Swelling of Thermosensitive Interpenetrating Polymer Networks Composed of Poly(vinyl alcohol) and Poly(acrylic acid)

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SYNOPSIS

The swelling behavior of interpenetrating polymer networks (IPNs) composed of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) in water was studied. The PVA/PAA IPN gels were prepared by four synthetic methods. The swelling behaviors of these IPNs made by different methods were compared. The differences in swelling behaviors of samples are discussed on the basis of their structural and physical differences. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogels of stimuli sensitive polymers have promising potential as intelligent materials that show structural and physical changes to external signals. Environmental stimuli factors include temperature,[1,2] pH,[3-7] electric field,[8,9] light,[10] and ion or certain chemical species.[11] Among these, thermally sensitive polymers receive much attention because body temperature may increase when people get sick.

Much of the fundamental swelling behaviors of the hydrogels has been investigated since Tanaka suggested the swelling theory with respect to the change in temperature.[12] A hydrogel could be described as containing either a negative or positive temperature-sensitive system. In a negative temperature-sensitive system, a phase transition or gel shrinking occurs at lower temperature. The temperature where the phase separation occurs is called a lower critical solution temperature (LCST). Poly(*N*-isopropyl acrylamide) (PNIPAAm) hydrogel is a well-known negative temperature-sensitive polymer showing LCST at 30–32°C.[13] Many attempts have been made to change LCST of polymers in an aqueous system through a variation in polymer–water and polymer–polymer interaction.[14-16]

In a positive temperature-sensitive system, a phase transition occurs at higher temperature called an upper critical solution temperature (UCST). Al-Alaw and Saeed[17] first reported on positive temperature-dependent polymer gels showing UCST based on interpenetrating polymer networks (IPNs) from poly(acryl amide) (PAAm) and poly(acrylic acid) (PAA). These gels have been used for drug delivery systems.[18] This phenomenon is closely related to the polymer–polymer complex between PAAm and PAA through hydrogen bonding. Recently, Jung et al. reported positive swelling behavior of IPNs composed of poly(*N*-vinyl pyrrolidone-*co*-butyl methacrylate) and PAA.[19]

PAA is known to form a complex with polyoxyethylene (POE) in IPN form.[20] PAA/POE IPN shows maximum swelling at pH 9 and demonstrates that swelling–deswelling and mechanochemical reactions proceed reversibly for the full IPN, but irreversibly for the semi-IPN upon changing pH. Aoki et al.[21] reported that PAA/poly(*N,N*-dimethyl acrylamide) IPN hydrogels showed a UCST behavior due mainly to the presence of PAA. A PVA and PAA composite hydrogel was prepared by repeatedly freezing and thawing a mixed solution of PVA and PAA.[22,23] Their structure was investigated by pulsed NMR.[24] However, PVA/PAA IPNs have not been reported so far.

In this study, we wish to report on the swelling behavior of IPNs composed of PVA and PAA. PVA

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hydrogels were chosen because they have been used for biomedical and pharmaceutical materials and because the gels are innocuous, noncarcinogenic, and have good biocompatibility.[25] PVA hydrogels were prepared by using the freeze–thaw method.[22,23,26–28] Hydrogels formed a matrix of physically crosslinked polymeric chain. These gels are elastic in nature and have a high degree of swelling without the use of a crosslinking agent. Effects of IPN preparation methods on the IPN hydrogels were investigated. In this study involving various synthetic methods, novel positive temperature-dependent polymer gels composed of PVA/PAA IPN gels were first prepared and are reported here.

EXPERIMENTAL

Materials

AAm, dimethylacrylamide (DMAAm), butylmethacrylate (BMA), acrylic acid (AA), dimethyl sulfoxide (DMSO), and ammonium persulfate (AP) were purchased from Junsei Chemicals Co. Methylenebisacrylamide (MBAAm) and *N,N*-azobisisobutyronitrile (AIBN) were purchased from Tokyo Chemical Industry Co. (TCI). Indomethacin was purchased from Aldrich Chem. Co. AAm was purified by recrystallization. AA, DMAAm, BMA, and DMSO were distilled under reduced pressure before use.

