

# Preparation and Optical Properties of an All-Polymer Light Modulator Using Colored *N*-Isopropylacrylamide Gel Particles in a Gel-in-Gel System

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**ABSTRACT:** A novel all-polymer light modulator with a gel-in-gel system was developed. The gel-in-gel system was constructed with colored gel particles responsive to stimuli held independently in another stimuli-nonresponsive gel matrix. Well-known thermoresponsive *N*-isopropylacrylamide (NIPAM) gel particles containing a pigment were dispersed and fixed in an outer stimuli-nonresponsive gel matrix. When poly(vinyl alcohol)-styrylpyridinium (PVA-SbQ) was used for the outer gel matrix, the light modulator showed excellent color-changing properties because the PVA-SbQ matrix was selectively formed around the NIPAM gel particles and the particles exhibited a large volume change in the matrix. The temperature when the outer gel matrix was formed affected the haze of the light modulator.

When the outer gel matrix was formed in the swollen state of the NIPAM gels, the haze of a light modulator increased with heating. On the contrary, the haze of a light modulator prepared in the shrunken state of the NIPAM gels decreased with heating. The response time of the color change was less than 1 s. The gel-in-gel system made a very fast macroscopic color change, taking advantage of the fast response of the micrometer-sized gel particles. We believe that a light modulator with a gel-in-gel system may find various applications in optical devices. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2295–2303, 2007

**Key words:** biomimetic; dyes/pigments; hydrogels; stimuli-responsive polymers

## INTRODUCTION

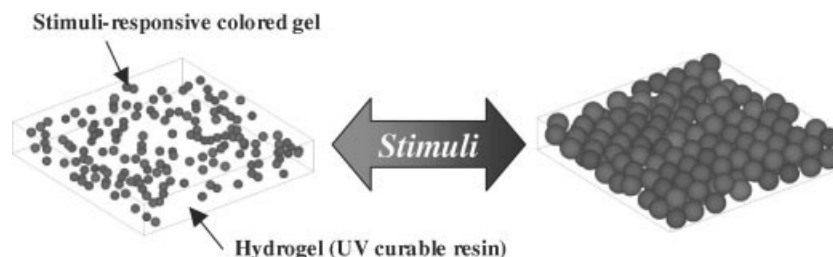
Advances in material science can come from what we learn from the structure and function of natural materials that have evolved and adapted over time. Materials that are modeled on those from the natural world are called *biomimetic materials*. For example, a super-water-repellent surface was developed by the imitation of the microstructure of lotus leaves.<sup>1</sup> Mimicking the wing-material structure of the blue morpho butterfly, which lives in rainforests of South and Central America, led to the invention of artificial fibers with iridescent luster.<sup>2</sup>

Stimuli-responsive polymer gels are among the most important prospective biomimetic materials because these gels are wet and soft like the tissue of living things and show abrupt and vast changes in volume in response to various stimuli from the surrounding environment,<sup>3–12</sup> such as temperature, pH, electricity, and exposure to light. There have been numerous attempts to apply these gels as artificial muscles and actuators.<sup>13–17</sup>

Our group has focused on the function of stimuli-responsive gels as artificial muscles and has been developing a novel light-modulation material—a smart-gel light-modulation material—by imitating the pigment cells of cephalopods,<sup>18</sup> which enable these animals to change their skin color rapidly. This material consists of stimuli-responsive gel particles containing high pigment concentrations. A preliminary experiment has revealed that the array or dispersion of the gel particles changes the color drastically with changes in the volume of the gel particles caused by external stimuli (Fig. 1) and shows rapid and excellent color-changing properties, just like cephalopod skin.<sup>18</sup> This light-modulation material has strong advantages over other light-modulation materials such as polymer dispersed liquid crystals (PDLCs),<sup>19</sup> aqueous dispersions of *N*-isopropylacrylamide (NIPAM) gels,<sup>20</sup> and thermochromic and electrochromic materials.<sup>21</sup> In the case of a light modulator using PDLCs, the light modulator alters only between transparent and opaque states according to the electric field applied. Suzuki et al. reported that a light modulator consisting of NIPAM gel particles dispersed and fixed in acrylamide (AAm) bulk gels showed a transmittance change from transparent and opaque states when heated.<sup>20</sup> In contrast, the smart-gel light-modulation material can change from a densely colored state to a transparent state

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**Figure 1** Design concept of a gel-in-gel light modulator: stimuli-responsive gel particles containing a high concentration of a pigment are dispersed and fixed in a stimuli-nonresponsive hydrogel matrix.

according to external stimuli. In addition, simply choosing a pigment dispersed in stimuli-responsive gel particles, we can decide the color of the light modulator freely. The wide varieties and freedom of choice of colors for a light modulator are also fundamental advantages of this smart-gel light-modulation material in comparison with conventional thermochromic and electrochromic materials. For these chromic compounds, the range of color choice is limited because their color and stimuli responsiveness are strongly dependent on their chemical structure.

