Controlling Optical Properties of a Novel Light-Modulation Device Consisting of Colored *N*-Isopropylacrylamide Gel Particles Dispersed in a Poly(vinyl alcohol) Solution

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ABSTRACT: The optical properties of a novel light modulator consisting of colored particles of *N*-isopropylacrylamide (NIPAM) gel, a well-known thermoresponsive gel, dispersed in an aqueous poly(vinyl alcohol) solution were examined. The performance of the light modulator was mainly defined by two factors: the NIPAM gel properties and device compositions. The NIPAM gel properties included the amount of the volume change, the volume-change temperature, and the pigment concentration in the NIPAM gels. The larger the volume change was of the NIPAM gel particles, the wider the transmittance change became. The color-change temperature was controlled by the manipulation of the volume-change temperature of the NIPAM gels with the addition of sodium dodecyl sulfate (SDS). The volume-change temperature of the NIPAM gels became higher with an increasing concentration of SDS. The pigment concentration also had a significant effect. The higher the pigment concentration was in the NIPAM gels, the wider the breadth of the transmittance changes became. This occurred because, in the case of low pigment concentrations, absorbed water diluted the pigment, and this led to low absorption at each NIPAM gel particle. The properties of light modulation could also be controlled by the composition of the light-modulation layer. The two main parameters were the concentration of the gel particles in the layer and the thickness of the layer. The transmittance of the light modulators decreased as the thickness and/or concentration of the gel particles increased. Light modulators with various colors were obtained with NIPAM gel particles containing pigments of different colors. J Appl Polym Sci 102: 362–368, 2006

Key words: biomimetic; dyes/pigments; hydrogels; optics; stimuli-sensitive polymers

INTRODUCTION

Reversible color-changing or light-modulating materials are drawing intense interest because they are a fundamental technology for various optical devices such as displays, optical filters, recording media, and various types of sensors. There have been numerous attempts to develop such materials as electrochromic compounds, thermochromic compounds, photochromic compounds, and guest–host liquid crystals.

Recently, we designed and developed novel reversible light-modulation materials, smart-gel light-modulation materials (called LM gels hereafter),[1] which we devised by observing the mechanism of pigment cells in cephalopods, which can rapidly change their skin color and reverse the process. LM gels use the volume-change properties of stimuli-responsive gels. Stimuli-responsive gels[2,3] are smart materials and are of great interest from both fundamental and technological viewpoints because these gels reversibly change their volume according to external stimuli, such as the temperature, pH, electricity, and exposure to light.[4–11] The applications of these gels to artificial muscles,[12] actuators,[13–16] and drug delivery systems[17–20] are being intensively researched.

We have recognized that stimuli-responsive gels can be applied to unique light-modulation materials imitating pigment cells because these gels function as specifically as artificial muscles. These novel LM gels consist of stimuli-responsive gel particles and highly concentrated pigment dispersed in the gel. The optical properties of the LM gels can be modulated by a simple mechanism: the volume change of the colored gel alters the area in which light is absorbed. That is, the transmittance of a light modulator is directly controlled by the microscopic motion of the colored gel particles. Enclosing a high concentration of a pigment inside stimuli-responsive gels helps us to obtain a wide range of transmittance changes because gels can absorb sufficient light for color changes even in the swollen state, in which the solvent absorbed by the gel

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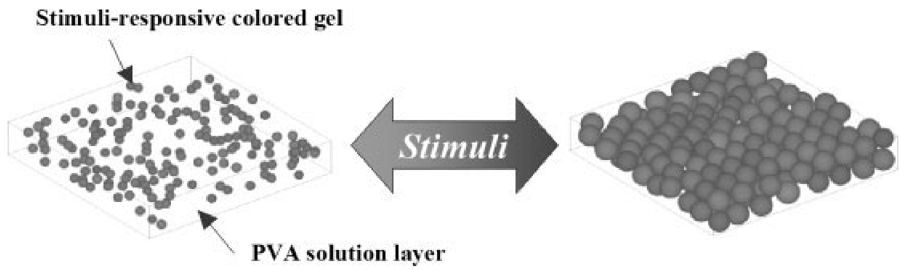

Figure 1 Design concept of the light modulator. Colored gel particles were dispersed in a viscous PVA solution.

dilutes the concentration of the pigment. Extensive work by many researchers has generated many kinds of stimuli-responsive gels that respond to various types of stimuli.[4–11] Consequently, we believe that LM gels may have strong potential for various optical devices with a wide variety of stimuli responsiveness.