Synthesis of PVA and PAA Hydrogels

PVA hydrogels were prepared by the freeze–thaw method. PVA powder (Shinetsu, DP_N 2500, degree of saponification 99.5 mol %) was dissolved in water at 80°C (5, 7.5, and 10.0 wt %). PVA aqueous solutions were poured into petri dishes, frozen at −20°C for 6 h, and thawed at room temperature for 2 h. Freeze–thaw cycles were repeated five times to manufacture elastic PVA hydrogels.

PAA hydrogel was prepared by a chemical method. AAc, 20 wt %, (Junsei Chemicals Co.) aqueous solutions containing 0.2 wt % AP (Junsei Chemicals Co.) and 0.5 mol % MBAAm (Tokyo Chemical Industry Co.) as a crosslinking agent were injected between two glass plates, separated by a silicone rubber spacer (1-mm thickness), and stored at 50°C for 24 h to obtain PAA hydrogel.

Synthesis of PVA/PAA IPNs

Chemical Method (IPNs-C)

PVA hydrogels were cut in a circular shape where the diameter of the hydrogel was 3 cm. The matrices were dried and swollen in AA aqueous solutions containing 0.2 wt % AP as an initiator and 0.5 mol % MBAAm as a crosslinking agent for 12 h. AA in these swollen matrices was polymerized at 50°C for 24 h to prepare IPNs. Matrices looked transparent and glassy.

Sequential Method (IPNs-Se)

AA (20 wt %) aqueous solutions, 0.2 wt % AP, and 0.5 mol % MBAAm were injected between two glass plates, separated by a silicone rubber spacer (1-mm thickness), and polymerized at 50°C for 24 h. PAA hydrogels prepared by thermal polymerization were cut in a square form (1 × 2 cm) and dried. These matrices were swollen in 5, 7.5, and 10.0 wt % PVA aqueous solutions, respectively, for 24 h. PAA/PVA gels were frozen at −20°C for 6 h and thawed at room temperature for 2 h. These freeze–thaw cycles were repeated five times to prepare PAA/PVA IPNs.

Simultaneous Method (IPNs-S)

Each of the 5, 7.5, and 10.0 wt % PVA solutions and 20 wt % AA aqueous solution containing 0.2 wt % AP and 0.5 mol % MBAAm were mixed at a ratio of 1 : 1 and injected between two glass plates separated by a silicone rubber spacer (1-mm thickness). Molds were maintained in an oven at 50°C for 24 h and later freeze–thawed five times to prepare IPNs-S.

UV Method (IPNs-UV)

PVA hydrogels prepared by the freeze–thaw method were immersed in AA monomer solution containing a photoinitiator (dimethylphenylacetophenone, 0.2 wt %) and a crosslinking agent (MBAAm, 0.5 mol %). These swollen gels were placed on a petri dish stored in a box and exposed to a 450-W UV lamp (Ace Glass Co.) for 10 min after dry nitrogen blowing. The distance between the UV lamp and the gels was 18 cm.

Swelling Measurement

After immersion in water at the desired temperature, the IPNs were removed and tapped with filter paper to remove any excess water that remained on the sample surfaces. The polymer samples were weighed at a fixed temperature until the hydrated weight reached a constant value. After equilibration at a certain temperature, samples were reequilibrated at a higher temperature. The weight ratio, W_s/W_p, was used to evaluate the swelling ratio, where W_s and W_p are the weight of absorbed water and dry polymer, respectively.