In a previous study,<sup>18</sup> we reported that the smart-gel light-modulation material exhibited excellent color-change properties and that these color change showed good reproducibility because a high concentration of the pigment was tightly fixed to the networks of the stimuli-responsive gel. We believe this light-modulation material has strong potential for applications in devices such as optical switches, optical filters, displays, and various kinds of sensors. Recently, we summarized our findings on a light modulator with a gel-in-gel system,<sup>22</sup> in which smart gel particles are dispersed and fixed within another stimuli-nonresponsive polymer gel matrix to prevent the deterioration of the light-modulation properties during repeated cycles of the color change due to aggregation of the gel particles. In this article, we describe the material design, preparation methods, and optical properties of the light modulators with the gel-in-gel system in more detail.

## RESULTS AND DISCUSSION

We chose NIPAM gel as a thermoresponsive gel that shows an abrupt change in volume at its lower critical solution temperature (LCST; 34°C). Colored NIPAM gel spherical particles containing 20 wt % pigment were prepared by inverse-phase suspension polymerization.<sup>23</sup> Here, we define *pigment concentration* as the weight ratio of the pigment to the NIPAM monomer used in the polymerization. The diameter of the 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 light path through which visible light is absorbed. In this work, we used particles averaging approxi-

mately 30  $\mu\text{m}$  in diameter in their swollen state (25°C) in aqueous media to obtain good absorption properties and to avoid granularity.<sup>18</sup>

In the gel-in-gel system, stimuli-responsive gel particles are dispersed and confined in a stimuli-nonresponsive gel matrix. That is, the light modulator consists entirely of semisolid gels. The gel-in-gel system has various advantages over a simple dispersion of colored gel particles: (1) leakage of the solvent and aggregation among the gel particles are efficiently prohibited because the solvent and colored gel particles are tightly fixed in a stimuli-nonresponsive gel matrix, (2) the light modulator can be very flexible with plastic films as substrates, and (3) the light modulator is expected to be appropriate for mass production using polymer coating technology.

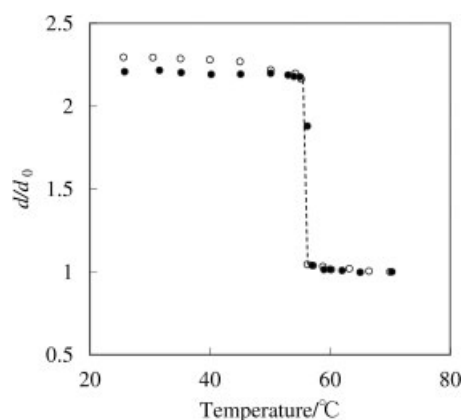
The outer gel matrix of the gel-in-gel system is formed by a crosslinking reaction of the gel precursor in a dispersion of gel particles. There are two possible kinds of gel precursors: monomers and polymers. For the formation of the outer gel matrix, a polymer precursor is considered more suitable. If a monomer precursor were used, the monomers would penetrate the colored gel particles and form interpenetrating polymer networks with gel particles that would likely restrict the volume change of the gel particles. Polymer precursors, on the other hand, are too large to easily infiltrate the matrices of gel particles; thus, the outer gel matrix is expected to form around the gel particles selectively. Another advantage of a polymer precursor is that the dispersion of NIPAM gel particles is easily coated onto a substrate because the viscosity of the dispersion containing a polymer precursor can be easily controlled by the adjustment of its concentration and molecular weight. Moreover, the dispersion state of gel particles becomes stable because of the viscosity. UV-curable compounds are also considered important because they can be polymerized by short exposure to UV irradiation without heating; this minimizes evaporation of the solvent during curing.

On the basis of these considerations, we chose poly(vinyl alcohol)-styrylpyridinium (PVA-SbQ),<sup>24</sup> a UV-curable polymer, as the precursor for the outer gel matrix. PVA-SbQ has been reported to have excellent photosensitivity, and it is curable at a polymer concen-

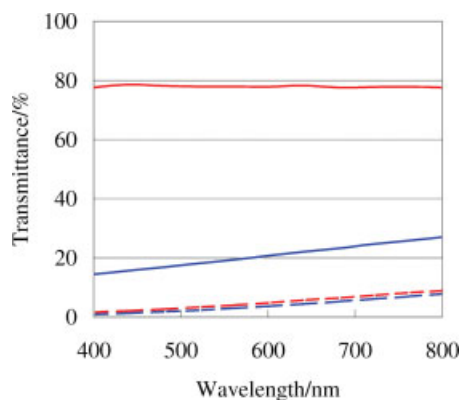
tration of less than 5 wt %. A lower curable concentration is also important for this system to maintain the amount of the volume change of the NIPAM gel particles because the amount of the volume change of the NIPAM gels is restricted by the osmotic pressure of high-concentration polymer solutions.

