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

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To cite this Article Kim, Seon Jeong , Lee, Ki Jung and Kim, Sun I.(2004) 'Thermo-sensitive Swelling Behavior of Poly(2-Ethyl-2-oxazoline)/Poly(Vinyl Alcohol) Interpenetrating Polymer Network Hydrogels', Journal of Macromolecular Science, Part A, 41: 3, 267 — 274

To link to this Article: DOI: 10.1081/MA-120028206

URL: http://dx.doi.org/10.1081/MA-120028206

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A41, No. 3, pp. 267–274, 2004

Thermo-sensitive Swelling Behavior of Poly(2-Ethyl-2-oxazoline)/Poly(Vinyl Alcohol) Interpenetrating Polymer Network Hydrogels

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ABSTRACT

Interpenetrating polymer network (IPN) hydrogels composed of poly(2-ethyl-2-oxazoline) (PEtOz) and poly(vinyl alcohol) (PVA) were prepared using radical polymerization. Swelling behavior of IPN hydrogels is observed at various pH conditions. The low critical solution temperature (LCST) behavior of PEtOz is measured with various composition bain. The properties of temperature–responsive IPN hydrogels are reported.

Key Words: Hydrogel; Poly(2-ethyl-2-oxazoline); Poly(vinyl alcohol); IPN; Swelling.

INTRODUCTION

Hydrogels are crosslinked, then form three-dimensional hydrophilic polymer networks that swell, but do not dissolve when brought into contact with water. In the swollen state they are soft and rubbery, resembling a living tissue, some of them also possess excellent biocompatibility.[1,2] The water uptake of these hydrogels may be

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DOI: 10.1081/MA-120028206
1060-1325 (Print); 1520-5738 (Online)
www.dekker.com

sensitive to temperature and pH, the ionic strength of the swelling solution, or even to the presence of a magnetic field or ultraviolet light.[3] It is mainly used in the fields of medicine, pharmacy, biotechnology, and agriculture. In recent years, hydrogels, due to their versatile application in biomedicine and biotechnology, have been used for the immobilization of enzymes, proteins, antibodies and antigens.[4]

Interpenetrating polymer networks (IPNs) are defined as a composition in which one or more polymers are crosslinked, linear or branched.[4,5] Many hydrogels are generally formed from water-soluble polymers by crosslinking them either using radiation or chemicals, or by polymerizing hydrophilic monomers in the presence of a crosslinker. Crosslinked polymers seem to be good candidate to improve wet strength. The IPN hydrogels have been studied with a particular emphasis on their reversible volume changes in response to external stimuli, such as pH, solvent composition, temperature, ionic concentration, and electric field.[6]

Poly(2-ethyl-2-oxazoline) (PEtOz) is an amorphous non-ionic tertiary polyamide, soluble in water as well as in a wide range of organic solvents.[7,8] It is swelled in polar solvent, water, and shrunk with increasing temperature of solvent, indicating low critical solution temperature (LCST) behavior due to hydrogen bonding.[9] Due to these properties, it can be used in various fields as surfactants, stabilizers, biomaterials, and specific drug delivery, etc.

Poly(vinyl alcohol) (PVA) is used as a basic material for a variety of biomedical applications including contact lens material,[10] skin replacement material,[11] vocal cord reconstruction,[12] artificial cartilage replacement,[13] etc., as a result of its inherent non-toxicity, non-carcinogenicity, good biocompatibility, and desirable physical properties such as its elastic nature and a good film-forming property.[14]

In this study, we prepare IPN hydrogels composed of PEtOz and PVA. We study the characterization of the pH/temperature dependence of swelling behavior and thermo-responsive swelling behavior of IPN hydrogels.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) with an average molecular weight 1.24×10^5–1.86×10^5 and a hydrolyzed ratio of 99+%, and 2-ethyl-2-oxazoline (EtOz), as monomer, were purchased from Aldrich Chemical Co., Milwaukee, WI, USA. The EtOz was refluxed twice over CaH_2/KOH, and then distilled. Acrylic acid was purchased from Junsei Chemical Co., Tokyo, Japan and used after purification with an inhibitor removal column. 1,4-Dibromo-2-butene (DBB) (Aldritch Chemical Co., Milwaukee, WI, USA) was dried in vacuum before use. 2,2′-Azoisobutyronitrile (AIBN) (Junsei Chemical Co., Tokyo, Japan) is used as an initiator. Glutaraldehyde (GA) (Yakuri Pur Chemicals Co., Kyoto, Japan) was used as a cross-linking agent. Acetonitrile (Aldritch Chemical Co., Milwaukee, WI, USA) was purified by distillation over calcium hydride. All other chemicals used were reagent grade and used as purchased without further purification.

