

Surfactant-Free Thermochromic Hydrogel System: PVA/Borax Gel Networks Containing pH-Sensitive Dyes

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ABSTRACT: The well-known pH-indicators, phenolphthalein and bromothymol blue, exhibit an outstanding thermochromism, when they are embedded in aqueous polyvinyl alcohol/borax gel networks. The color of phenolphthalein in hydrogels changes gradually from colorless at 20°C to dark red at 70°C. The pH change in a hydrogel system was from 8.0 to 8.9 with increasing temperature. In

the case of bromothymol blue, the color was optically clear green at room temperature and changed to clear blue with increasing temperature. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 890–893, 2004

Key words: crosslinking; hydrogels; networks; pH-sensitive dye; polymer thermochromism

INTRODUCTION

Recent advances in intelligent hydrogels have resulted in the development of new materials that have found applications in many areas of optics and materials science.^{1–12} One novel application presently being considered is as thermochromic materials in thermally adjustable smart windows, large-area displays for information and traffic engineering, and temperature-sensing applications in medical technologies.^{13–15} In the last decade, so-called intelligent hydrogels that are sensitive to external stimuli such as temperature or electric fields have been extensively investigated, although thermochromic hydrogels have rarely been described. Recently, the reversible thermochromism of phenol-substituted dyes embedded in the polyvinyl alcohol (PVA)/borax/surfactant gel network was reported by Seeboth et al.¹³ The advantages of hydrogels are that they are biologically degradable, innocuous, free of an organic solvent, inexpensive, available in large quantities, and nonflammable. Furthermore, these hydrogels allow for high transparency and they have a reasonable color-transition temperature. However, it is not easy to select an appropriate surfactant that enables organic dyes to be miscible with aqueous hydrogel networks. Therefore, we present a surfactant-free system that may simplify the manufacturing

process and improve the maintenance of transparency over time.

In this article, we report the thermochromic behaviors of surfactant-free hydrogels containing two cheap and common dyes¹⁶: phenolphthalein, which has a color transition from colorless at pH 8.3 to red at pH 10.0; and bromothymol blue, which has a color transition from yellow at pH 6.2 to blue at pH 7.6.

EXPERIMENTAL

Materials

Borax (sodium tetraborate decahydrate, Na₂B₄O₇·10H₂O) and polyvinyl alcohol (PVA, $M_w = 13,000$ – $18,000$ hydrolyzed to 88%) were purchased from Aldrich Chemical (Milwaukee, WI). PVA with a high degree of hydrolysis ($M_w = 74,000$ hydrolyzed to 99.95%) was kindly supplied by Hyosung Corp. (Korea). pH-sensitive dyes (phenolphthalein, bromothymol blue, and bromophenol blue) were purchased from Acros Chemical Co. All chemicals were supplied by Aldrich (USA), TCI (Japan), or Acros (Belgium) and were used without further purification.

Preparation

Preparation of borax solution

A 3% aqueous solution of borax, which totally dissociated into equal amounts of borate [B(OH)₄⁻] and boric acid [B(OH)₃], was prepared.

Preparation of phenolphthalein, bromothymol blue, and bromophenol blue solution

Normal 1% butanolic solutions of phenolphthalein, bromothymol blue, and bromophenol blue were prepared, respectively.

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Preparation of the first thermochromic hydrogel (1)

The resulting gel (1) was prepared by mixing 36 g of a 20% aqueous solution of PVA (Aldrich; $M_w = 13,000$ – $18,000$ hydrolyzed to 88%), 2 mL of the prepared borate solution, 2 mL of a 1M sodium hydroxide solution, 1 mL of the prepared phenolphthalein solution, and refluxing the gel mixture for 60 min.

Preparation of the second thermochromic hydrogel (2)

The resulting gel (2) was prepared by mixing 43 g of a 7.5% aqueous solution of PVA (Hyosung; $M_w = 74,000$ hydrolyzed to 99.9%), 1 mL of the prepared borate solution, 0.3 mL of a 1M sodium hydroxide solution, 0.5 mL of the prepared phenolphthalein solution, and refluxing the gel mixture for 60 min.

Preparation of the third thermochromic hydrogel (3)

The resulting gel (3) was prepared by mixing 43 g of a 7.5% aqueous solution of PVA (Hyosung, $M_w = 74,000$ hydrolyzed to 99.9%), 1 mL of the prepared borate solution, 0.2 mL of the prepared bromothymol blue solution, and refluxing the gel mixture for 60 min.

Preparation of the fourth thermochromic hydrogel (4)

The resulting gel (4) was prepared by mixing 43 g of a 7.5% aqueous solution of PVA (Hyosung, $M_w = 74,000$ hydrolyzed to 99.9%), 1 mL of the prepared borate solution, 0.3 mL of a 0.5M hydrochloric acid solution, 0.2 mL of the prepared bromophenol blue solution, and refluxing the gel mixture for 60 min.