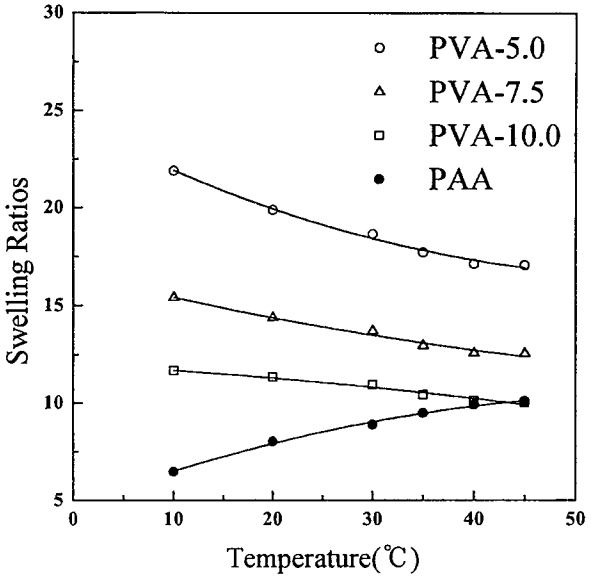

Figure 1 Swelling behavior of PVA and PAA gels.

RESULTS AND DISCUSSION

Swelling ratios of PVA and PAA hydrogels at pH 7 are shown in Figure 1. Numbers after PVA indicates PVA concentrations in the hydrogel in weight percent (wt %). Swelling degree of PVA hydrogels decreased with increasing swelling temperature and exhibited a so-called negative swelling behavior. The negative swelling behavior was observed in other polymeric systems such as the one containing *N*-isopropylacrylamide.[13] In the present study, the swelling degree of PVA gels decreased because the interaction between polymeric chains became stronger and the chemical affinity with water became weaker as temperature increased. However, the swelling ratio of PAA gels increased with temperature, indicating a UCST behavior as shown in other reports.[17–19,21]

Swelling experiments using IPN-Se hydrogels failed because they broke at above 30°C during the swelling test. It seemed that PVA macromolecules did not penetrate into PAA hydrogels during the IPN-Se preparation period. It was observed that PVA molecules accumulated and crosslinked on the surface of PAA gels. Above 30°C, the swelling ratios of PAA in the inner part of the matrix increased and that of PVA, forming the outer part of the matrix, decreased. The opposite swelling ratios of PVA and PAA hydrogels caused extensive shrinkage of the outer part which broke the expanding inner layer.

Swelling behaviors of IPNs prepared by chemical method (IPNs-C) at pH 7 are shown in Figure 2. Swelling ratios of all the matrices increased with temperature. Swelling behaviors of these IPNs were not on the order of PVA concentrations. One of the possible reasons might be that during the synthesis of the matrices at 50°C, PVA gels did not maintain their shape but they became liquid. At this stage it was speculated that the PVA chain was uncoiled due to the loss of hydrogen bonding and AA was polymerized in a random fashion. Therefore, the final IPNs-C seemed to become phase separated polymeric structures, the so-called heterogeneous IPNs. This might lead to irregular swelling of PVA/PAA IPNs. Figure 3 shows swelling behaviors of IPNs-S at pH 7. Swelling ratios of IPNs-S increased with temperature. With more PVA in these IPNs, the swelling ratios were smaller, which is similar to that of virgin PVA hydrogels. Because AA was polymerized prior to the crosslinking of PVA, the PAA matrix hindered PVA from crosslinking. Compared with less crosslinked PVA, PAA played a major role in the positive swelling behaviors of these IPNs.

Swelling behaviors of IPNs-S measured at pH 2 (Figure 4) were similar to those measured at pH 7. However, the extent of the change in swelling ratios of these IPNs as much smaller at pH 2 than those at pH 7. The pK_a value of PAA is 4.28.[23,24] Therefore at pH 2, PAA is in a carboxylic acid form that hydrogen bonds with the hydroxyl group of PVA and subsequently swells as temperature increases due to the dissociation of hydrogen bonding between them. However, at pH 7 PAA is in a carboxylate ionic form that causes a repulsion between them.

