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Electrochemical Behavior of an Interpenetrating Polymer Network Hydrogel Composed of Poly(propylene glycol) and Poly(acrylic acid)

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ABSTRACT: An interpenetrating polymer network (IPN) hydrogel based on poly(propylene glycol) and poly(acrylic acid) was prepared by UV irradiation. The swelling behavior of the IPN hydrogel was studied by the immersion of the gel in aqueous NaCl solutions of various concentrations. The swelling ratio decreased with an increase in the NaCl concentration. The electrically sensitive behavior of the IPN hydrogel in electric fields was also investigated. The IPN hydrogel also showed a stepwise bending behavior that

depended on the electric stimulus. The bending angle and bending speed of the IPN hydrogel were greatest in 0.6 wt % aqueous NaCl and increased with an increase in the applied voltage. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2301–2305, 2003

Key words: interpenetrating polymer networks (IPN); hydrogels; electric

INTRODUCTION

Hydrogels are hydrophilic polymer networks that have a large capacity for adsorbing water and that are characterized by the presence of crosslinks, crystalline and amorphous regions, entanglements, and rearrangements of hydrophobic and hydrophilic domains.^{1,2} Hydrogels can change their volume and shape reversibly, according to several external physicochemical factors, such as the temperature, solvent composition, pH, ionic concentration, and light.³ Environmentally sensitive hydrogels are also called intelligent or smart hydrogels.⁴ Polymer hydrogels have been proposed for many applications, such as the controlled delivery of medicinal drugs, artificial muscles, sensor systems, and bioseparations, because of their good biocompatibility, stimuli-responsive properties, and water permeation properties.

The stimuli-response mechanism of the gels in direct-current electric fields has been discussed frequently, but it is still controversial. Grimshaw et al.⁵ applied an electrodiffusion theory to explain the

swelling pattern of a poly(methacrylic acid) gel. De Rossi et al.⁶ explained the anisotropic deswelling of poly(vinyl alcohol) (PVA)/poly(acrylic acid) (PAAc) membranes at the anode by a local pH decrease associated with water electrolysis. Kim et al.⁷ adopted a theory involving depletion polarization to explain gel bending in a direct-current electric field. Tanaka et al.⁸ reported anisotropic contraction of negatively charged gels when electrodes were in contact with the gels. This gel contraction was explained by the electrophoretic migration of the negatively charged gel toward the anode.

Interpenetrating polymer networks (IPNs) are a combination of two or more network polymers synthesized in juxtaposition.⁹ IPNs are an important class of materials attracting broad interest from both fundamental and industrial points of view. IPNs are normally made up of two or more incompatible crosslinked polymers in which crosslinking is used to increase the extent of mixing of the networks.^{10–12}

PAAc has a very high charge density based on carboxyl groups, which can also be suitable as crosslinking sites. Therefore, PAAc has polyelectrolyte properties and the possibility of a wide range of applications on account of these properties. Kim and Lee¹³ reported on the synthesis of a semi-IPN composed of poly(ethylene glycol) macromer and β -chitin.

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Kim and coworkers reported on PAAc/PVA IPN hydrogels crosslinked by UV irradiation and their swelling kinetics,³ on electric stimulus,¹⁴ and on the permeation of solutes.¹⁵ PAAc is known to form a complex structure with polyoxyethylene (POE) in an IPN form. PAAc/POE IPNs show that swelling–deswelling and mechanochemical reactions proceed reversibly for full IPNs. It was also reported that PAAc/poly(*N,N*-dimethyl acrylamide) IPN hydrogels showed an upper critical solution temperature behavior that was due mainly to the presence of PAAc.¹⁶ Poly(propylene glycol) (PPG) is a more hydrophobic polyether than poly(ethylene glycol) and has been used in various biomedical applications, such as lubricious coatings on absorbable sutures and soft segments for biocompatible polyurethanes.¹⁷

In this study, the PPG/PAAc IPN hydrogel was characterized by its swelling behavior in aqueous NaCl solutions. We observed the deformation of the PPG/PAAc IPN hydrogel by an electric stimulus.

EXPERIMENTAL

Materials

PPG (number-average molecular weight = 3500) was purchased from Aldrich Chemical Co. (USA) and was dried by azeotropic distillation with benzene. Acryloyl chloride and 2,2-dimethoxy-2-phenylacetophene (DMPA), a photoinitiator, were obtained from Aldrich Chemical and were used without further purification. Acrylic acid (AAc) monomer was purchased from Junsei Chemical Co. (Japan) and used after purification with an inhibitor removal column. Methylenebisacrylamide (MBAAm) was used as a crosslinking agent. All other chemicals used were reagent-grade and were used as purchased without further purification.