Synthesis of *bis*-Macromonomers

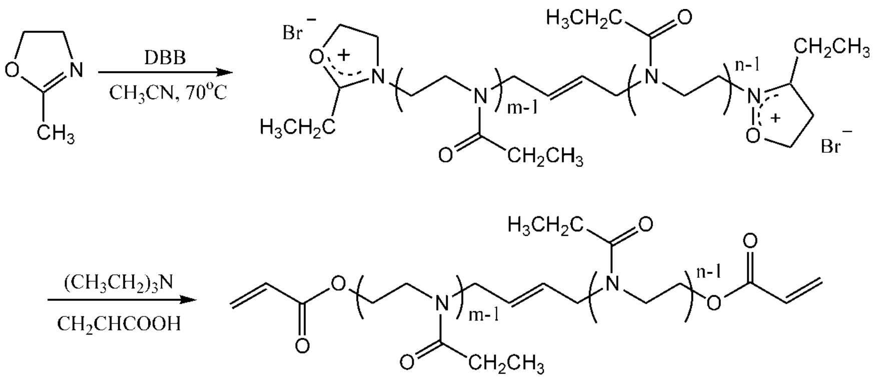
A mixture of 1.25 g of DBB and 5.73 g of EtOz in 20 mL of acetonitrile was stirred at 70°C for 6 hr. After cooling to 0°C, 2.10 g of acrylic acid and 2.95 g triethylamine were added and the reaction mixture was stirred at 60°C for 24 hr. The mixture was cooled to room temperature, poured into cooled diethyl ether and the polymeric product was collected and dried. To remove unreacted terminating agent, the product was dissolved in 100 mL chloroform and stirred with 1 g of Amberlyst 15 ion-exchange resin at room temperature for 24 hr. After filtration off the ion-exchange resin, the filtrate was concentrated in vacuum and precipitated in cooled diethyl ether. The *bis*-macromonomer, thus, obtained was purified by reprecipitation from methanol solution in diethyl ether and dried in vacuum. Scheme 1 shows the method of synthesizing *bis*-macromonomer. This reaction is reported by Christova et al.[15] The producing yield of synthesizing them has very good yield, and so we used it without further purifying.

Synthesis of Interpenetrating Polymer Network Hydrogel

bis-Macromonomer was dissolved in 2 mL of methanol and 10 mol% of initiator, AIBN were added. It is mixed with a PVA aqueous solution (1 wt%). The mixture was held in an oven at 60°C for 15 hr. Then, 1 wt% GA for PVA and HCl, catalyst, were added in the mixture for crosslinking PVA. The mixture was poured into a Petri-dish and reacted for 10 hr at room temperature. The synthesized film is then torn from the Petri-dish. The film was washed in deionized water and dried at room temperature. The samples were prepared as a composition of PEtOz and PVA. The designation of each sample is listed in Table 1.

Characterization

The dried gel films were immersed in 50 mL of deionized water at 20°C. The swelling ratio was obtained by weighing the initial and swollen samples at various time intervals. To measure the swelling ratio, pre-weighed dry samples were immersed in deionized water. After excessive surface water was removed with filter paper, the weight of the swollen samples was measured at various pH, temperature, and time intervals.



Scheme 1. Synthesis of PEtOz *bis*-macromonomer.

Table 1. Design of synthesized samples.

Sample	Composition of PEtOz and PVA (ratio of weight) PEtOz	 PVA
OV11	1	1
OV21	2	1
OV31	3	1

The swelling ratio was determined according to the following equation:

$$\text{Swelling ratio (\%)} = \left(\frac{W_s - W_d}{W_d}\right) \times 100 \tag{1}$$

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

RESULTS AND DISCUSSION

Figure 1 shows the swelling ratio of PEtOz/PVA IPN hydrogel films with composition of PEtOz and PVA at 25°C. All samples swelled rapidly and reached at

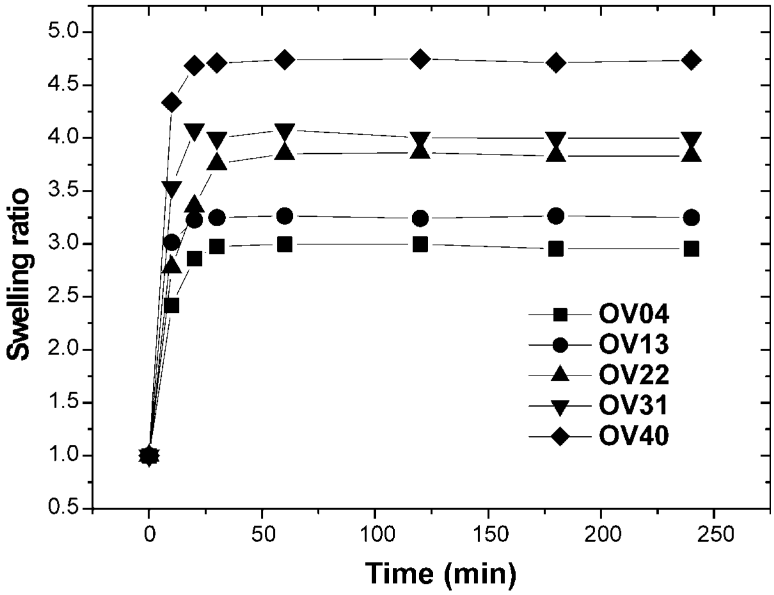


Figure 1. Swelling ratio of PEtOz/PVA IPN hydrogels as a function of time.

