Electroactive Characteristics of Interpenetrating Polymer Network Hydrogels Composed of Poly(vinyl alcohol) and Poly(*N*-isopropylacrylamide)

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ABSTRACT: An interpenetrating polymer network (IPN) composed of poly(vinyl alcohol) (PVA) and poly(*N*-isopropylacrylamide) (PNIPAAm) was prepared by the sequential IPN method. The equilibrium swelling ratio and bending behavior under electric fields of the IPN hydrogel were measured in an aqueous NaCl solution. The IPN exhibited a high equilibrium swelling ratio, in the range 280–380%. When the IPN in aqueous NaCl solution was subjected to an electric field, the IPN showed significant and quick bending toward the cathode. The IPN hydrogel also showed stepwise bending behavior, depending on the electric stimulus. In addition, the ionic conductivity of the IPN hydrogel was measured using dielectric analysis, and its conductive behavior followed the Arrhenius equation. The conductivity of the IPN hydrogel and the activation energy for the form of the IPN were 1.68×10^{-5} S/cm at 36°C and 61.0 kJ/mol, respectively. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 890–894, 2003

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INTRODUCTION

Hydrogels are among the most promising types of polymers being used for new material development.[1] They are polymeric materials that do not dissolve in water at a physiological temperature and pH but swell considerably in an aqueous medium.[1,2] Hydrogel transitions, or volume changes, occur in response to changing environmental conditions such as temperature,[3,4] pH,[5] solvent composition,[6] and electrical stimuli.[7] The system, which undergoes shape change and produces contractile force in response to environmental stumuli, can transform chemical free energy directly into mechanical work to give isothermal energy conversion. This can be seen in living organisms, for example, in muscle, flagella, and in ciliary movement.[8] Hydrogels have been studied for use in a variety of fields, such as in chemical engineering, medicine and pharmaceuticals, food processing or preparation, and agriculture, in applications such as controlled drug delivery systems, musclelike soft linear actuators, robotics, sensors, biomimetic energy transducing devices, and separation techniques.[9–11]

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer employed in practical applications because of its easy preparation, excellent chemical resistance and physical properties, and because it is completely biodegradable. Chemically crosslinked PVA hydrogels have received increasing attention in biomedical and biochemical applications because of their permeability, biocompatibility, and biodegradability.[12–15]

Poly(*N*-isopropylacrylamide) (PNIPAAm) is noted for exhibiting a lower critical solution temperature (LCST) at around 32°C in an aqueous solution; that is, it dissolves in water below the LCST and precipitates from the solution above the LCST. PNIPAAm hydrogels with a crosslinked structure are characterized by a temperature-responsive nature in which they swell in water below the LCST and shrink in water above the LCST.[16]

Many researchers have reported on electrically induced phenomena in charged polymer networks. Tanaka et al.[7] reported that a hydrolyzed acrylamide gel collapsed in an acetone/water binary mixture on application of an electric field. Kim et al.[9] reported that interpenetrating polymer networks (IPNs) composed of PVA and poly(acrylic acid) (PAA) exhibited electrical-sensitive behavior. Sun et al.[17,18] reported on the mechano-electrochemical behavior of chitosan/

poly(propylene glycol) composite fibers. Okano et al.[19] reported on comb-type graft hydrogels composed of poly(ethylene oxide) graft chains in a PNIPAAm crosslinked network. Kim et al.[20] reported on the bending behavior of a chitosan/polyallylamine IPN hydrogel under electric field. These results showed rapid gel swelling/deswelling kinetics. A fast response is necessary for applications such as artificial muscles and/or rapidly acting actuators.

In the present study, we prepared a PVA/PNIPAAm IPN hydrogel exhibiting pH sensitivity and studied the electrolyte concentration/pH dependency of its swelling behavior, its bending behavior under an electric field, and its ionic conductivity.

EXPERIMENTAL

Materials

PVA (average molecular weight, $1.24–1.86 \times 10^5$; degree of saponification, 99 mol %), N-isopropylacrylamide (NIPAAm), N,N'-methylenebisacrylamide (MBAAm), and ammonium peroxydisulfate (APS) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Glutaraldehyde (GA; 25 wt % solution in water), hydrochloric acid (HCl), and N,N,N',N'-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chemical Co. (Japan). These were used for hydrogel preparation without further purification and all other chemical reagents used were extra pure grade.