LM gels have the potential for applications in large-area light modulation achieved by the fabrication of a dispersion layer of LM gel particles. Figure 1 illustrates the mechanism of large-area light modulation with the LM gel particles. This light-modulation system has the following advantages:

1. The transmittance and contrast can be controlled easily by the adjustment of the contents of the LM gel particles in the light-modulation layer or the thickness of the layer.
2. The light modulator can easily be produced with polymer-coating technology, which reduces the production cost.

In addition, the color of the light modulator does not change when it is viewed from any angle, unlike liquid-crystal displays, because the color of the light modulator originates in the pigment itself contained in the LM gel.

In this work, we describe the properties of a light modulator using LM gel particles dispersed in a poly-(vinyl alcohol) (PVA) solution as a thermochromic light-modulation device. As the LM gel, we have chosen *N*-isopropylacrylamide (NIPAM) gel, which shows abrupt changes in volume at the lower critical solution temperature (LCST; 34°C), containing a high concentration of a pigment.[1] Specifically, we have investigated how to control the light-modulation temperature and how the various parameters of the light modulator, such as the volume-change amount of the LM gels, the concentration of the pigment, the concentration of the LM gels, and the thickness of the gel layer, affect the optical properties of the light modulator.

EXPERIMENTAL

Materials

PVA (Poval C-25GP; degree of polymerization = 2300) was supplied by Shin-Etsu Chemical Co., Ltd. Sodium dodecyl sulfate (SDS) was purchased from Wako Pure Chemical Industries, Ltd. As colorants, self-dispersed pigments [Dai Nippon Ink Co., Ltd.; black pigment MC black 082-E (carbon black; average particle diameter = 85 nm), blue pigment MC blue 182-E (CI pigment no. Blue 15:3; average particle diameter = 104 nm), and magenta pigment MCM-44-T (CI pigment no. Red 122; average particle diameter = 152 nm)] were used. NIPAM gel particles containing a specific concentration of a pigment were prepared by an inverse-phase suspension polymerization process. The concentrations of the pigment were expressed as the weight percentage against the weight of the NIPAM monomer used in the polymerization reaction. The details of the synthetic method have been reported elsewhere.[21]

Preparation of a light modulator using a dispersion of NIPAM gel particles

An aqueous dispersion of colored NIPAM gel particles and a specific amount of SDS were added to an aqueous PVA solution. NIPAM gel particles were dispersed homogeneously by vigorous stirring. A glass plate ($50 \times 50 \times 0.9$ mm^3) was coated with the colored NIPAM gel dispersion. The glass plate was laminated to another glass plate. Monodispersed polystyrene particles (110 μm in diameter) were used to maintain the space between the glass plates. The edges of the glass plates were sealed with ultraviolet-curable adhesive. Thus, a light modulator using colored NIPAM gel particles was obtained.

Measurement of the volume-change properties

The diameters of the gel particles were measured with a Nikon ME600 optical microscope with a calibrated scale. The amount of the volume change of the gel was defined as d/d_0, where d and d_0 express the equilibrium diameter (d) under certain conditions and the diameter of the fully shrunken state (d_0) of the NIPAM gel particles, respectively. The temperature was controlled within 0.1°C by a Mettler FP 82HT hot plate.

Measurement of the transmittance change

The transmission spectra in the visible-light region of the light-modulation layer of the light modulator were measured with a Hitachi U-4000 ultraviolet–visible spectrometer. The temperatures at which the light-modulator spectra were observed for NIPAM gel particles in their swollen and shrunken states were 25 and 60°C, respectively. As a reference, a sample made with 110 μm of distilled water between the same glass plates was used to obtain transmittance spectra of the light-modulation layer.

