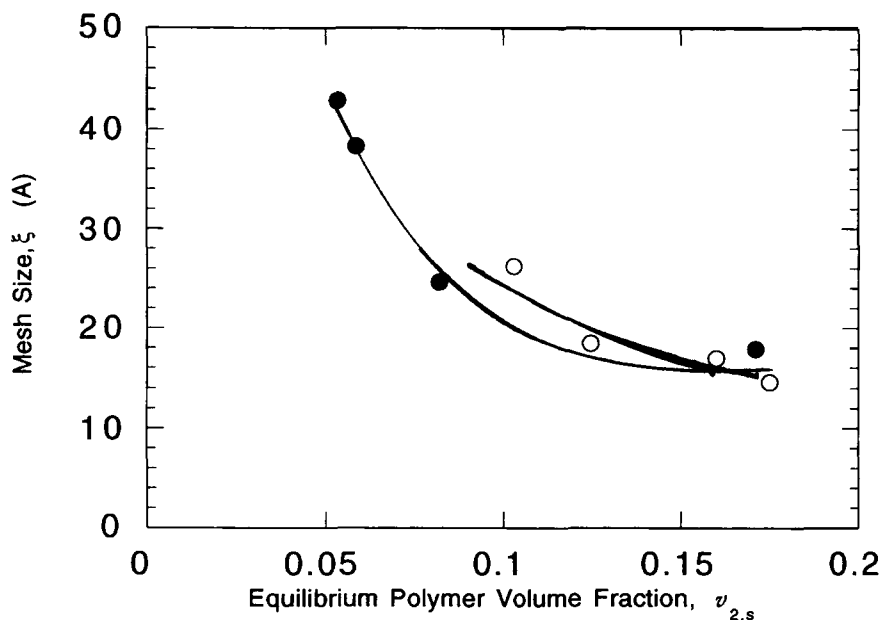
Figure 3 Effect of equilibrium polymer volume fraction, $v_{2,s}$, on the mesh size, ξ, for PVA/PAA IPN hydrogels cross-linked by EGDMA and glutaraldehyde and with a PAA content of (●) 50 mol % and (○) 60 mol %.

and PVA homopolymer membranes indicates that the former swelled significantly more at pH 8 because of the presence of the ionizable component PAA. The influence of ionic content is also seen in the greater weight swelling ratio of the samples containing 60 mol % PAA at a pH of 6, as compared to the samples containing 50 mol %, in spite of the slightly higher cross-linking ratios of the former samples.

The effects of the external pH and ionic strength on the swelling behavior of IPN samples of varying PAA content are summarized in the results of Table

VI. Below the pK_a, the membranes swelled significantly less than above the pK_a. An increase in ionic strength decreased the swelling because the presence of ions in the solution surrounding the network counteracted the mutual repulsion of the fixed ions on the network itself. The data in Table VI show that while ionic strength had little effect on the swelling at pH 3 it had a dramatic effect at pH 6, at which point the network was ionized. The observed effects of pH and ionic strength swelling behavior were in agreement with the results of Hariharan and Peppas[2] and Khare and Peppas.[3]

Table V   The Effects of pH and Temperature on the Equilibrium Swelling Ratio of PVA/PAA Samples with Varying PAA Content and Cross-linking Ratio

Sample Code No.	PAA Content (Mol %)	Nominal Cross-linking Ratio, X (mol/mol)	Equilibrium Weight Swelling Ratio			
			$T = 25°C$		$T = 37°C$	
			pH 3	pH 8	pH 3	pH 8
I1d	50	0.014	3.35	17.3	3.38	19.9
I4	50	0.014	3.38	17.1	3.76	22.4
L2	60	0.016	3.55	19.0	4.07	30.5
L3	60	0.016	3.74	26.8	4.05	34.1
PVA	0	0.019	5.67	5.32	4.31	4.35

Table VI   The Effects of pH and Ionic Strength on the Equilibrium Weight Swelling Ratio, q, of PVA/ PAA IPN Hydrogels at 25°C

Sample Code No.	PAA Content (Mol %)	Nominal Cross-linking Ratio, X (mol/mol)	Equilibrium Weight Swelling Ratio, q		
			pH 3 $I = 0.1N$	pH 3 $I = 0.01N$	pH 3 $I = 0.0N$
I1d	50	0.014	3.05	3.16	3.21
I4	50	0.014	3.48	3.66	3.73
L2	60	0.016	3.37	3.59	3.57
L3	60	0.016	3.31	3.46	3.49
			pH 6 $I = 0.1N$	pH 6 $I = 0.01N$	
I1d	50	0.014	5.00	19.1	
I4	50	0.014	7.94	31.8	
L2	60	0.016	7.33	26.6	
L3	60	0.016	6.43	27.9	

Table VII presents the results of equilibrium swelling studies for samples of varying ionic content and $\bar{M}_c$. Again, swelling increased as pH was increased and ionic strength decreased; the swelling ratio also increased as $\bar{M}_c$ became larger. The effect of ionic content (mol % PAA) can become evident by comparing the swelling ratio of sample L2b ($\bar{M}_c$ = 1200) to those of samples I4b ($\bar{M}_c$ = 5700) and I1e ($\bar{M}_c$ = 1700). Despite a smaller value of $\bar{M}_c$, and therefore a more highly cross-linked structure, the former specimen swelled to a greater degree in the ionized state (pH 6). This difference was due to the use of 60 mol % PAA in the synthesis of L2b, compared to 50 mol % in the other two samples.