Figure 2 shows the volume-change properties of the NIPAM gel particles before and after curing in the PVA-SbQ solution in the presence of 50 mM sodium dodecyl sulfate (SDS). SDS was used as a surfactant to disperse NIPAM gel particles homogeneously in the PVA-SbQ solution. Here we measured the volume change 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. In both cases, the NIPAM gels showed drastic change in diameter at 55°C. Because of the effect of SDS,<sup>25</sup> the LCST of the NIPAM gel particles in PVA-SbQ before and after curing increased from 34 to 55°C. The  $d/d_0$  values of the NIPAM gel particles were almost the same before and after the curing of PVA-SbQ. It was confirmed that NIPAM gels showed sufficient volume change for light modulation in aqueous PVA-SbQ before and after curing.

A light modulator with a gel-in-gel system using PVA-SbQ was fabricated in the following manner. The NIPAM gel particles were homogeneously dispersed in a 5 wt % PVA-SbQ solution in the presence of 50 mM SDS. The dispersion of the NIPAM gel particles in PVA-SbQ was coated on a glass plate or plastic film. Then, the coated substrate was laminated to another substrate and cured by UV irradiation at the ambient temperature (25°C). The space of the glass plates was maintained with monodispersed polystyrene beads (110 μm in diameter). Thus, we obtained a light modulator with a gel-in-gel system. In this structure, the solvent and NIPAM gel particles were tightly held in the PVA-SbQ matrix and did not leak from the composite. To confirm the importance of the poly-



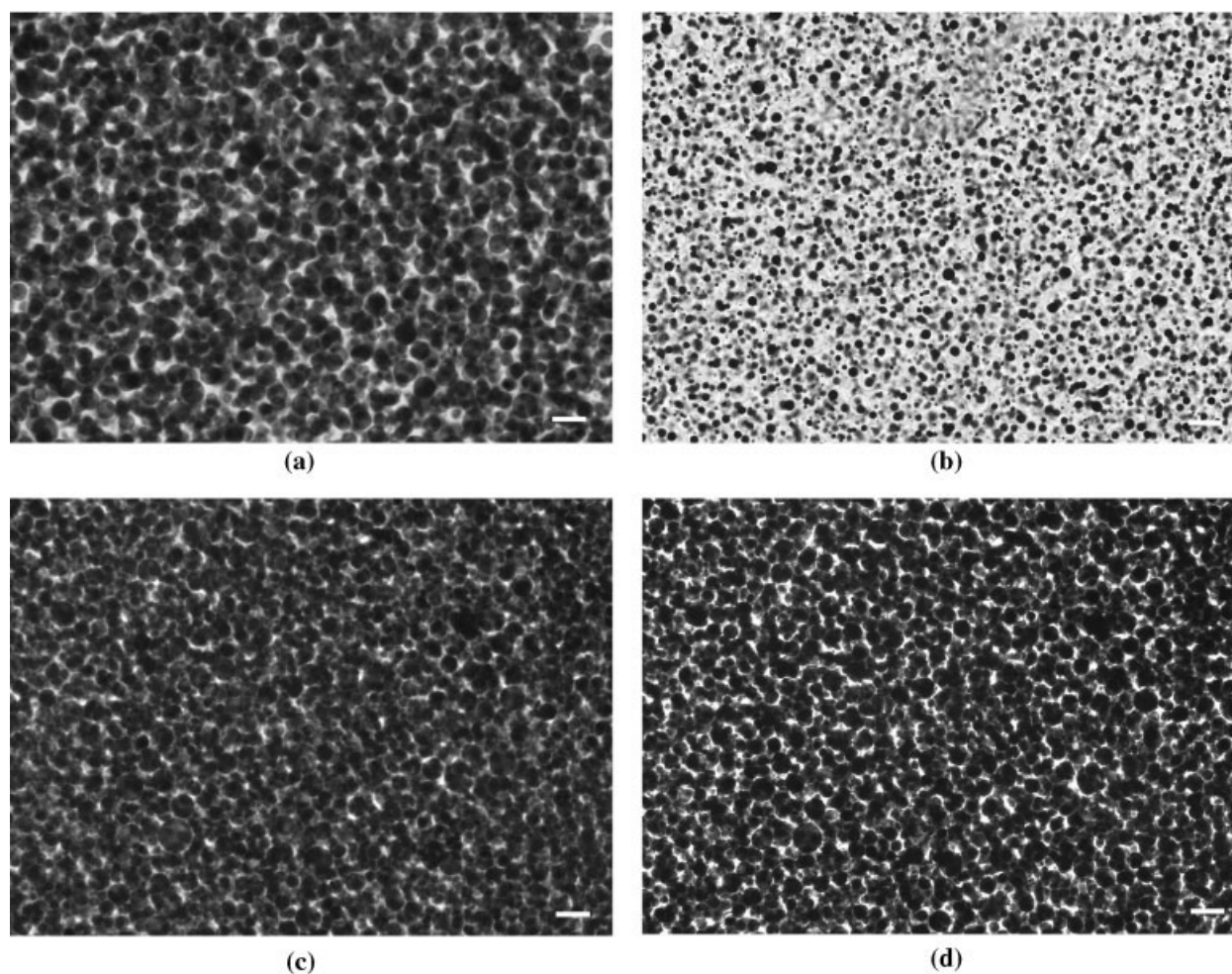
**Figure 2** Dependence of the diameter change of NIPAM gel particles in a PVA-SbQ solution as a function of temperature: (○) before UV curing and (●) after UV curing.