RESULTS AND DISCUSSION

Preparation of the colored nipam gel particles and light modulators

Colored NIPAM gel spherical particles containing 5, 10, or 20 wt % black (carbon black) pigment against the weight of the NIPAM monomer used in the polymerization reaction were prepared by inverse-phase suspension polymerization.[21] Here we define the pigment concentration as the weight ratio of the pigment to the NIPAM monomer used in the polymerization. The diameter of NIPAM gel particles is one of the most important characteristics for light modulation because it determines both the granularity of the particles and the length of the path through which visible light is absorbed. In this work, we used particles averaging 30 μm in diameter in their swollen state (25°C) in aqueous media to obtain good absorption properties and to avoid granularity.

Light modulators consisting of colored NIPAM gel particles dispersed in a polymer layer were prepared in the following manner. The colored NIPAM gel particles were dispersed homogeneously in an aqueous solution of PVA. A specific amount of the surfactant (SDS) was used when necessary, both to improve the dispersibility of the NIPAM gel particles and to control the color-change temperature of the light modulator. Ionic surfactants have been reported to increase the LCST of NIPAM gels.[22,23] The resulting dispersion of the NIPAM gel particles was enclosed between two glass plates through monodispersed polystyrene spacer beads to maintain the necessary gap between the glass plates. Finally, the edges of the glass plates were sealed with adhesive to obtain a light modulator in which NIPAM gel particles were dispersed as the light-modulation layer.

The performance of the light modulator was determined by two key factors: the LM gel properties and device compositions. The LM gel properties include the amount of volume change, the volume-change temperature of the gel particles, and the pigment concentration in the LM gels, all of which are determined by the polymerization conditions of the LM gel particles. The device compositions include the concentration of the gel particles and the thickness of the light-modulation layer, both of which can be controlled when the light modulator is fabricated. Details of the effects of these parameters are described in the following sections.

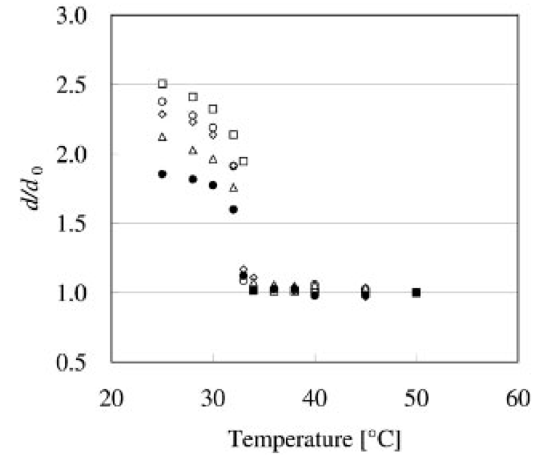

Figure 2 Volume-change properties of the colored NIPAM gel particles in various concentrations of PVA as a function of temperature: (□) 0, (○) 1, (◇) 2.5, (△) 5, and (●) 7.5 wt %.

Amount of the volume change and transmittance change

First, the LM gel properties were carefully investigated. The relationship between the volume-change property of the LM gel particles and the light-modulation ability of the device was examined. We used NIPAM gel particles containing 20 wt % carbon black pigment for the experiments. Figure 2 shows the volume-change properties of the black NIPAM gel particles in aqueous PVA solutions at concentrations that varied from 0 to 7.5 wt %. Here, we define the volume-change ratio as d/d_0, where d and d_0 represent the diameters of the gel particles in the equilibrium state under certain conditions and in the fully shrunken state, respectively. When the concentration of the PVA solution was increased, d/d_0 continuously decreased. The reason is that the swelling of the NIPAM gel particles became limited by the osmotic pressure from the PVA solution.

