A Novel Fluorescence Temperature Sensor Based on a Surfactant-free PVA/Borax/2-Naphthol Hydrogel Network System

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ABSTRACT: This article is a report about the novel fluorescence temperature sensor based on a surfactant-free Poly (vinly alcohol)/borax/2-naphthol hydrogel system. The well-known fluorescence indicator, 2-naphthol, exhibits a change of fluorescence intensity when it is embedded in aqueous PVA/borax gel networks at various temperatures. The blue color emission intensity(PL:λ_{max} = 426 nm) of 2-naphthol in a basic hydrogel changed gradually to strong from 30°C to 80°C when excitation wavelength was 365 nm. The pH change in the hydrogel system was in the range from 8.50 at 30°C to 9.35 at 80°C with rising temperature. In the case of salicylic acid, the blue color emission intensity in the acidic gel decreases with rising temperature when excitation wavelength was 365 nm in all cases. The pH change in the hydrogel system was from 2.80 at 30°C to 2.40 at 80°C with rising temperature. J Appl Polym Sci 93: 2114–2118, 2004

Key words: crosslinking; fluorescence temperature sensor; hydrogels; fluorescence indicator

INTRODUCTION

Chemical sensors, such as fluorescence sensors, molecular sensors, ionic sensors, and pH sensors, have been extensively investigated.[1–3] Particularly, fluorescence sensors have proved to be very attractive from the scientific point of view because of the high demand in analytical chemistry, bioanalytical chemistry, medicine, the environment, LEDs, displays, etc.[4–6] Fluorescence sensors have many advantages in terms of sensitivity and selectivity. Moreover, fluorescence is an easily detectable property, which can be used to signal the occurrence of molecular events in real time and in real space.[7]

However, molecular sensors to detect changes in environmental properties, such as temperature and pressure, have been rarely described. Recently, it was reported that in the reversible thermochromism of pH indicators, dyes such as bromothymol blue and cresol red embedded in the PVA/borax/surfactant gel network system,[8–9] and a dual fluorescence temperature sensor based on perylene/exciplex interconversion was reported by Kelly et al.[10] Recent advances in the above intelligent hydrogels have resulted in the development of new materials that find applications in many areas of optics and material science. The advantages of hydrogels are that they are biologically degradable, innocuous, free of an organic solvent, inexpensive, available in large quantities, and nonflammable. Furthermore, the hydrogels should allow high transparency. The formation of complexes between a borate and a simple polyol is well known, and numerous studies have been carried out on interactions of simple polyols with borate ions.[11–17] PVA's properties in the hydrogel system depends on its molecular weight and degree of hydrolysis.[18] The polyhydroxy compound of PVA forms gels in the presence of anionic species such as a borate. The use of the borate ion is particularly attractive because the induced crosslinks are very labile and the system is easily brought to thermal equilibrium.

In this present work, we report a novel fluorescence temperature sensor based on a surfactant-free Poly (vinly alcohol)/borax/2-naphthol hydrogel network system.

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EXPERIMENTAL

Materials

Borax (sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$), 2-naphthol, and salicylic acid were purchased from Aldrich Chemical Company (Seoul, Korea). The PVA (Mw = 74,000 hydrolyzed to 99.95%) was kindly supplied by Hyosung Corp. (Seoul, Korea). The completely hydrolyzed PVA was used due to avoiding hydrolysis of an unhydrolyzed acetate group of the PVA. All chemicals were used without further purification of the PVA.

Sample 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 2-naphthol and salicylic acid solution

1% normal butanolic solutions of 2-naphthol and salicylic acid solution were prepared, respectively.

Preparation of the hydrogel with 2-naphthol

The hydrogel of the 2-naphthol was prepared by mixing 21.5 g of a 7.0% aqueous solution of poly vinyl alcohol(Hyosung, Mw = 74,000 hydrolyzed to 99.95%), 0.35 mL of aqueous borax solution, 0.05 mL of 2-naphthol solution, and 0.45 mL of a 1*M* sodium hydroxide solution. The mixture was refluxed for three hours at 90°C and cooled at room temperature.