Preparation of PPG/PAAc IPNs

PPG (12 g, 3.2 mM) dissolved in 150 mL of benzene was heated to 80°C. A total of 0.89 mL (3.2 mM) of triethylamine and 0.61 mL (7.5 mM) of acryloyl chloride were added, and the reaction mixture was stirred for 3 h at 80°C. After the filtration of triethylamine·HCl, the macromer was purified by the reaction mixture being poured into a large excess of hexane. The solvent from the filtrate was removed by rotary evaporation. The resulting syrup containing the viscous macromer was dried *in vacuo* for 1 day.

The IPN was prepared by a simultaneous method. The PPG macromer and AAc monomer were dissolved in ethyl alcohol. Then, the crosslinkers *N*-vinylpyrrolidone and MBAAm and the initiator DMPA were mixed with that solution. The solution was poured into a circular glass mold and irradiated with

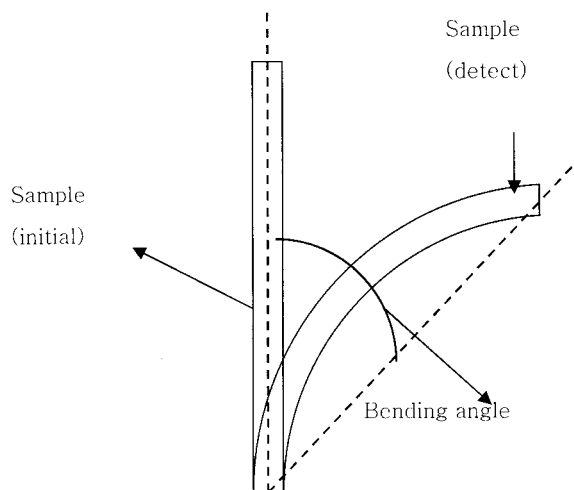


Figure 1 Illustration of the bending angle.

a 450-W UV lamp (Ace Glass Co., USA) placed 20 cm above it for 10–20 min until gelation occurred. The mold was then kept under reduced pressure to evaporate the solvent. After 24 h, a dry film was obtained, and it was washed for the removal of unreacted chemicals.

Swelling properties of the IPN hydrogel

For the measurement of the swelling ratio, pre-weighed dry samples were immersed in aqueous NaCl solutions of various concentrations. After excessive surface NaCl solution was removed with filter paper, the swollen samples were weighted. The procedure was repeated until there was no further weight increase and was then repeated five more times. The swelling ratio was determined according to the following equation:

$$\text{Swelling ratio} = \frac{W_s}{W_d} \quad (1)$$

where W_s and W_d represent the weights of swollen-state and dry-state samples, respectively.

Bending-angle measurements under an electric stimulus

The bending angle is defined as shown in Figure 1. An aqueous NaCl solution was poured into a petri dish equipped with two parallel carbon electrodes. The space between the electrodes was about 20 mm. The PPG/PAAc IPN hydrogel was swollen in NaCl aqueous solutions at room temperature and cut into 20-mm-long and 2-mm-wide strips. A hydrogel specimen 20 mm long, picked up with plastic tongs, was placed in the center of a petri dish filled with 20 mL of the

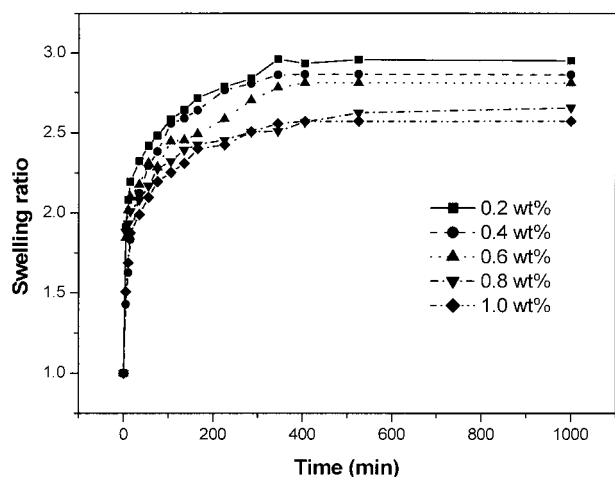


Figure 2 Swelling ratio of the PPG/PAAc IPN hydrogel as a function of the concentration of the aqueous NaCl solution at room temperature.

solution. A voltage was then applied across the solution between the electrodes. The deformation was recorded with a video screen via a charged-coupled device camera (Mitsubishi, Japan) interfaced to a Compaq Pentium computer (Compaq Co., USA). The deflection was expressed in terms of the curvature at the midlength of the hydrogel at various times. For reversible bending to be tested, one end of the specimen was fixed between the two electrodes. The amount of bending was recorded with a manual counter. A protractor style scale was drawn on white paper and was placed beneath the petri dish. When an electric stimulus was applied, we measured the degree of bending by reading the deviated angle from the vertical position. The applied electric potentials were set at 3, 5, 10, and 15 V. The bath medium was a 0.6 wt % NaCl solution.