Preparation of the PVA/PNIPAAm IPN

PVA/PNIPAAm IPN was prepared by the sequential IPN method. PVA was dissolved in deionized water and heated at 80°C for 2 h to make a 5 wt % aqueous solution. The NIPAAm monomers were then mixed. PVA was crosslinked in the presence of NIPAAm, using GA and HCl as a crosslinking agent and catalyst, respectively. Next, NIPAAm was polymerized with APS, TMEDA, and MBAAm as an initiator, accelerator, and crosslinking agent, respectively, at room temperature for 24 h under a nitrogen atmosphere. The contents of the initiator and accelerator were 1 wt % of monomer and the contents of the crosslinking agent were 3 mol % of monomer. The IPN was prepared from 50 : 50 weight ratio of PVA : NIPAAm. The dry film was washed with distilled water to remove any nonreactive materials that were not incorporated into the network.

Swelling experiment of the IPN hydrogel

To measure the equilibrium swelling ratio, pre-weighed dry IPN samples were immersed in various pH values and aqueous NaCl solutions until they swelled to equilibrium. It was confirmed that 24 h equilibration was enough to reach the equilibrium swelling for the samples. After excessive surface water was removed with filter paper, the fully swollen samples were weighed. The equilibrium swelling ratio was calculated from the following equation:

Equilibrium swelling ratio (%)

$$= [(W_s - W_d)/W_d] \times 100 \quad (1)$$

where W_s is the weight of the swollen state of a sample at equilibrium and W_d is the weight of the sample at the dry state. The swelling experiments were repeated five times.

Bending angle measurement under an electric stimulus

Bending angle measurement was carried out under the noncontact dc electric field. Aqueous NaCl solution was poured into an organic glass case equipped with two parallel carbon electrodes. The separation between the electrodes was about 30 mm. The PVA/PNIPAAm IPN hydrogel samples were swollen in aqueous NaCl solutions at room temperature and cut into 10×2 mm (length $\times$ width) strips. One end of the sample strip was fixed and the IPN hydrogel placed in the center of the organic glass case. A protractor-style scale was drawn on white paper and was placed underneath the petri dish. When an electric stimulus was applied, the degree of bending was measured by reading the deviated angle from the vertical position.

Conductivity measurement of the IPN hydrogel

Ionic conductivity of the IPN after equilibrium swelling with 0.8 wt % aqueous NaCl solution was measured using dielectric analysis (DEA). Measurements of the dielectric constant (ϵ') and the dielectric loss factor (ϵ'') were carried out using DEA (DEA 2970; TA Instruments, New Castle, DE) with a parallel plate ceramic sensor. The experiment was done from 30 to 40°C with dry nitrogen gas adjusted to a flow rate of 50 mL/min. The data were collected over a frequency range from 10 kHz to 10 Hz. Ionic conductivity was calculated from the dielectric loss factor obtained from the DEA:
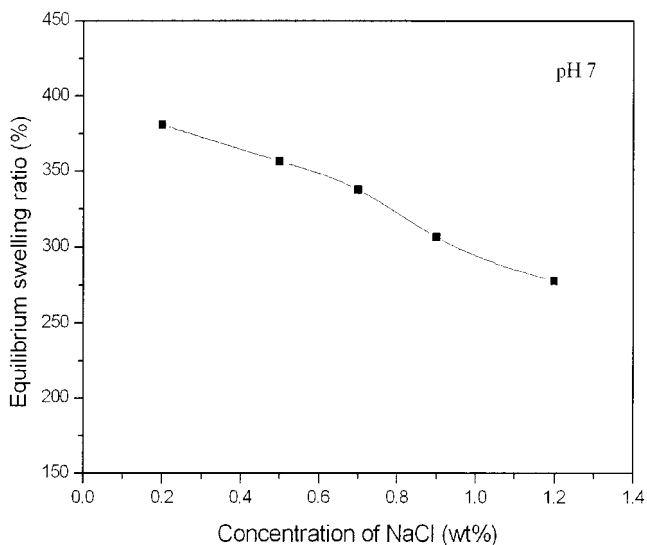
$$\sigma = \varepsilon'' 2\pi f \varepsilon_0 \quad (2)$$

where σ is the ionic conductivity, f is the frequency, and ϵ_0 is the absolute permittivity of free space of the parallel plate ceramic sensor (8.85×10^{-12} F/m).