We used the PVA concentration effect to clarify the correlation between d/d_0 and the transmittance changes. Light modulators containing the same concentration of NIPAM gel particles dispersed in a PVA solution (solid concentration of the NIPAM gel = 1.25 wt %) at various PVA concentrations were prepared. Figure 3 shows the relationship between the transmittance changes of the light modulators and the PVA concentrations. Here, transmittances of colored and bleached states were measured at 25 and 60°C, respectively, at a fixed wavelength (500 nm). The lower the PVA concentration was, that is, the larger the d/d_0 values were of the NIPAM gel particles, the wider the transmittance change became. This result clearly

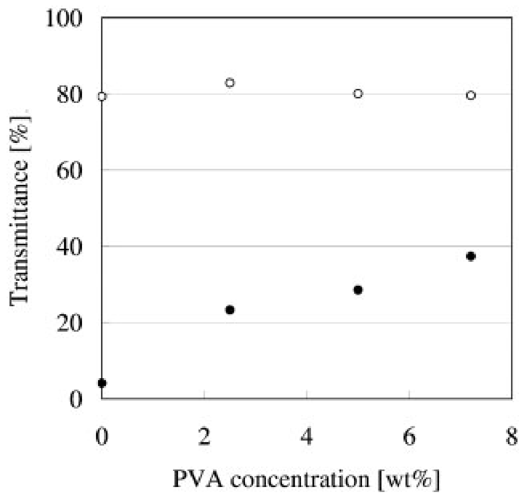

Figure 3 Relationship between the PVA concentration and transmittance changes of light modulators in which NIPAM gel particles containing 20 wt % carbon black pigment were dispersed. The transmittances of (●) the colored state and (○) bleached state at 500 nm were measured at 25 and 60°C, respectively.

showed that d/d_0—the amount of the volume change—directly controlled the breadth of the transmittance change of this light modulator. In addition, the transmittances in the bleached state were almost the same. We assume that the diameters of the NIPAM gels in the swollen state become smaller as the concentration of the PVA solution increased because of the osmotic pressure, whereas the NIPAM gels could shrink to the same extent, regardless of the PVA concentration. These results indicate that d/d_0 is an important parameter of this light-modulation system for determining the breadth of the transmittance change and that the breadth can be easily controlled by the adjustment of the concentration of PVA.

Manipulating the color-change temperature with an ionic surfactant

The color-change temperature of the light modulator can be controlled by the manipulation of the LCST of the NIPAM gels because changes in the light-absorption area caused by the volume-phase transitions of NIPAM gels at LCST are what induce the color change.[21] There are several methods for controlling the LCST of NIPAM gels, such as the introduction of hydrophobic[24] and/or ionic moieties[25] into the NIPAM polymer chain, the addition of an ionic surfactant,[22,23] and variations in the solvent composition.[26] Above all, the addition of an ionic surfactant is a convenient method because light modulators with different color-change temperatures can be obtained from the same NIPAM gel particles. On the basis of these considerations, we investigated the volume-change properties of NIPAM gel particles in 5 wt % aqueous PVA solutions in the presence of various concentrations of SDS, an ionic surfactant. Figure 4 shows the effect of SDS on the volume-change properties of the NIPAM gel particles. The LCST of the NIPAM gel particles rose as the concentration of SDS was increased. These results indicate that the addition of SDS to a NIPAM gel dispersion can control the color-change temperature of light modulators. In addition, SDS has the effect of increasing the amount of the volume change in the polymer solution.

Tanaka's group[25] and Tsujii's group[26] comprehensively investigated the effects of ionic surfactants and the mechanism of their interaction with NIPAM gel (not containing a pigment) in distilled water. The researchers explained the effect of SDS as follows. SDS molecules absorb to the hydrophobic part of the NIPAM polymer chain at temperatures below the LCST of the NIPAM gel; the ionic part of SDS absorbed in the NIPAM gel leads to an increase in the osmotic pressure inside the NIPAM gel. Thus, the diameter of the NIPAM gel particle in the swollen state increases. In addition, they assumed that electric repulsion between the SDS molecules and the NIPAM polymer chain competes with the hydrophobic interactions among the NIPAM polymer chains, causing the LCST to rise. Our results showed that SDS had the same effect on a NIPAM gel containing a high concentration of a pigment in a PVA solution.