RESULTS AND DISCUSSION

Figure 2 shows the swelling ratio of the PPG/PAAc IPN hydrogel in aqueous NaCl solutions at room temperature. The hydrogel swelled rapidly at the initial point and reached equilibrium within about 7 h. The IPN hydrogel exhibited a high swelling ratio in the range of 2.57–2.95. The swelling ratio decreased with increasing concentrations of the NaCl solution. Generally, the swelling ratio of a polyelectrolyte gel depends on the association state of ionic groups within the polymer and on the affinity of the hydrogel for water.¹⁸ However, according to the Donnan osmotic pressure equilibrium,¹⁹ an increase in movable counterions in solution leads to a decrease in the osmotic pressure within the gel and causes shrinkage of the gel.

A constant electric potential across two parallel-plate electrodes can cause the PPG/PAAc IPN hydrogel to bend toward the anode in an electrolyte solution. The mechanism for this kind of behavior is not completely understood because there is still a lack of well-developed theories for such behavior. However, it is generally thought that the deformation of a polymer hydrogel under an electric field is due to the voltage-induced motion of ions and the concomitant expansion of one side of the polymer and the contraction of the other. In concrete terms, the counterion of the polyion, which is an ionic group in the polymer network, moves toward the negative electrode, whereas the polyion remains immobile, and an electric field is applied to the negatively charged gel in the aqueous solution. Also, the free ions in the surrounding solution move toward their counter electrode and come into the gel. Therefore, the osmotic pressure of the gel polymer network near the positive electrode increases and becomes larger than that of the negative electrode side. Consequently, the osmotic pressure difference occurs within the gel and is the driving force that controls bending toward the negative electrode.

A sample was allowed to reach its swelling equilibrium in the corresponding bath medium before the electric stimulation. As soon as an electric field was applied, equilibrium could not be maintained. The influence of the medium ionic concentration on the bending behaviors of the IPN hydrogel in response to an electric stimulus with NaCl solutions of various concentrations (from 0.2 to 1.0 wt %) and the other condition kept constant was examined. The time to reach 90° from 0° on the protractor style scale (RT_{90}) was measured. As shown in Figure 3, RT_{90} of the IPN hydrogel showed an apparent peak with a 0.6 wt % aqueous NaCl solution. RT_{90} decreased with an in-

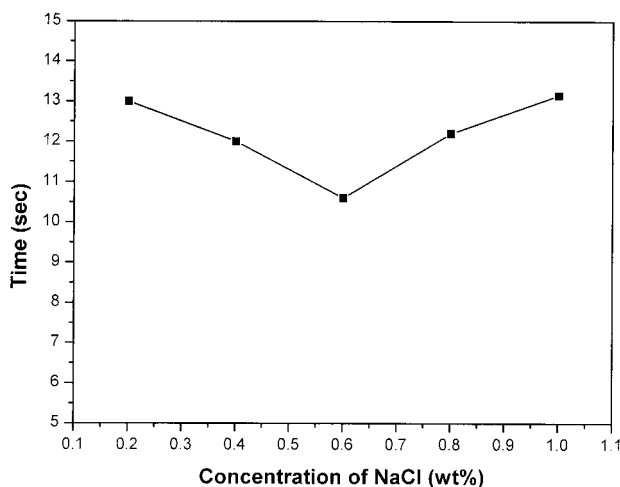


Figure 3 Effect of the concentration of the NaCl solution on RT_{90} at a constant voltage of 10 V.

crease in the concentrations of the NaCl solution when the concentrations of NaCl solutions were less than 0.6 wt %, and the bending degree increased with NaCl solutions greater than 0.6 wt %. This is because an increase in the electrolyte concentration in a solution induces an increase in the free ions moving from the surrounding solution toward their counter electrode or into the IPN hydrogel. As a result, RT_{90} of the IPN hydrogel could decrease. However, when the concentration of the NaCl solution was greater than the critical concentration, a shielding effect of the polyions by the ions in the electrolytic solute occurred, leading to a reduction in the electrostatic repulsion of the polyions and an increase in RT_{90} . As shown in Figure 2, the swelling ratio of the IPN hydrogel in the solution with a lower concentration of electrolytes was greater than that of a solution with a higher electrolyte concentration. Therefore, if the swelling ratio is compared with the bending results according to the concentrations of the solution (Fig. 3), it could be found that the swelling of the IPN hydrogel according to the concentration of the NaCl solution did not significantly affect the bending behavior of the IPN hydrogel.