RESULTS AND DISCUSSION

Swelling behavior of IPN hydrogel

The PVA/PNIPAAm IPN hydrogel exhibited swelling behavior that was sensitive to both electrolyte concen-

Figure 1 Equilibrium swelling ratio of IPN hydrogel as a function of concentration of aqueous NaCl solution at room temperature.

tration and pH. The effect of concentration of aqueous NaCl solution on the equilibrium swelling was investigated for the IPN hydrogel. The IPN swelled rapidly and reached equilibrium within 3 h. All swelling behaviors are plotted as the average of five trials. Figure 1 shows the equilibrium swelling ratio of the IPN hydrogel in various aqueous NaCl solutions at room temperature. It is shown that the equilibrium swelling ratio decreased with increasing concentration of aqueous NaCl solution. Generally, the swelling ratio of polyelectrolyte gels depends on the association state of ionic groups within the polymer and on the affinity of hydrogel for water.

According to the Donnan osmotic pressure equilibrium,[21] an increase of movable counterions in solution leads to a decrease of osmotic pressure within the gel and causes shrinkage of the gel.

The pH-dependent swelling behavior was observed at room temperature with changes in pH 2–10 buffer solutions, as shown in Figure 2. By increasing the pH, the polymer network becomes more hydrophilic because the degree of ionization of the hydroxyl group in the PVA increases. However, as the pH increases further, the ionic strength also increases. The osmotic pressure difference of free ions between the internal and external solution decreases and the hydrogel tends to deswell.[22] By increasing the pH range from 2 to 7, the equilibrium swelling ratio gradually increased because the degree of ionization of the hydroxyl group in the PVA increased gradually; the equilibrium swelling ratio then abruptly swelled and reached a maximum value at pH 9 because the hydroxyl groups were fully ionized. However, the equilibrium swelling ratio decreased at pH 10 because the

effect of the ionic strength surpassed the effect of the electrostatic repulsion between the hydroxyl groups.

Bending behaviors under electric fields

When an electric field was applied to a strip of PVA/PNIPAAm IPN hydrogel in an aqueous NaCl solution, the IPN hydrogel showed significant and quick bending toward the cathode. When the electric stimulus was removed, the IPN hydrogel returned to its original position. Moreover, when the polarity of the electric field was altered, the IPN hydrogel bent in the opposite direction. This behavior is generally thought of as the deformation of a polymer hydrogel under an electric field as a result of the voltage-induced motion of ions and the concomitant expansion of one side of the polymer hydrogel and the contraction of the other side.

The influence of the medium ionic concentration on the bending behavior of the IPN in response to an electric stimulation by varying the concentrations of aqueous NaCl solution from 0.2 to 1.2% by weight, while keeping the pH level and other conditions constant, was measured. As shown in Figure 3, the equilibrium bending angle (EBA) of the IPN hydrogel shows an apparent peak with 0.9 wt % aqueous NaCl solution. The bending degree increased according to the concentration of aqueous NaCl solution when the concentration of aqueous NaCl solution was less than 0.9% by weight, whereas the bending degree decreased when the concentration of aqueous NaCl solution was greater than 0.9% by weight. As described above, an increase in the electrolyte concentration in a solution induces an increase of the free ions moving from the surrounding solution toward their counter-
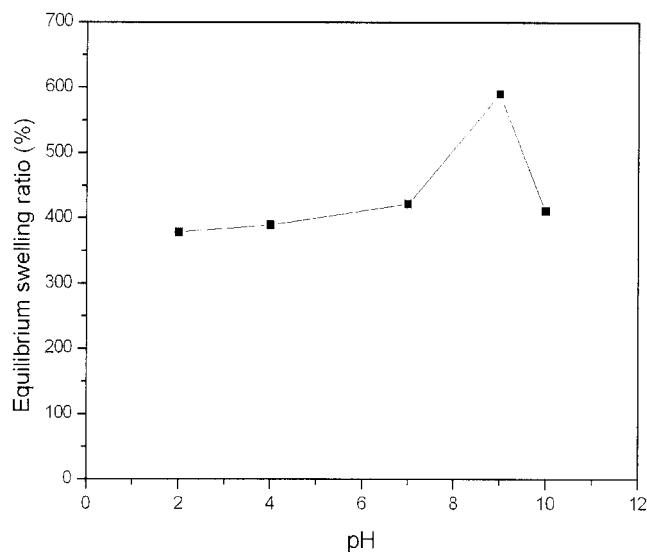