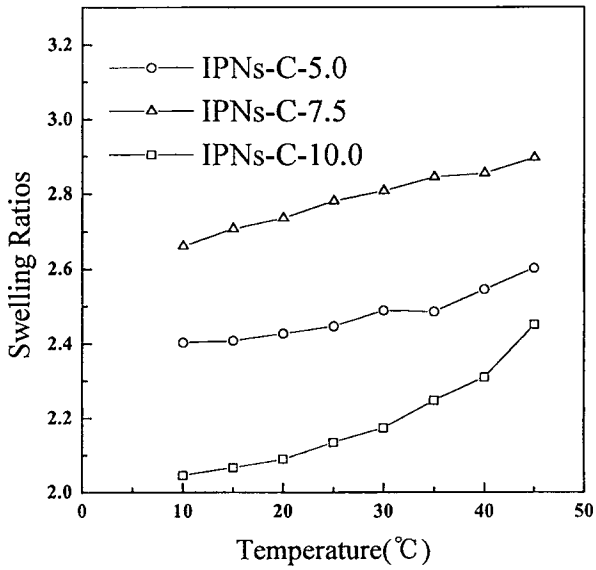

Figure 2 Swelling behavior of IPNs-C.

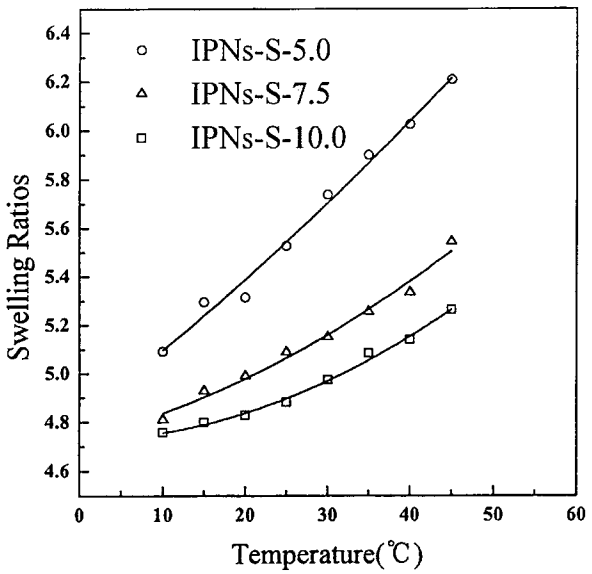

Figure 3 Swelling behavior of IPNs-S.

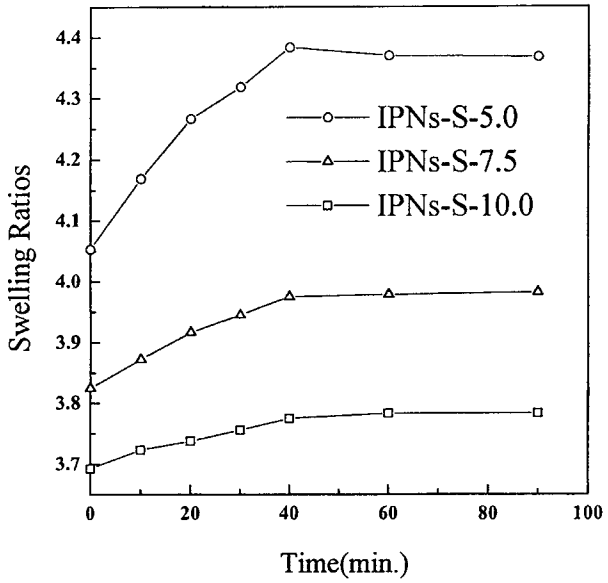

Figure 5 Kinetic swelling behavior of IPNs-S (20–40°C).

Swelling kinetics of IPNs-S hydrogels are shown in Figure 5. First, IPNs-S were swollen at 20°C to reach an equilibrium, put into a 40°C water bath, and their swelling was measured every 20 min. All the IPNs-S samples reached equilibrium after 1 h. IPNs-S-5.0 showed steeper swelling kinetics compared with the remaining IPNs-S samples.