**Figure 3** Transmittance change of light modulators with the gel-in-gel system using a (—) polymer precursor and (---) a monomer precursor. The swollen and shrunken states were measured at 20 (blue line) and 60°C (red line), respectively. The thickness of the gel-in-gel layer was 110 μm, and the NIPAM gel solid concentration was 1.25 wt %. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

meric structure of the precursor of the outer gel matrix, another light modulator using a monomer precursor was also fabricated. AAm (monomer) and *N,N*-methylene bisacrylamide (crosslinker) were used for forming the outer gel matrix of the light modulator.

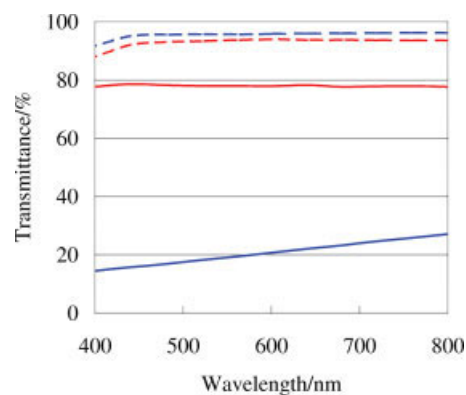
Figure 3 shows the total transmittance changes of these light modulators with the gel-in-gel system using the polymer precursor and the monomer precursor. The light modulator using PVA-SbQ (polymer precursor) exhibited drastic changes in transmittance when heated. The average transmittance change in the visible-light region was approximately 60%. In contrast, the average transmittance change of the light modulator using AAm (monomer precursor) was only 2%. A microscopic inspection revealed that the NIPAM gel particles in an AAm gel matrix showed hardly any volume change and were distorted in the shrunken state (Fig. 4). In this case, it was assumed that interpenetration polymer networks between the NIPAM gel particles and the outer AAm gel matrix were formed and that the AAm matrix that formed inside and at the interface of the NIPAM gel particles restricted the volume change of the gel particles. On the other hand, in the polymer-based modulator, interfacial walls were observed between the PVA-SbQ matrix and the solvent when the NIPAM gel particles were shrunken. This result indicates that polymeric PVA-SbQ could not penetrate the NIPAM gel particles, and the PVA-SbQ matrix was selectively formed around NIPAM gel particles. Consequently, each NIPAM gel particle was confined in the PVA-SbQ matrix independently. These results demonstrated that with a polymeric precursor for the outer gel matrix, NIPAM gel particles can be fixed and still maintain their volume-change properties. With this structure, the transmittance change of the light modu-



**Figure 4** Microphotographs of gel dispersion layers: (a) with a polymer precursor (PVA-SbQ) at 25°C, (b) with a polymer precursor at 60°C, (c) with a monomer precursor (AAM) at 25°C, and (d) with a monomer precursor at 60°C. The scale bars are 50  $\mu\text{m}$ .

lator was highly reproducible. The gel-in-gel structure effectively prevented the NIPAM gel particles from aggregation, which became sticky in their shrunken state, during repeated cycles of swelling and shrinking. We have confirmed that the optical properties of a light modulator with a gel-in-gel system were maintained after 50 heating and cooling cycles.<sup>22</sup>

We also noted that the gel-in-gel system using colored NIPAM gel particles exhibited excellent and opposite transmittance-change properties in comparison with that obtained with NIPAM gel particles not containing pigment (colorless NIPAM gel particles). Figure 5 compares light modulators using colored and colorless NIPAM gel particles. With the colorless NIPAM gel particles, the light modulator remained almost transparent, becoming slightly opaque when heated at 60°C. The transmittance decreased only 3%, from 95 to 92%. The colorless NIPAM gel particles began to scatter the incident light when they shrank. The reason for the small transmittance change was that



**Figure 5** Transmittance change of light modulators with the gel-in-gel system using (—) colored and (---) colorless NIPAM gel particles. The swollen and shrunken states were measured at 20 (blue line) and 60°C (red line), respectively. The thickness of the gel-in-gel layer was 110  $\mu\text{m}$ , and the NIPAM gel solid concentration was 1.25 wt %. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
**Total Light Transmittance and Haze of Light Modulators Cured at 25 and 70°C**