Preparation of the hydrogel with salicylic acid

The hydrogel of salicylic acid was prepared by mixing 21.5 g of a 7.0% aqueous solution of poly vinyl alcohol (Hyosung, Mw = 74,000 hydrolyzed to 99.95%), 0.35 mL of borax solution, 0.05 mL of salicylic acid solution, and 0.30 mL of a 1*M* hydrochloric acid solution. The mixture was refluxed for three hours at 90°C and cooled at room temperature.

Measurements

The photoluminescence spectra were obtained on a RF-5301DC SHIMADZU fluorescence spectrophotometer (Seoul, Korea) using a quartz cell. The spectra of the fluorescence thermometer gel were measured by changing temperature.

The pH values of solutions were checked using a digital pH meter (Istek Inc., Seoul, Korea) calibrated with standard buffers of pH 4.00, 7.00, and 10.00 at 25 ± 2°C.

RESULTS AND DISCUSSION

Fluoroscence temperature sensor based on the hydrogel in the basic solution

In our system, 2-naphthol was used as a fluorescent indicator that displays a color transition from nonfluorescence at pH 8.5 to blue at pH 9.5.[19] It offers more sensitivity than classical pH indicators such as phenolphthalein, bromothymol blue, etc., based on color change.[4]

As opposed to the previous study in thermochromism using a surfactant,[8–9] the surfactant-free system was chosen for preventing turbidity in our system, and instead of a surfactant, normal butanol was used as an excellent candidate that exhibited the fluorescence behavior of dyes in the hydrogel networks without turbidity.

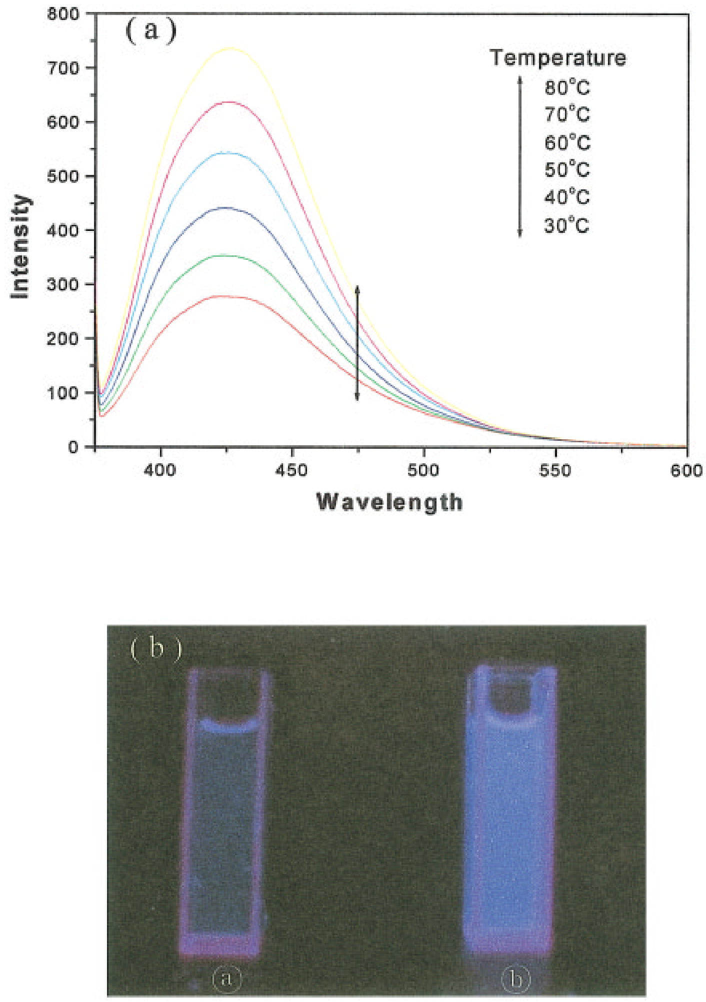
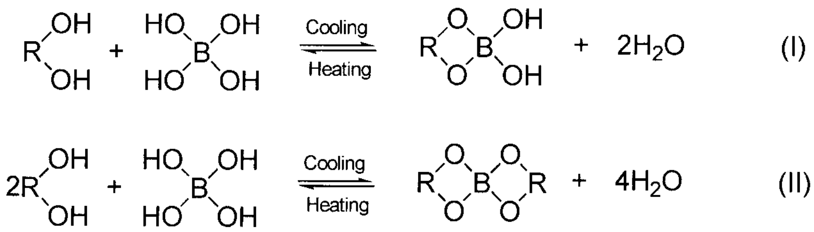


Figure 1 (a) The emission spectrum of the 2-naphthol in the gel network at 30°C, 40°C, 50°C, 60°C, 70°C, and 80°C. (b) The photograph of the 2-naphthol containing gel at two different temperatures: at 30°C and at 80°C.