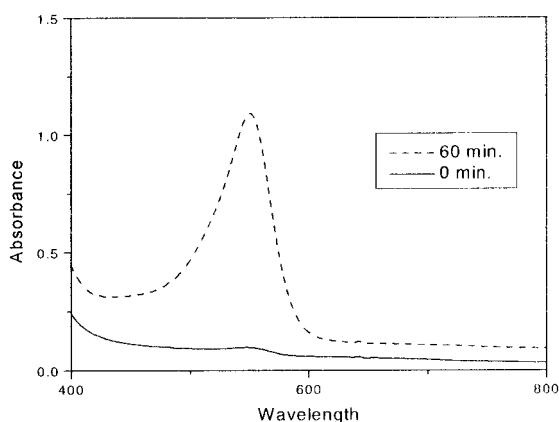


Figure 1 UV-vis absorption spectra of gel (1), which contains phenolphthalein and PVA (hydrolyzed to 88%), at 70°C for different times.

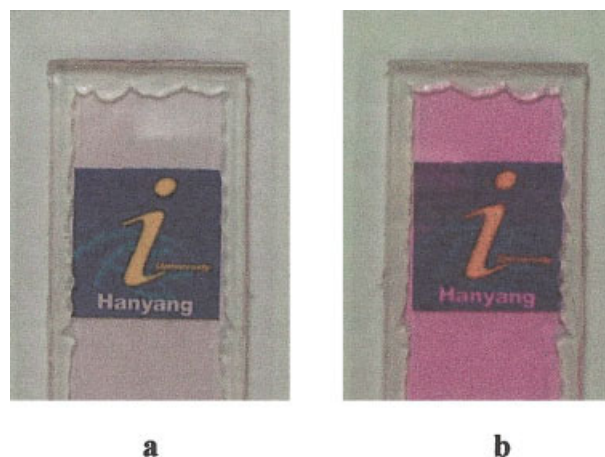


Figure 2 (a) Photograph of gel (2) between two glass plates (2 mm thickness) at room temperature. (b) Thermochromic behavior of gel (2) by increasing temperature to 70°C. The transparent clear state becomes transparent red. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Measurements

The absorption spectra were obtained with a Scinco UV S-2100 UV-visible spectrometer (Korea). The spectra of the thermochromic gels were measured at different temperatures.

The pH values of solutions were measured using a digital pH meter (Istek Inc., Korea) calibrated with standard buffers of pH 4.00, 7.00, and 10.00 at $20 \pm 2^\circ\text{C}$.

RESULTS AND DISCUSSION

Hydrogel (1) was prepared from 88% hydrolyzed PVA as reported by Seeboth et al.¹³ However, the color intensity attenuated gradually with time at 70°C. The UV-vis absorption spectrum of gel (1) is shown in Figure 1. Data from Figure 1 indicate that an incompletely hydrolyzed gel may not be appropriate for thermochromic applications because the pH decreases from 8.4 at 0 min to 6.5 at 60 min. This pH change might be caused by acetic acid produced by the hydrolysis of an unhydrolyzed acetate group of the polymer. We believe that using completely hydrolyzed PVA could avoid this problem.

Hydrogel (2) was fully transparent and colorless at room temperature. On heating, the color changed gradually from colorless at 20°C to dark red at 70°C (Fig. 2). The attenuation of color intensity was not detected after 3 days with a reflux. The temperature-dependent visible absorption spectrum of gel (2) in the temperature range from 20 to 70°C is shown in Figure 3. The absorption intensity of the gel (2) at $\lambda_{\text{max}} = 550$ nm increases with increasing temperature, indicating that the phenol form of phenolphthalein is converted

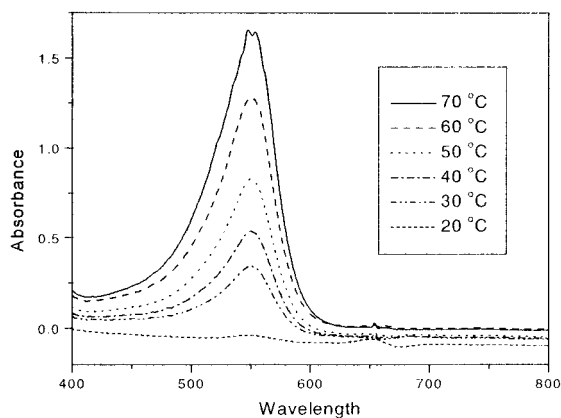


Figure 3 Temperature-dependent UV-vis spectra of gel (2), which contains phenolphthalein.

to the phenolate form. The pH value in the hydrogel increased with increasing temperature and with decreasing viscosity of the hydrogel. It is known that the crosslink density in the hydrogel decreases when the temperature is increased (Fig. 4).^{17,18} The reactions between borate ions and hydroxyl groups of PVA led to the monodiol-borate complex formation and didiol-borate complexes, so-called crosslinks, governed by change of temperature.