UV-irradiation temperature (°C)	Total light transmittance (%)		Haze (%)	
	Colored	Bleached	Colored	Bleached
25	18	75	12	17
70	24	78	14	10

coverage of the light-modulation layer by the NIPAM gel particles became low at a higher temperature because of the shrinkage of the NIPAM gel particles, even though the colorless NIPAM gel particles could scatter incident light in their shrunken states. In addition, some of the light scattered by the shrunken NIPAM gel was assumed to pass through a light-modulation layer as thin as 110  $\mu\text{m}$ . Thicker light-modulation layers are regarded as necessary for wider transmittance changes. In contrast, the light modulator with the same thickness as the light-modulation layer using the colored NIPAM gel particles changed its color intensity drastically from dark to transparent when heated. The average transmittance increased from approximately 20 to 78%. The larger transmittance change was achieved because the incident light was absorbed by the colored NIPAM gel particles in their swollen state, which covered a large part of the light-modulation layer. The colored NIPAM gel particles realized larger transmittance changes with smaller amounts of the gel particles. These results clearly showed that the gel-in-gel system using colored gel particles was an effective light-modulation system.

The temperature during UV irradiation is considered important in forming the gel-in-gel structure because the temperature determines the swelling state of the NIPAM gel particles. More specifically, when

UV irradiation occurs at temperatures below the LCST of the NIPAM gel, the gel particles are held in the polymer matrix in their swollen state. On the other hand, when UV irradiation occurs at temperatures above the LCST, the NIPAM gel particles are held in the polymer matrix in their shrunken state. Here we attempted to elucidate the effect of the temperature conditions on the light-modulation properties of the gel-in-gel system.

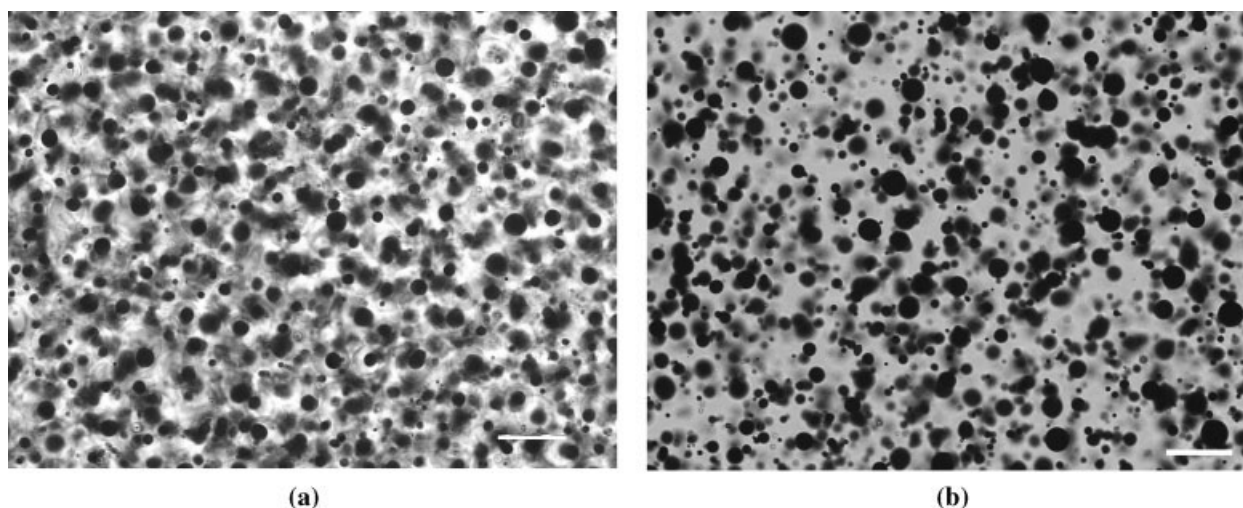
We fabricated light modulators cured at 25 and 70°C, temperatures below and above the LCST of NIPAM gel, respectively, in the presence of 50 mM SDS in 5 wt % PVA-SbQ (see Fig. 2). The changes in the transmittance and haze of the light modulators were measured in their colored and bleached states. Here *haze* is used to express the turbidity of the light modulators, which is the ratio of the diffuse light transmittance to the total light transmittance through a specimen expressed as a percentage:

$$\text{Haze}(\%) = T_d/T_t \times 100 \quad (1)$$

where  $T_d$  and  $T_t$  represent the diffuse light transmittance and total light transmittance, respectively.

As shown in Table I, the tendency of the change in haze was different for each light modulator, although the total light transmittances of the two light modulators were almost the same. The haze of the light modulator cured at 25°C increased when heated (bleached state). In contrast, the haze of the light modulator cured at 70°C decreased when heated.