Oscillatory Swelling Behavior

In addition to the equilibrium swelling experiments, oscillatory swelling behavior at 25°C, with pH alternating between 3 and 6, was investigated to confirm the reversibility of the swelling process. Figure 4 presents such swelling data for IPN hydrogel samples with 50 mol % PAA and varying degrees of cross-linking. An increase in X led to a decrease of both the degree and the rate of swelling. For networks of 67 mol % PAA (Fig. 5), both the degree and rate of swelling were greater than in the samples with 60 mol % PAA. The data in Figures 4 and 5 demonstrate that the swelling process was reversible

Table VII   The Effects of pH and Ionic Strength on the Equilibrium Weight Swelling Ratio, q, of PVA/PAA IPN Hydrogels at 25°C

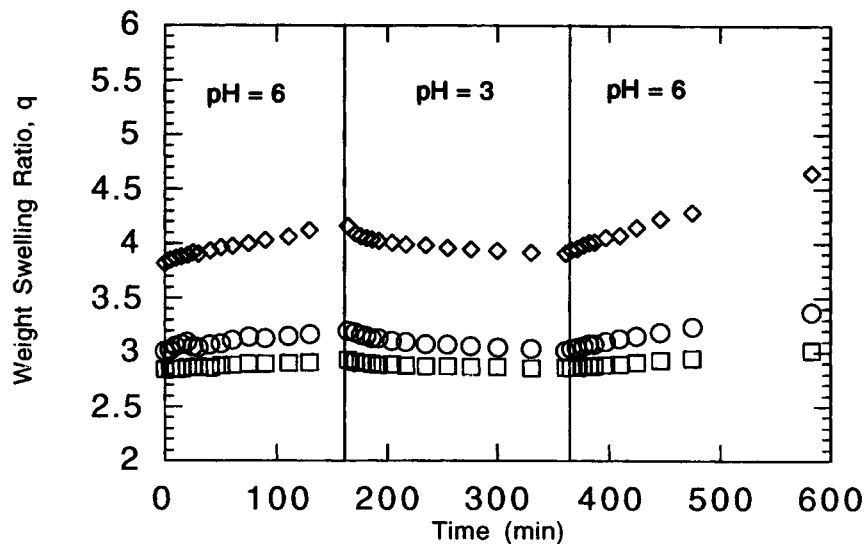| Sample Code No.	PAA Content (Mol %)	Experiment Molecular Weight Between Cross-links $\bar{M}_{c,e}$ (g/mol)	Equilibrium Weight Swelling Ratio, q			
			pH 3 $I = 0.1N$	pH 3 $I = 0.01N$	pH 6 $I = 0.1N$	pH 6 $I = 0.01N$
I4b'	50	22,000	4.47	4.75	27.9	66.7
I5'	50	16,000	4.15	4.34	16.37	
I4b	50	5,700	3.52	3.53	11.24	16.38
I1e	50	1,700	3.30	3.28	12.0	18.7
L4'	60	5,400	4.28	7.35		
L2b'	60	3,500	4.06	4.14	15.6	
L2b	60	1,200	3.50	3.63	13.3	25.8

Figure 4 Effect of pH on the dynamic swelling of PVA/PAA IPN network samples of 50 mol % PAA and varying cross-linking ratio: (◇) X = 0.01; (○) X = 0.02; (□) X = 0.03.

as the pH was repeatedly raised and lowered and that the swelling behavior was reproducible for membranes with the same value of $\bar{M}_c$.

CONCLUSIONS

The preparation of IPN hydrogels of PVA and PAA was investigated. Hydrogels with varying cross-