equilibrium within 1 hr. The swelling ratio of hydrogels films is from 200% to 350% and changes with the composition of the PEtOz and PVA network. The swelling ratio of OV31 was higher than those of the OV22 and OV13 films. It was observed that an increase in the PEtOz fraction in the films led to an increase in the equilibrium swelling ratio. This is attributed to the fact that PEtOz has a hydrophilic content. This behavior may be due not only to the complex degree of PEtOz and PVA network, but also to the content of PEtOz having a large number of water-binding sites.

The swelling behavior in the PVA/PEtOz hydrogels was directly linked to the pH value in aqueous solutions. To diminish the effect of hydrolysis at a high pH, we measured the swelling ratio with increasing pH values in standard buffer solution (Shinyo Pure Chemicals Co., Ltd., Osaka, Japan), and the results can be seen in Fig. 2. Unlike other basic polymer networks, the hydrogels were swollen at higher pH values but collapsed at lower pH values under a fixed condition, when the ionic strength ($I = 0.01$) and room temperature were held at a constant value. At pH values lower than 5.3, the amide groups of PEtOz were ionized, thereby inducing hydrogen-bonded complexes to be formed between different PEtOzs. The subsequent increase in cohesion restricted the swelling of the hydrogels. Therefore, the equilibrium swelling ratio of the polymeric network was determined by a balance among the swelling forces, elastic forces, and hydrogen bonding. In addition, elastic forces and hydrogels at low pH values were observed to increase slightly with a decreasing pH value. This behavior was based on the fact that the networks slightly expanded because the residual amide groups had ionized and were repulsive. At low pH values, the swelling ratio of OV31 was smaller than that of OV22 because of the formation of hydrogen. When the pH value increased, hydrogen bond formations were

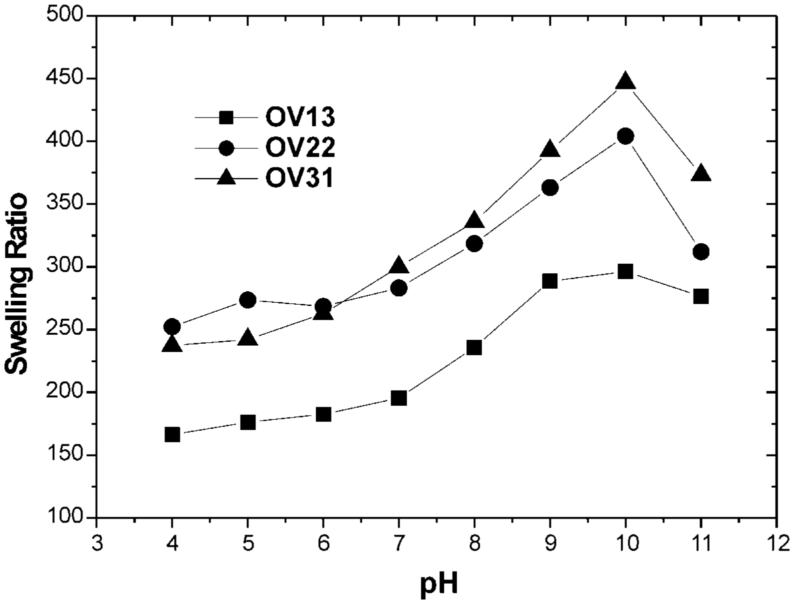


Figure 2. Equilibrium swelling ratio of PEtOz/PVA IPN hydrogels as a function of pH.

broken because the amide group of PEtOz was disassociated with hydrogen ions. Shrunken polymers should begin to expand, causing the hydrogels to swell.

The changes in the swelling behavior of the segmented polymer networks as a function of temperature are summarized in Fig. 3. The highly hydrophilic PVA/PEtOz hydogels exhibit considerable volume shrinkage in the temperature range of 35–65°C. The shrinkage is more abrupt in the case of PEtOz containing gels. The networks with higher PEtOz content display a higher equilibrium water uptake and the most spectacular volume change. As increasing PVA content, thermo-responsive behavior of IPN hydrogels was reduced. It is obvious that this observation should be attributed to the presence of a PVA matrix, which does not allow PEtOz segments, even long enough, to display their LCST features.