To clarify this phenomenon, microscopic observations of the gel dispersion layers were conducted. Figure 6 shows microphotographs of each light modulator in the shrunken state of the gel particles. In the light modulator cured below the LCST of the NIPAM gels, interfacial walls were observed between the outer gel matrix and the water released from the NIPAM gel



**Figure 6** Microphotographs of light modulators in the shrunken state: (a) cured at 25°C (swollen state of NIPAM gels) and (b) cured at 70°C (shrunken state of NIPAM gels). The scale bars are 50  $\mu\text{m}$ .

particles [Fig. 6(a)]. In the case of the light modulator cured above the LCST, however, such interfacial walls did not appear [Fig. 6(b)]. It was assumed that the generation of interfacial walls at which incident light was scattered led to the increase in haze in the light modulator cured at 25°C. In contrast, the light modulator cured at 70°C showed less haze in the bleached state than that in the colored state because interfacial walls were not generated and superficial areas of NIPAM gel particles, which also scattered the incident light, became smaller in the bleached state. We found that the difference in haze was attributable to the formation of these interfacial walls and that the curing temperature was an important factor for determining the haze of the light modulator.

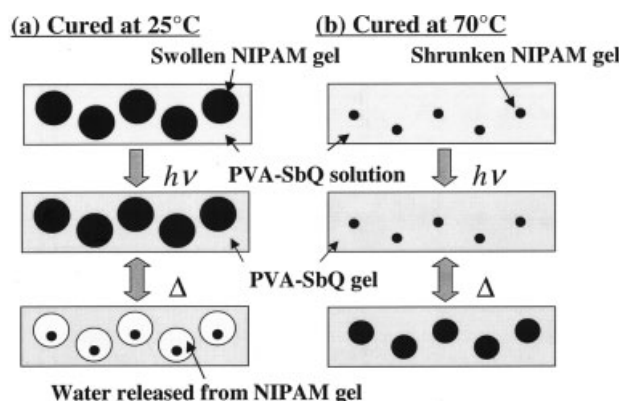
The mechanism of the generation of the interfacial walls can be explained as follows. Some researchers have reported that polymer gels can memorize their initial macroscopic and mesoscopic shapes during polymerization.<sup>26–29</sup> On the basis of this shape-memory effect of gels, when the outer gel matrix is cured in the swollen state of NIPAM gel particles, the outer gel memorizes the structure. Thus, when PVA–SbQ was cured below the LCST of the NIPAM gels (NIPAM gels were swollen), the PVA–SbQ gel matrix maintained this original structure even when NIPAM gel particles were shrunken with heat. As a result, interfacial walls between the PVA–SbQ gel matrix and water released from the gel particles were formed [Fig. 7(a)]. In contrast, when, as shown in Figure 7(b), the PVA–SbQ gel matrix was cured above the LCST (NIPAM gels were shrunken), the PVA–SbQ gel matrix memorized the shape of the shrunken NIPAM gel particles. We assumed that the NIPAM gel particles swelled by absorbing water in the PVA–SbQ gel matrix after cooling. When this light modulator was heated above the LCST, the PVA–SbQ gel matrix immediately absorbed

the water released from the NIPAM gel particles because the PVA–SbQ gel matrix had memorized the shape of the shrunken NIPAM gel particles. As a result, interfacial walls did not form, and the haze of the light modulator in the bleached state was lower than that of the light modulator cured in the swollen state of the NIPAM gel particles.