Figure 4 shows the variation of the bending angle of the IPN hydrogel as a function of the applied voltage in 0.6 wt % aqueous NaCl. The equilibrium bending angle and bending speed increased with increasing voltage across the gel. The rate of the bending angle was fast and reached its maximum in 3.96 s. When the IPN hydrogel in the NaCl electrolyte solution was subjected to an electric field, the IPN hydrogel bent toward the anode. However, bending was not found in pure water, and this indicates that bending was induced by the electric current. It is generally thought that the deformation of a polymer hydrogel under an electric field is due to the voltage-induced motion of ions and the concomitant expansion of one side of the

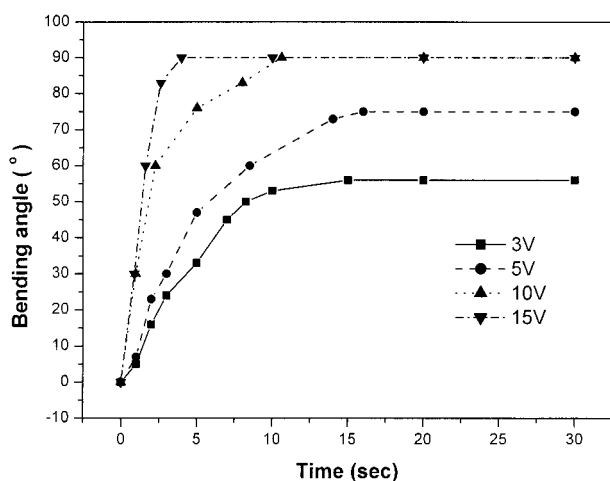


Figure 4 Bending kinetics of the IPN hydrogel as a function of the applied voltage in 0.6 wt % aqueous NaCl.

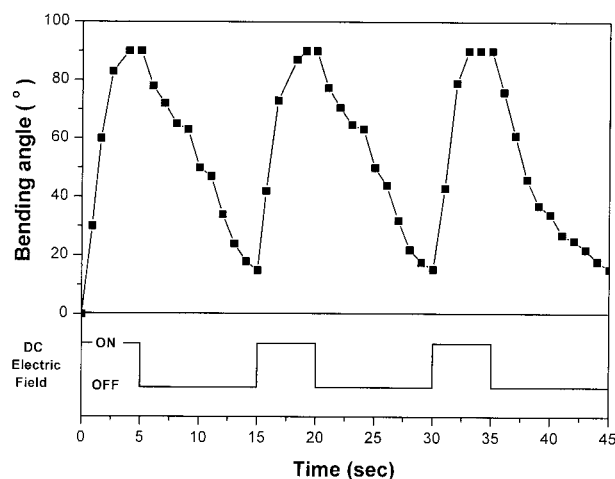


Figure 5 Reversible bending behavior of the IPN in a 0.6 wt % NaCl solution with changes in the applied voltage of 15 V.

polymer and contraction of the other side. As shown in Figure 5, the PPG/PAAc IPN hydrogel exhibited reversible bending behavior according to the application of the electric field, and this is important to the application of artificial muscles. Although the voltage between the electrodes was 15 V, the response rate of the PPG/PAAc IPN hydrogel was faster than those of fast-responding pH-sensitive^{20,21} and electrosensitive materials²² that we previously reported.

CONCLUSIONS

An IPN hydrogel based on PPG and PAAc was prepared by UV irradiation. The PPG/PAAc IPN hydrogel exhibited a high swelling ratio in the range of 2.57–2.95. The swelling ratio decreased with an increase in the NaCl concentration. When the IPN hydrogel in an NaCl electrolyte solution was subjected to an electric field, it showed significant and quick bending toward the anode. When the electric stimulus was removed, the gel approached its original position. The bending angle of the IPN was measured in NaCl solutions of different concentrations. The bending angle and bending speed of the IPN were greatest in 0.6 wt % aqueous NaCl and increased with an increase in the applied voltage. The IPN also showed a stepwise bending behavior that depended on the electric stimulus. Therefore, this PPG/PAAc IPN hydrogel system could be useful for artificial organic components such as musclelike contractile structures, sensors, switches, and electric-current-modulated drug delivery systems.

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