Figure 2 Equilibrium swelling ratio of IPN hydrogel as a function of pH at room temperature.
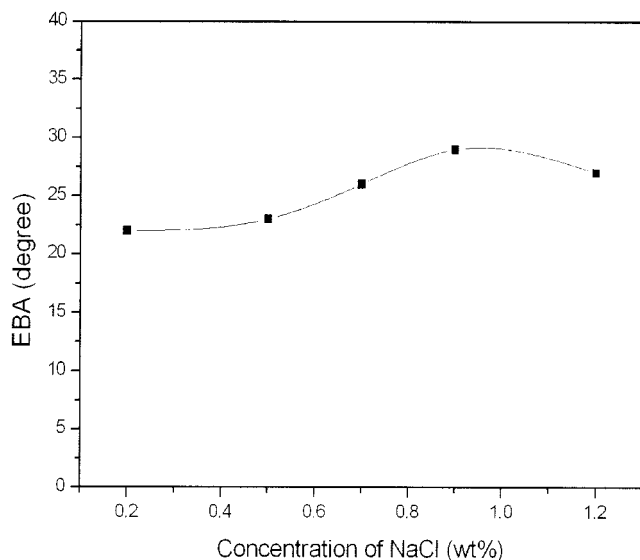
Figure 3 Effect of concentration of aqueous NaCl solution (pH 7) on the equilibrium bending angle (EBA) at room temperature (10 V constant).

Figure 4 Bending and relaxation kinetics of IPN hydrogel as a function of the applied voltages in a 0.8 wt % aqueous NaCl solution (pH 7) at room temperature.

electrode or into the IPN. As a result, the bending degree of the IPN hydrogel could increase. However, if the concentration of aqueous NaCl solution is greater than a critical concentration, the shielding effect of the polyions by the ions in the electrolytic solute occurs, leading to a reduction in the electrostatic repulsion of the polyions and a decrease in the degree of bending. A similar result was reported in our previous study of bending behaviors of an IPN hydrogel based on chitosan and polyallylamine. As shown in Figure 1, the equilibrium swelling ratio of the IPN hydrogel in the solution with the lower concentration of NaCl was greater than that of the IPN hydrogel in the solution with a higher NaCl concentration. Therefore, if the equilibrium swelling ratio of the IPN hydrogel is compared with the bending results depending on the concentrations of the aqueous NaCl solution in Figure 3, we could consider that the swelling of the IPN hydrogel in various concentrations of aqueous NaCl solution does not significantly affect the bending behavior of the IPN hydrogel.