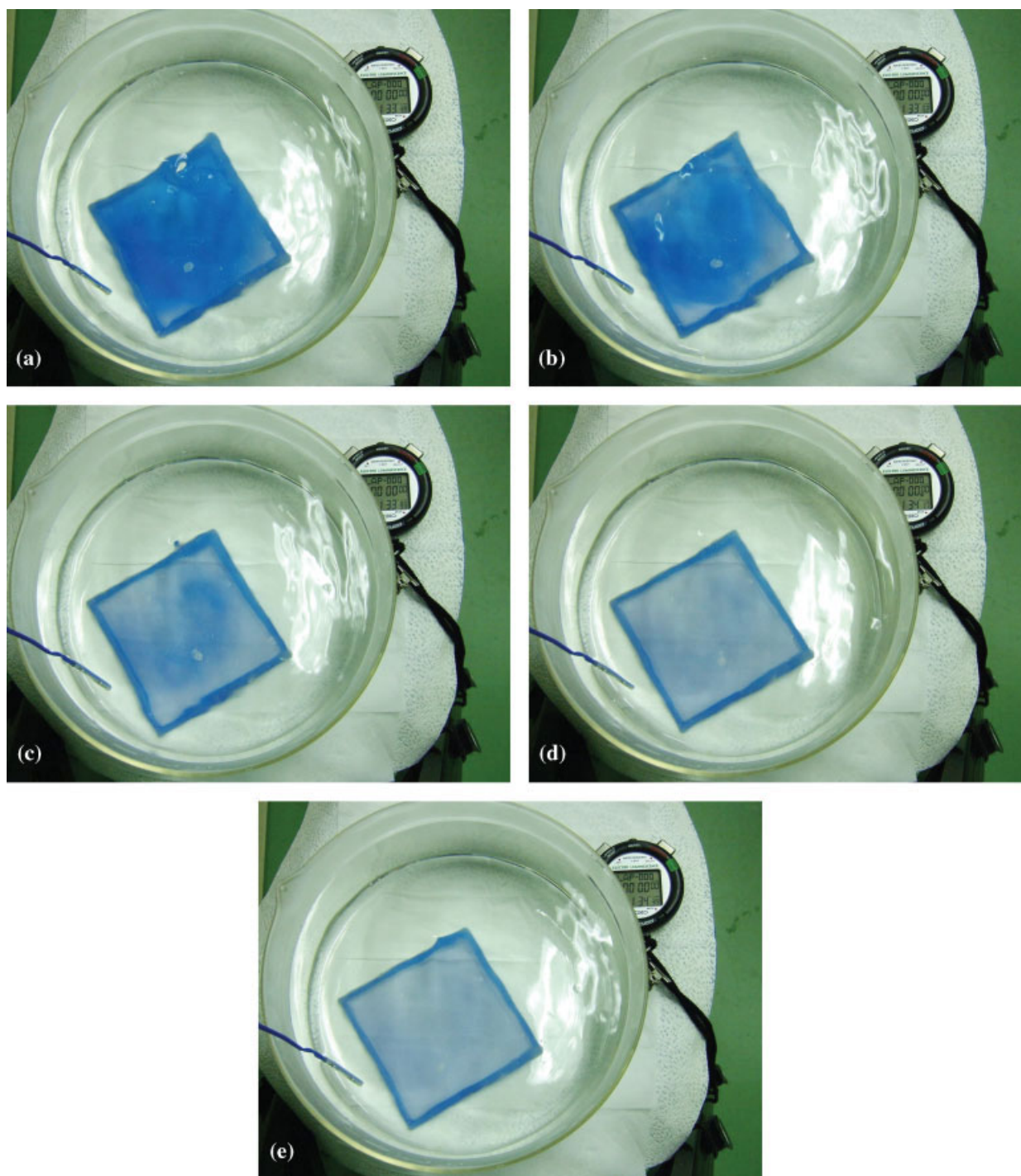
Basically, light modulators with the gel-in-gel system were transparent in both their colored and bleached states. The reason is as follows. In the colored state, the building blocks of the gel-in-gel system are hydrogels that contain up to 95 wt % water; the reflective indices of both the PVA–SbQ matrix and NIPAM gel particles are near that of water. In the bleached state, although the difference in the reflective indices between water and the NIPAM gel particles become larger, the superficial areas of the NIPAM gel particles, which scatter incident light, decrease with the volume change.

Moreover, the temperature during UV curing had another effect on the light-modulation properties. The total light transmittance of the light modulators was affected by the curing temperature. As shown in Table I, the light modulator cured at 70°C showed higher total light transmittance than that cured at 25°C. When UV irradiation occurred at a temperature above the LCST of the NIPAM gels, the PVA–SbQ matrix was formed and covered the NIPAM gel particles in their shrunken state. It was assumed that the PVA–SbQ matrix that formed in the shrunken state of the NIPAM gel particles restricted the gel particles from swelling freely. Consequently, the light modulator cured at the temperature above the LCST exhibited higher total light transmittance than that cured at the temperature below the LCST.

A light modulator with the gel-in-gel system has various advantages. One of the chief merits of the gel-in-gel system is a fast response time. In reality, applications of stimuli-responsive gels in macroscopic devices have been obstructed by long response times. The interval required for the volume change of a gel is principally governed by the collective diffusion of the polymer network of the gel.<sup>30</sup> Consequently, the response time is proportional to the square of the characteristic length of the gel. As a result, bulk gels generally show very slow volume changes. For example, a complete volume change takes more than 1 month in the case of a bulk gel of a centimeter size. In contrast to the bulk gel, our gel-in-gel system responds very quickly. The color-change property of the light modulator with the gel-in-gel system was measured by the temperature-jump method. Figure 8 shows the bleaching process of the light modulator when there was a sudden temperature jump from 25 to 70°C. The light modulator exhibited a fast color change. Approximately after 0.5 s, the color almost disappeared. The whole area of the light modulator finished the color change within 1 s. The actual response time of each gel



**Figure 7** Effect of the temperature during the curing of the outer gel matrix and a plausible mechanism for the formation of interfacial walls between the water and outer gel matrix: (a) curing at the ambient temperature (NIPAM gel particles are swollen) and (b) curing at a high temperature (NIPAM gel particles are shrunken).