In summary, the concentration of SDS can both control the LCST of the NIPAM gel and increase the volume-change amount. This means that we can control the color-change temperature and the breadth of the transmittance change of the light modulator at the same time simply by adding slight amounts of SDS. We used an aqueous PVA solution (3.75 wt %) with 10 m*M* SDS for further investigation.

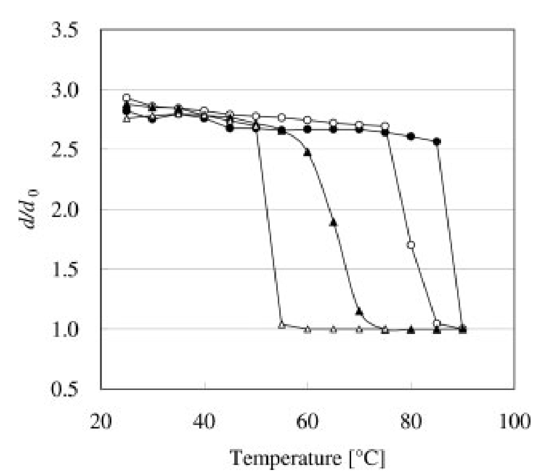

Figure 4 Volume-change properties of NIPAM gel particles in the presence of various concentrations of SDS as a function of temperature: (△) 10, (▲) 20, (○) 50, and (●) 100 m*M*.

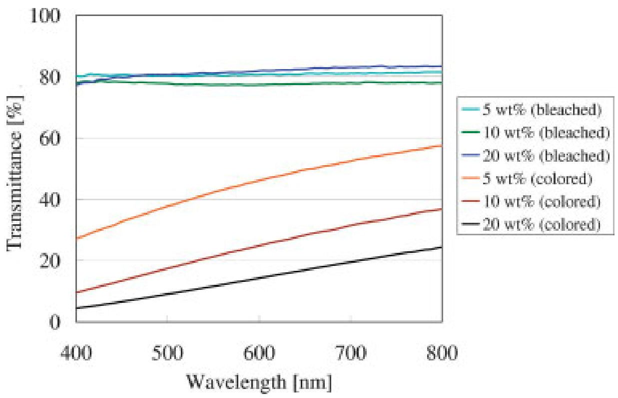

Figure 5 Effect of the pigment concentration in NIPAM gel particles containing black pigment (carbon black) on the transmittance change of light modulators. The colored and bleach states were measured at 25 and 60°C, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

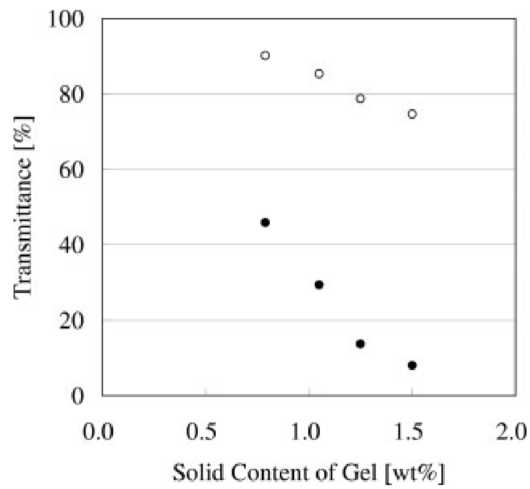

Figure 6 Dependence of the transmittance changes of light modulators on the concentration of NIPAM gel particles containing 20 wt % carbon black pigment in the light-modulation layer (thickness of the light-modulation layer = 110 μm). Transmittances were measured at 500 nm. The (●) colored and (○) bleached states were measured at 25 and 60°C, respectively.