Swelling behavior of IPNs-S-10.0 was measured at 30°C and in pH 2–7 buffer solutions and is shown in Figure 6. Because the pK_a value of PAA is 4.28, at pH 2 and 3 carboxyl groups in PAA form hydrogen bonds with the PVA chain. Therefore, the swelling ratio of IPNs-S-10.0 below pH 3 was small. However, carboxylate ions of PAA formed at pH greater than 5, inducing the repulsion between them. Thus, the hydrogen bonding between PVA and PAA should break and the free volume in the matrix will increase, resulting in a rapid increase in swelling ratios.

Typical stepwise swelling behavior of IPNs-S hydrogels at pH 7 was investigated by varying the temperature from 10 to 40°C and measuring swelling ratio every hour (Fig. 7). Generally, swelling ratios

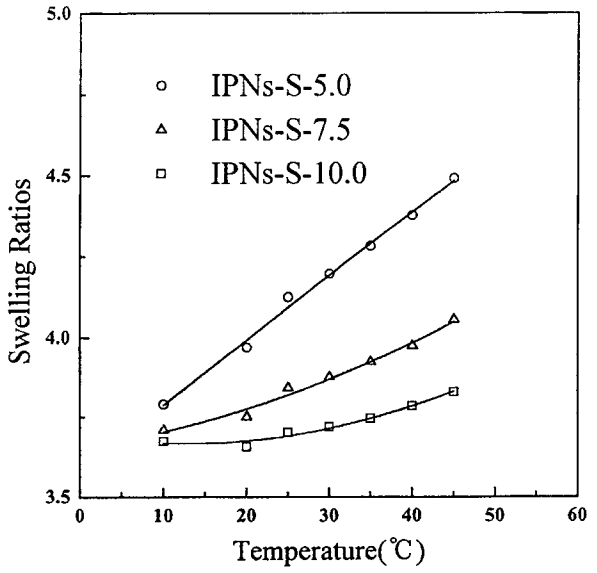

Figure 4 Swelling behavior of IPNs-S at pH 2.

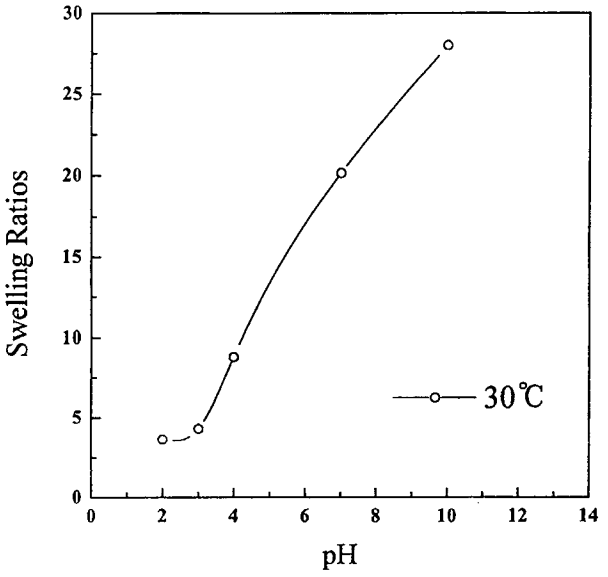

Figure 6 Swelling behavior of IPNs-S-10.0 through different pH.

were small at 10°C but became large at 40°C. Pulsatile swelling behavior of IPNs-S confirmed that PVA in the hydrogel was crosslinked and did not come out of the IPNs system.

Figure 8 shows swelling behavior of IPNs-UV hydrogels. IPNs-UV showed different swelling behavior compared with IPNs-S. At below 40°C, the swelling ratios of IPNs-UV hydrogels were almost constant. However, above 40°C they increased very rapidly. To prepare IPNs-UV samples, PVA was crosslinked by the freeze–thaw method followed by an immersion in AA monomer solution and subsequent UV irradiation. It was believed that the crosslinking degree of PAA prepared by the UV irradiation method was somewhat greater than that by the simultaneous method. Therefore, up to 40°C the PVA network hindered swelling of PAA in IPNs-UV, a result of the hydrogen bonding between PVA and PAA. Above 40°C PAA may start to swell and increase the overall swelling ratios because of the weaker hydrogen bonding between them. It is not clear at this point why the transition temperature is at 40°C, but it may be dependent on the PVA content in the IPNs. We expect that the transition temperature will decrease as the AA content in the IPNs increases.