The temperature-dependent emission spectra of the basic gel of 2-naphthol in the temperature range from 30 to 80°C is shown in Figure 1(a). The emission intensity of the gel at λ_{max} = 426 nm increased with rising temperature when excitation wavelength was 365 nm in all cases. Figure 1(b) is a photograph giving a visual demonstration of the gel at two different temperatures. On heating, the blue color intensity changed gradually to strong from 30°C to 80°C.



Scheme 1 The monodiol-borate complex formation (reaction I) and the didiol-borate complex, that is, cross-link, formation (reaction II). These complexation reactions are reversible and exothermic.

The pH value in the hydrogel was increasing with rising temperature and with decreasing the viscosity of the hydrogel[20–21]; pH 8.50 (30°C), pH 8.68 (40°C), pH 8.87 (50°C), pH 9.02 (60°C), pH 9.19 (70°C), and pH 9.35 (80°C). It was known that the crosslink density in the hydrogel decreases when the temperature is raised. The mechanism of the formation of crosslinks in this system is relatively simple and is governed by complexation equilibria between borate ions and hydroxyl groups of PVA.[16–17] It means that the reactions between borate ions and hydroxyl groups of PVA lead to the monodiol-borate complex formation and didiol-borate complexes, so called crosslinks, governed by change of temperature. The hydrogel system tends to lose its viscosity when raising the temperature, owing to decrease in the number of the didiol complexes as well as the shrinkage of the PVA chains (Scheme 1).[15] These complexation reactions are reversible and exothermic.[11–14]

The basic solution acts as a proton acceptor. The acidic properties in the ground state and in the excited state of 2-naphthol that absorb light may not be the same.[22–23] Acids are stronger in the excited state than in the ground state, because excitation may trigger a photoinduced proton transfer.[4] Then, the acidic character of 2-naphthol can be enhanced upon excitation so that the pK of 2-naphthol in its ground state is 9.5, dropping to pK* = 2.8 in the excited state, nearly 7 orders of magnitude.[20] The pH value in the hydrogel was increasing with rising temperature, that is, the basicity of solution is increasing. It means when the temperature is raised, the emission intensity of the gel is getting higher than before.

Fluoroscence temperature sensor based on the hydrogel in the acidic solution

We observed a significant decrease of pH value in the acidic hydrogel networks with rising temperature, in contrast to basic PVA-gel networks where the pH value was increasing with rising temperature. Generally, the borax aqueous solution is a buffer, pH about 9.5, and there is no change of pH value with rising temperature, as shown in Figure 2. According to this