linking ratio and ionic content were prepared from the IPNs. Equilibrium swelling studies were conducted for characterization of the cross-linked structure of the membranes, and the average molecular weight between cross-links, cross-linking density, and average mesh size were determined. These studies showed that the molecular weight between cross-links varied from 1200 to 22,000, and the mesh size (in water), from 18 to 43 Å. The cross-
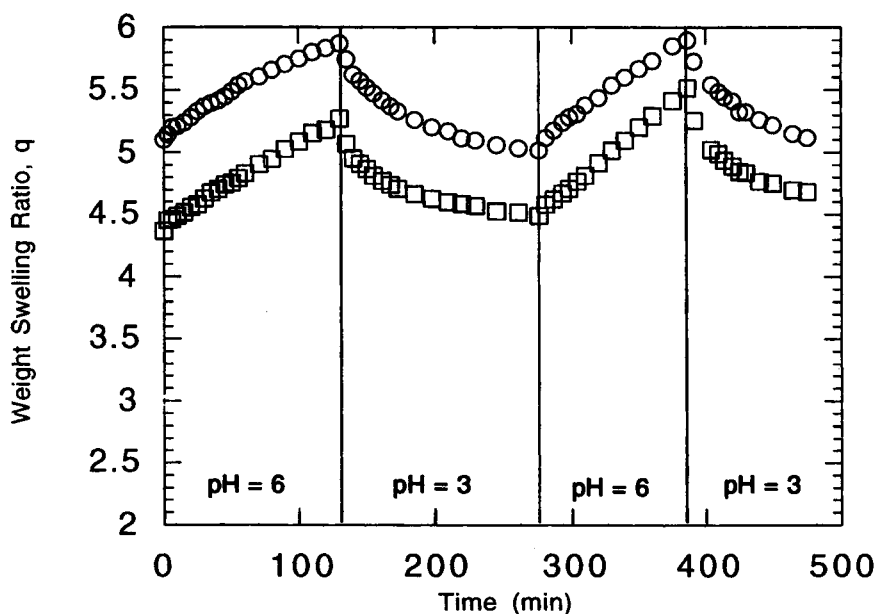

Figure 5 Effect of pH on the dynamic swelling of PVA/PAA IPN hydrogels of 67 mol % PAA and varying cross-linking ratio: (□) X = 0.01; (○) X = 0.03.

linking density increased with an increase in the cross-linking ratio. Equilibrium and oscillatory swelling behavior was investigated in response to changes in the pH and ionic strength of the swelling medium. The oscillatory swelling studies showed that membranes with a more loosely cross-linked structure (higher $\bar{M}_c$) swelled and deswelled more quickly than did denser membranes.

REFERENCES

1. D. L. Meadows and N. A. Peppas, *Chem. Eng. Commun.*, **31**, 101 (1984).
2. D. Hariharan and N. A. Peppas, *J. Membr. Sci.*, **78**, 1 (1993).
3. A. Khare and N. A. Peppas, *J. Biomater. Sci. Polym. Ed.*, **4**, 275 (1993).
4. H. L. Greenwald and L. S. Luskin, in *Handbook of Water Soluble Gums and Resins*, R. L. Davidson, Ed., McGraw-Hill, New York, 1980, p. 1.
5. M. T. am Ende and N. A. Peppas, to appear.
6. S. Dumitriu, *Br. Polym. J.*, **21**, 295 (1989).
7. X. Zhang, K. Takegochi, and K. Hikichi, *Polymer*, **33**, 718 (1992).
8. F. J. Liou, G. C. C. Niu, and Y. J. Wang, *J. Appl. Polym. Sci.*, **46**, 1967 (1992).
9. J. W. Rhim, M. Y. Sohn, and K. H. Lee, *J. Appl. Polym. Sci.*, **52**, 1217 (1994).
10. T. Yamauchi, E. Kokufuta, and Y. Osada, *Polym. Gels Networks*, **1**, 247 (1993).
11. T. Shiga, K. Fukumori, Y. Hirose, A. Okada, and T. Kurauchi, *J. Polym. Sci. Polym. Phys.*, **32**, 85 (1994).
12. T. Shiga, Y. Hirose, A. Okada, and T. Kurauchi, *J. Appl. Polym. Sci.*, **47**, 113 (1993).
13. H. Vazquez-Torres, J. V. Cauich-Rodriguez, and C. A. Cruz-Ramos, *J. Appl. Polym. Sci.*, **50**, 777 (1993).
14. T. Shiga, Y. Hirose, A. Okada, and T. Kurauchi, *Kob. Ronbunshu*, **46**, 709 (1989).
15. T. Shiga, Y. Hirose, A. Okada, and T. Kurauchi, *Polym. Prepr.*, **30**(1), 310 (1989).
16. H. Tsujinaka, T. Hirai, T. Suzuki, and S. Hayashi, *Polym. Prepr. Jpn.*, **39**, E370 (1990).
17. H. Tsujinaka, T. Hirai, T. Suzuki, and S. Hayashi, *Polym. Prepr. Jpn.*, **39**, E943 (1990).
18. M. Suzuki, M. Matzuzawa, M. Saito, and T. Tateishi, *Polym. Prepr. Jpn.*, **39**, E1292 (1990).
19. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York, 1981.
20. N. A. Peppas and B. D. Barr-Howell, in *Hydrogels in Medicine and Pharmacy*, N. A. Peppas, Ed., CRC Press, Boca Raton, FL, 1979, p. 27.
21. N. A. Peppas and E. W. Merrill, *J. Polym. Sci. Polym. Chem.*, **14**, 441 (1976).
22. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Wiley, New York, 1989.