CONCLUSIONS

The PVA/PAA IPNs gels were prepared by four synthetic methods. The swelling behaviors of these IPNs made by different methods were compared.

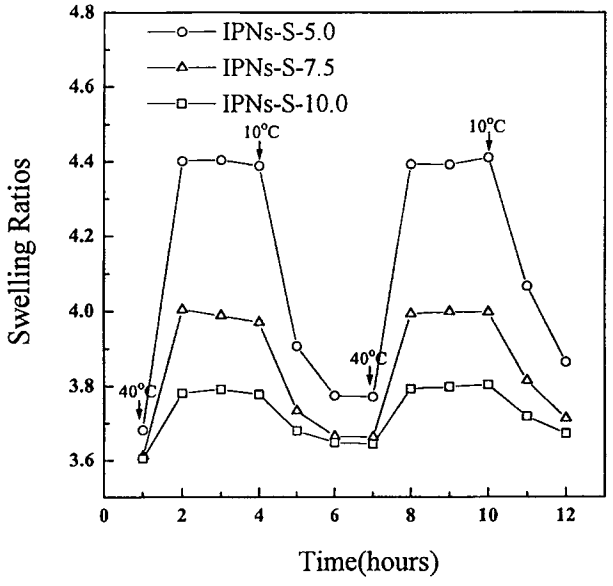

Figure 7 Stepwise swelling behavior of IPNs-S.

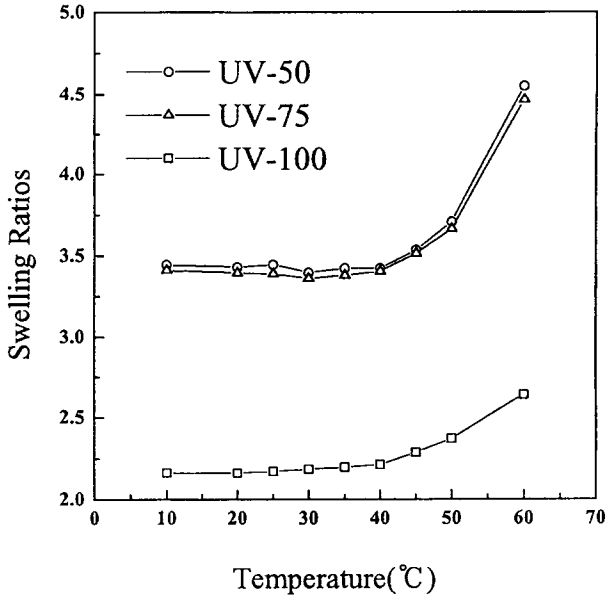

Figure 8 Swelling behavior of IPNs-UV.

The difference in swelling behavior between them was attributed to the structural differences. Positive swelling changes with temperature were observed in the PVA/PAA IPNs gels whereas negative swelling changes with temperature were observed in the PVA hydrogels. Swelling experiments using IPNs-Se were not successful because they broke during the swelling test, a result of the heterogeneous hydrogel. IPNs-S measured at pH 2 and 7 were pretty much similar but the extent of the change in swelling ratios of these IPNs was much smaller at pH 2 than at pH 7 due to their association and dissociation capability at different pH regions. IPNs-S hydrogels reached an equilibrium within 1 h. IPNs-UV hydrogels showed different swelling behavior compared with IPNs-S hydrogels. IPNs-UV hydrogel swells rapidly above 40°C. It was considered that the crosslinking degree of PAA prepared by the UV irradiation method was somewhat greater than that by the simultaneous method. Further experimentation on mechanisms of IPNs and hydrogen bonding is ongoing.

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