Another candidate dye and widely used indicator, bromothymol blue, was also used in the thermochromic hydrogel. With increasing temperature, the absorption behavior of the bromothymol blue in the visible spectra range shows an increase in the intensity of the absorption band at $\lambda_{\max} = 610$ nm, whereas that at $\lambda_{\max} = 405$ nm is reduced. The temperature-dependent UV-vis spectra of the hydrogel (3) are shown in Figure 5, which also shows that the pH value in the hydrogel increased with increasing temperature. This gel was optically clear green at room temperature and changed to clear blue with increasing temperature.

Instead of the using a surfactant to prevent turbidity, normal butanol was used. Butanol exhibited the same striking thermochromic behavior of phenolphthalein and bromothymol blue in the hydrogel networks without turbidity. Unlike these surfactant-free hydrogel networks, thermochromic hydrogels that contain surfactant can become turbid when an unsuit-

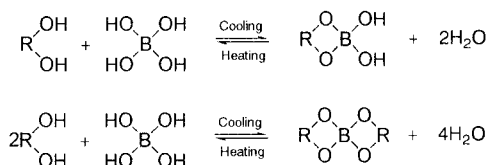


Figure 4 Monodiol-borate complex formation (reaction I) and didiol-borate complex (i.e., crosslink) formation (reaction II). These complexation reactions are reversible and exothermic.

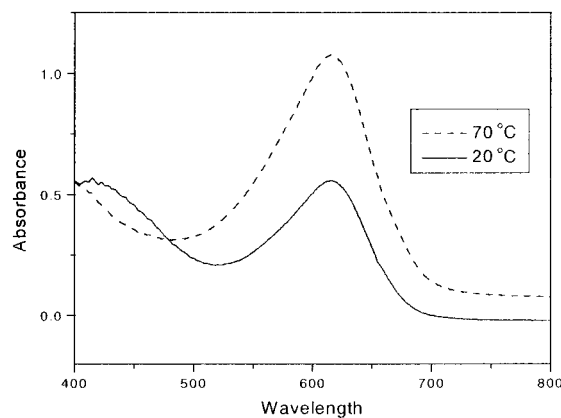


Figure 5 Temperature-dependent UV-vis spectra of gel (3), which contains bromothymol blue.

able surfactant is used. A suitable surfactant can be selected only experimentally. In contrast to the neutral or basic PVA-gel networks where the pH value increased with increasing temperature, we observed a significant decrease in pH of the acidic hydrogel networks with increasing temperature. Generally, the borax aqueous solution acts as a buffer (pH \sim 9.5), and there is no change in pH with increasing temperature (Fig. 6). Because of this buffering, we assumed that appropriate indicators, which change their color under acidic conditions, could show the thermochromic behavior in the acidic hydrogel networks. Bromophenol blue, which has a color transition from purple at pH 4.6 to yellow at pH 3.0, was applied to the acidic PVA-gel network (4), but the bromophenol blue in our investigation exhibited no significant color change with increasing temperature in the hydrogel networks. A temperature-induced decrease in pH might not be sufficient to change their color.

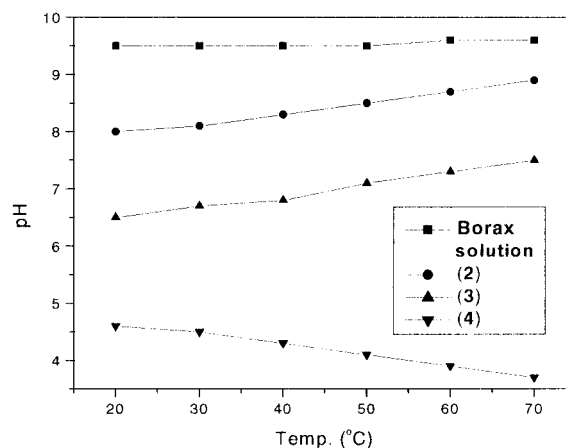


Figure 6 Plots of the variation of the pH values of the hydrogel networks depending on the variation of temperatures. (■) 0.003M borax aqueous solution; (●) basic gel (2), which contains 0.3 mL of 1M NaOH; (▲) neutral gel (3); (▼) acidic gel (4), which contains 0.3 mL of 0.5M HCl.

However, it may be possible to apply it to the acidic region of pH values according to the change in temperature.

CONCLUSIONS

The new surfactant-free thermochromic hydrogel system was made from PVA/borax gel networks containing phenolphthalein or bromothymol blue, which are cheap and common pH indicators. It is likely that other pH-sensitive dyes will show a similar behavior in hydrogel networks. Additional studies are currently being conducted on the thermochromic gels having improved properties and more desirable colors. In the future, these networks with high transparency will be economical substitutes in electrochromic¹⁹ or photochromic²⁰ applications, such as car rear-view mirrors, large-scale traffic direction boards, sun-protecting smart windows, and optical memory cells.

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