Pigment concentration effect

The pigment concentration in the NIPAM gel particles is another important factor in this light-modulation system. Light modulators containing black NIPAM gel particles (1.25 wt %) in 110 μm of a light-modulation layer were prepared with various concentrations of the pigment (5–20 wt %), and the transmittance changes of these light modulators were measured. Figure 5 shows the effect of the pigment concentration on the transmittance change of the light modulators. The higher the pigment concentration was, the wider the breadth of the transmittance changes became. In particular, the transmittance of the colored state (swollen state of the gel particles) dropped from 50 to 6% as the pigment concentration increased from 5 to 20 wt %. On the other hand, the transmittances in the bleached state (shrunken state of the gel particles) were almost the same (80%). As expected, in low concentrations of the pigment in the NIPAM gel particles, absorbed water diluted the pigment, and absorption at each NIPAM gel particle became low. On the contrary, the pigment was densely concentrated in the shrunken gel particles, and the light absorption in the NIPAM gel particles became saturated, regardless of the pigment concentration. As a result, the three light modulators showed the same transmittance in the bleached state. As previously shown, the pigment concentration is a significant factor in this light-modulation system, determining the dynamic range of transmittance change and the transmittance in the colored state of the light modulators.

Other parameters for controlling the light-modulation properties

The properties of light modulation can also be controlled by the composition of the light-modulation layer. The two main factors are the concentration of the gel particles in the layer and the thickness of the layer. We investigated the effects of these two factors on the light-modulation properties. First, the effect of the concentration of the NIPAM gel particles was investigated. Figure 6 shows the transmittance of the colored and bleached states of the light modulators with various concentrations of the NIPAM gel particles. The thickness of the light modulators was fixed at 110 μm. The transmittances in both the colored and bleached states became lower with increasing concentration of the NIPAM gel particles. Table I shows the effect of the thickness of the light-modulation layer on the transmittance change. The concentration of the NIPAM gel particles was fixed at 1.25 wt %. The transmittance of the light modulators decreased as the thickness increased. These results can be explained as follows. The concentration of the gel particles and the thickness of the light-modulation layer

TABLE I
Dependence of the Transmittance Changes of Light Modulators on the Thickness of the Light-Modulation Layer

Thickness of the light-modulation layer (μm)	Transmittance (%) Colored state (25°C)	Transmittance (%) Bleached state (60°C)
110	13.7	80.6
200	1.1	61.1

NIPAM gel particles containing 20 wt % carbon black were used for the measurements. The concentration of the NIPAM gel particles in the light-modulation layers was 1.25 wt %. Transmittances were measured at 500 nm.

(a)

(b)

Figure 7 Light modulators using NIPAM gel particles containing different color pigments: (a) colored state (25°C) and (b) bleached state (60°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

determine the number of gel particles per unit of area, which in turn determines the light absorption per unit of area of the light modulators. These two factors—the concentration of the gel particles and the thickness of the light-modulation layer—can control the position of the transmittance change, although there exists a suitable range for maximizing the breadth of change in the transmittance.

Color variety

Another feature of this light-modulation system is color variety. Light modulators with various colors were easily obtained with NIPAM gel particles with different colors. Figure 7 shows light modulators with various colors. The response time of the color change from the colored state [Fig. 7(a)] to the bleached state [Fig. 7(b)] was within a few seconds. The rate-determining factor of this color change was considered to be heat conduction through the glass plates of the light modulator. Much faster color change can be achieved with thinner glass plates. In this light-modulation system, traces of color remained in the bleached state because the colored NIPAM gel particles did not disappear but instead were shrunken into a tightly packed shape. Moreover, various color changes could be achieved through the mixing of several kinds of gel particles with different colors because the color and color-change temperature could be designed independently in this material system.[1] For example, mixing the magenta particles with the cyan particles led to a purple dispersion. This result means that full-color devices can be fabricated with LM gel particles with the three primary colors.

CONCLUSIONS

We have scrutinized important parameters of a thermoresponsive light modulator in which the dispersion of colored NIPAM gel particles in an aqueous PVA solution are laid as a thin layer. Three main properties of the light modulator—the color-change temperature, dynamic range of the transmittance change, and position of the transmittance change—can be controlled by the parameters as follows. The color-change temperature can be controlled by the addition of an ionic surfactant (SDS), the range of transmittance change is determined by the concentration of the PVA solution and the pigment concentration of the NIPAM gel particles, and the position of transmittance change can be manipulated by the concentration of NIPAM gel particles and the thickness of the light-modulation layer. These findings are important for designing light modulators with specific optical properties.

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