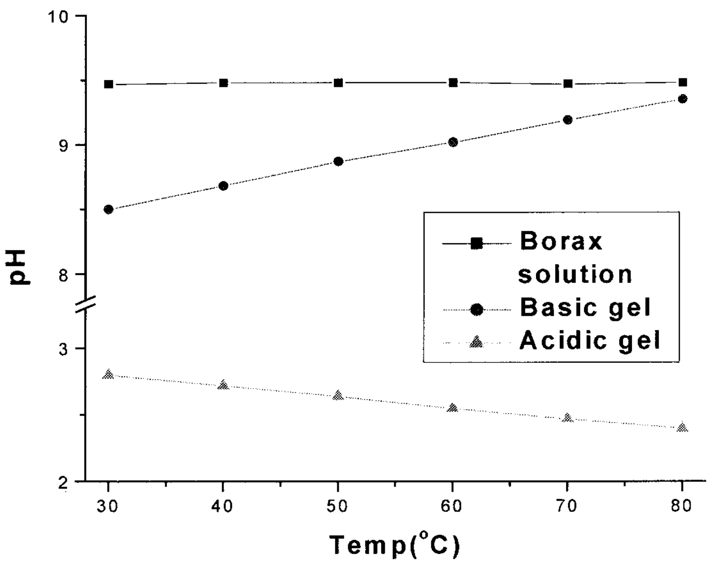


Figure 2 Plots of the variation of pH values of the hydrogel networks depending on the variation of temperatures. (■) 0.003M borax aqueous solution. (●) The basic gel, which contains 0.45 mL of a 1*M* NaOH. (▲) The acidic gel, which contains 0.3 mL of a 1*M* HCl.

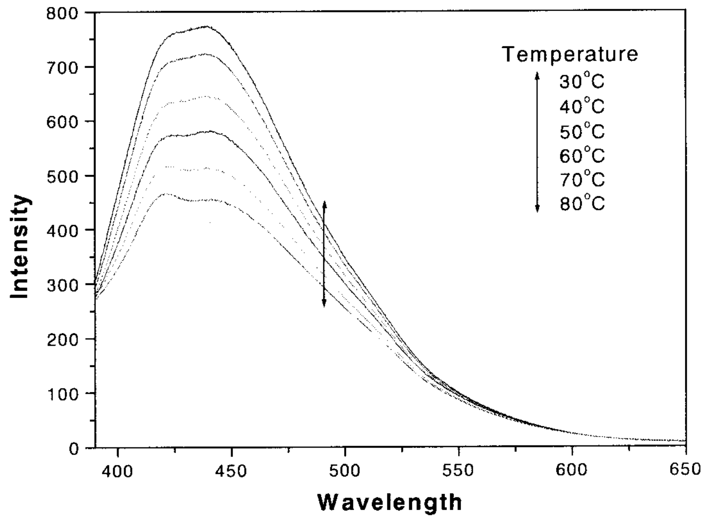


Figure 3 The emission spectrum of the salicylic acid in the gel network at 30°C, 40°C, 50°C, 60°C, 70°C, and 80°C.

explanation, we assumed that appropriate indicators, which change their emission color under an acidic condition, could show the fluorescence temperature sensor behavior in the acidic hydrogel network. So, we applied salicylic acid, which is the widely used fluorescence indicator, to the acidic PVA-gel network. The salicylic acid has a color transition from nonfluorescence at pH 2.5 to dark-blue at pH 4.0.[19]

As in the 2-naphthol, the salicylic acid, which absorbs light, may not be the same in the ground state and in the excited state because an intramolecular hydrogen bond is generally formed in the electronic ground state in salicylic acid, which contains both hydrogen-atom donor and acceptor groups in close proximity. The intramolecular redistribution of electronic charges due to photon absorption in salicylic acid induces an elementary and fast reorganization of the molecular structure, generally referred to as electronically excited-state intramolecular proton transfer (ESIPT).[24–28]

The temperature-dependent emission spectra of the acidic gel of salicylic acid in the temperature range from 30 to 80°C is shown in Figure 3. The blue color emission intensity of the gel at λ_{max} = 430 nm decreased with rising temperature when excitation wavelength was 365 nm in all cases. The pH value in the hydrogel was decreasing with rising temperature; pH 2.80 (30°C), pH 2.72 (40°C), pH 2.64 (50°C), pH 2.55 (60°C), pH 2.47 (70°C), and pH 2.40 (80°C) (Fig. 2).

It has been known that no gelling appears when the pH is lower than 7.5 at a similar borax complexion system and that no boric acid-diol complex has been formed.[11] However, in the case of our system, we observed change of the color intensity and the pH. The reason about it would be in progress.

CONCLUSION

In conclusion, the novel fluorescence temperature sensor was made from the PVA/borax hydrogel system containing 2-naphthol in the temperature range of 30–80°C. The hydrogel network whose emission intensity varies with temperature is very useful for many applications, such as fluorescence sensors, large area displays, and intelligent windows of surgical applications. Also, it can be expected that other fluorescence pH dyes will show a similar behavior in the hydrogel networks. Further works are underway involving other fluorescence gels with improved properties and desired colors.

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