Figure 4 shows the bending and relaxation kinetics of the IPN hydrogel as a function of applied voltage in an 0.8 wt % aqueous NaCl solution. Bending angle measurements with various applied voltages were carried out in an 0.8 wt % aqueous NaCl solution because extracellular fluid contains about 0.8 wt % NaCl. IPN hydrogels are thought to be useful for artificial organ components such as sensors and switches in a body. The equilibrium bending angle and bending speed increase with increasing the voltage across the IPN hydrogel, but bending is not found in pure water, indicating that bending is induced by the electric current. The bending behavior occurred by
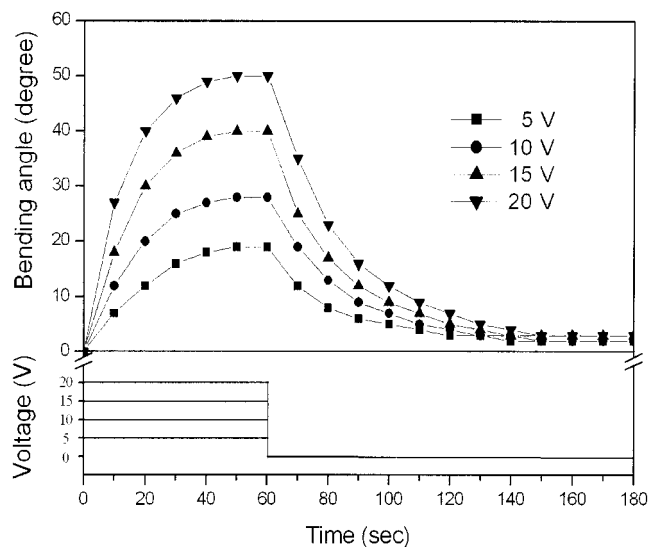
the deformation of a polymer hydrogel under an electric field as a consequence of the voltage-induced motion of ions. When the electric stimulus is removed, the voltage-induced free ions adsorbed into the hydrogel move toward the surrounding solution. Therefore, the relaxation of the hydrogel occurs. As shown in Figures 4 and 5, the relaxation time was longer than the bending time because the adsorption and desorption kinetics of voltage-induced free ions are different in the hydrogel/surrounding solution system. As shown in Figure 5, the PVA/PNIPAAm IPN hydrogel exhibited reversible bending behavior depending on whether the electric field was on.
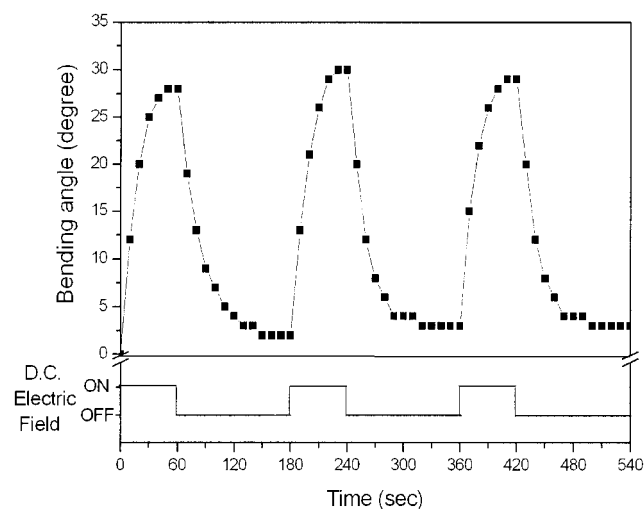
Figure 5 Reversible bending behavior of IPN hydrogel in a 0.8 wt % aqueous NaCl solution (pH 7) with changes in the applied voltages of 10 V at room temperature.
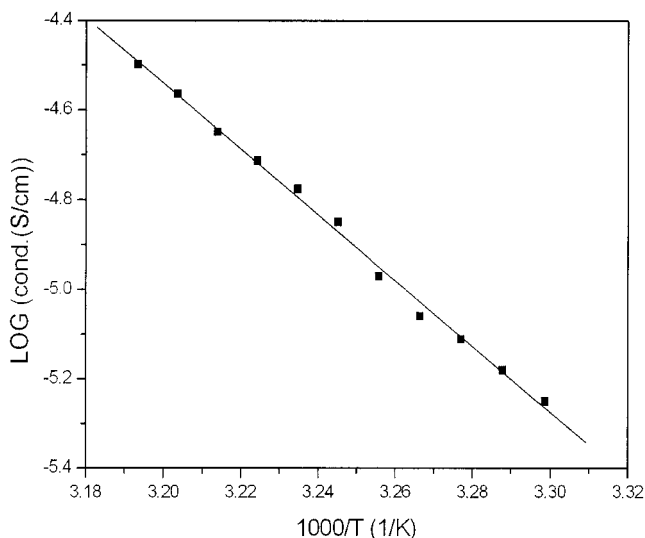
Figure 6 Temperature dependency of ionic conductivity of the PVA/PNIPAAm IPN hydrogel.

Ionic conductivity

The PVA/PNIPAAm IPN was immersed in 0.8 wt % aqueous NaCl solution and reached equilibrium in 24 h. The plot of ionic conductivity versus reciprocal of temperature for the IPN hydrogel is shown in Figure 6. It is noted that the conduction behavior of the IPN hydrogel obeys the Arrhenius law, which implies that the conductive environment of Na^+ ions in the IPN hydrogel is liquidlike and remains unchanged in the studied temperature region. The ionic conductivity at 36°C was measured to be 1.68×10^{-5} S/cm. The activation energy E_a is shown in eq. (3), as determined for the IPN hydrogel by the Arrhenius equation:

$$\sigma = A \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where A is a preexponential factor, R is the gas constant, and T is temperature on the Kelvin scale. The activation energy for the form of the PVA/PNIPAAm IPN is 61.0 kJ/mol.

CONCLUSIONS

The IPN exhibited a high equilibrium swelling ratio and the swelling ratio decreased with increasing the concentration of the aqueous NaCl solution. The EBA

and the bending speed of the IPN hydrogel were the greatest in 0.9 wt % aqueous NaCl and increased with increases in the applied voltage. The IPN also showed stepwise bending behavior depending on the electric stimulus. The ionic conductive behavior of IPN hydrogel follows the Arrhenius equation. The ionic conductivity of IPN hydrogel and the activation energy for the form of the IPN were 1.68×10^{-5} S/cm at 36°C and 61.0 kJ/mol, respectively. Therefore, the present IPN system can be useful for artificial organ components such as sensors, switches, and electric current–modulated drug delivery systems.

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