The swelling–deswelling kinetics of PEtOz hydrogels in response to stepwise changes in temperature, respectively, at 25°C and 65°C, was followed. A typical example has been shown in Fig. 4. As the time interval between every step is 30 min, the experimental data are not equilibrium values. However, kinetic data show that the biggest changes in the swelling and deswelling process already happen in the first 30 min. More detailed kinetic experiments as a function of network composition, film thickness, temperature, and pH are currently under investigation and will be subject to a forthcoming paper. The example shown in Fig. 4 already demonstrates the reversibility of the swelling–deswelling process and the mechanical stability of such hydrogels. It has been found that, by increasing the PEtOz-fraction or the step time, it is possible to get stable swollen and shrunken gels for many cycles. These properties make these water-swollen segmented polymer networks promising materials for applications as actuators and on–off switches.

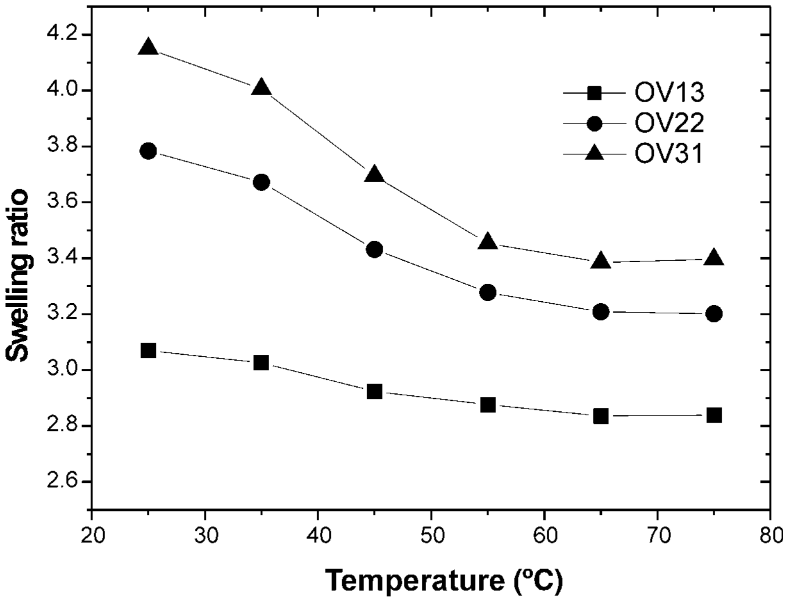


Figure 3. Equilibrium swelling ratio of PEtOz/PVA IPN hydrogels as a function of temperature.

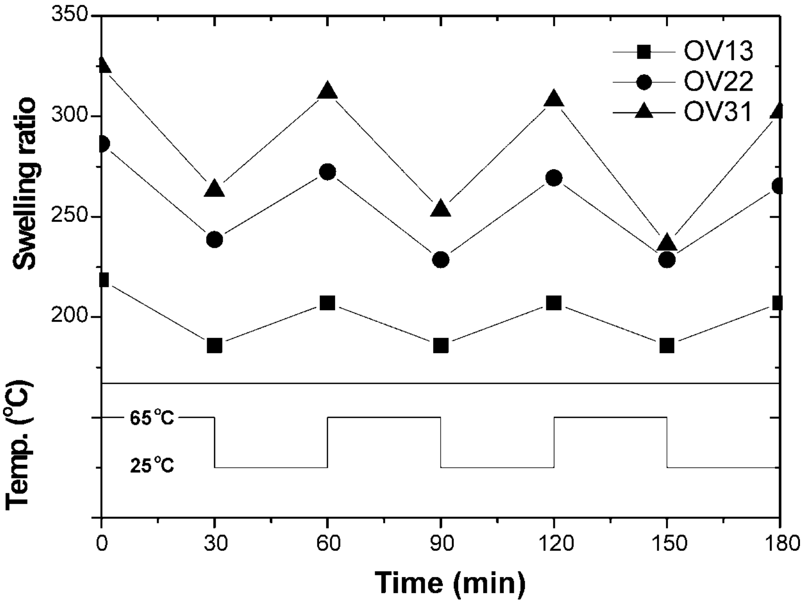


Figure 4. Swelling–deswelling cycles for PEtOz/PVA IPN hydrogel as a function of temperature.

CONCLUSION

PEtOz is more hydrophilic than PVA. PEtOz/PVA IPN hydrogels had a maximum swelling ratio at about pH 10. All PEtOz/PVA IPN hydrogels show LCST in an aqueous solution. With increasing the content of PEtOz, IPN hydrogels show a noticeable response in change in temperature.

ACKNOWLEDGEMENT

This work is the result of research activity of Advanced Biometric Research Center (ABRC) supported by Korea Science and Engineering Foundation (KOSEF).

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Received June 2003
Accepted September 2003

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