**Figure 8** Bleaching processes of a light modulator with the gel-in-gel system with a temperature jump. The time course of the photographs develops from parts a to e: (a) just after immersion in hot water, (c) after approximately 0.5 s, and (e) after approximately 1 s. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

particle to temperature change was assumed to be faster than that measured here because heat transfer through a glass substrate was the dominant factor in this system. The short response time was attributed to the structure of the gel-in-gel system, in which micrometer-sized gel particles were fixed in the outer bulk-gel matrix independently. In other words, the gel-in-gel system made a very fast macroscopic color change,

taking advantage of the fast response of the micrometer-sized gel particles.

The gel-in-gel system has other advantages, such as high durability to repetitive cycles of color change and flexibility. We have already reported that a light modulator with a gel-in-gel system shows excellent durability to repetitive cycles of color change and that a film-type light modulator can be fabricated with flexible

substrates such as poly(ethylene terephthalate) film<sup>22</sup> because the gel-in-gel system prevents NIPAM gel particles from aggregating and consists of whole-gel materials that are all soft and flexible. From a practical point of view, a flexible light modulator is quite useful in various applications, and this type of light modulator can be produced with roll-to-roll coating technology.

## CONCLUSIONS

We have designed and fabricated a light modulator with a gel-in-gel system, in which colored NIPAM gel particles are fixed and held in another, stimuli-nonresponsive polymer gel matrix. This work reveals that using a polymer-structured precursor for the outer gel of the gel-in-gel system maintains the volume-change properties of colored NIPAM gel particles and yields excellent light-modulation properties. The UV-curing temperature is an important factor in determining the light modulator's haze, a crucial factor, especially in applications for transmissive optical devices. We have also noted that the gel-in-gel system achieves a fast response time because the macroscopic color change is the result of synchronized motion of the micrometer-sized NIPAM gel particles. Through this work, we have found important factors for designing the optical properties of a light modulator with a gel-in-gel system. A light modulator with a gel-in-gel system has properties that will make it optimal for applications in sensors, optical switches, and displays. Attempts to develop such applications for optical devices are now under way.

## EXPERIMENTAL

### Materials

The PVA-SbQ solution (SPP-S-13; degree of polymerization = 2300; 1.3 mol % vinyl alcohol moieties were modified with styrylpyridinium) was a gift from Toyo Gosei Co., Ltd. (Ichikawa, Japan). SDS was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). As colorants, we used self-dispersed pigments [Dai Nippon Ink Co., Ltd. (Tokyo, Japan); MC black 082-E (black pigment) and MC blue 182-E (blue pigment) with average particle diameters of 85 and 104 nm, respectively]. NIPAM gel particles containing a specific pigment concentration were prepared by an inverse-phase-suspension-polymerization process. The details of the synthetic method have been reported elsewhere.<sup>20</sup>

### Preparation and optical properties of the light modulator with the gel-in-gel system using PVA-SbQ

An aqueous NIPAM gel dispersion (10.0 g, 2.3 wt % gel solid), an aqueous PVA-SbQ solution (10.0 g, 5.0 wt %), and SDS (260 mg) were mixed and stirred vigorously to

disperse the NIPAM gel particles homogeneously. The resulting viscous dispersion was coated onto a glass plate (100 × 100 × 0.9 mm<sup>3</sup>) and laminated with another glass plate. Monodispersed polystyrene particles (110 μm in diameter) were used to maintain the space between the glass plates. The plates were irradiated by UV light (ultrahigh-pressure mercury lamp, 75 mW/cm<sup>2</sup>) for 30 s at 25 or at 70°C. The edges of the light modulator were sealed with a UV-curable adhesive. Thus, we obtained a light modulator having a gel-in-gel structure. Transmittance spectra of the light modulator were measured with a Hitachi (Tokyo, Japan) U-4000 UV-vis spectrometer, and the haze of the light modulator was measured with an NDH2000 haze meter (Nippon Denshoku Industry Co., Ltd. (Tokyo, Japan)). Microphotographs of the gel-in-gel structure were taken with an optical microscope (Eclipse ME600, Nikon (Tokyo, Japan)) equipped with a charge-coupled-device camera (Axio Cam HRC, Carl Zeiss (Göttingen, Germany)).

### Preparation of the light modulator using AAm (monomer precursor) as the outer gel matrix

An aqueous NIPAM gel dispersion (10.0 g, 2.3 wt % gel solid) and SDS (260 mg) were mixed and were dispersed into an aqueous solution of AAm (0.5 g), methylene bisacrylamide (25 mg), a radical initiator (ammonium persulfate; 5 mg), and water (10.0 g). The dispersion was cooled to 0°C with an ice-water bath. The polymerization was initiated with *N,N,N',N'*-tetramethylethylenediamine (0.2 mL). The dispersion was coated onto a glass plate and laminated with another glass plate immediately. Monodispersed polystyrene particles (110 μm in diameter) were used to maintain the space between the glass plates. The edges of the light modulator were sealed with a UV-curable adhesive and allowed to stand for 3 h at the ambient temperature. Thus, we obtained a light modulator using AAm as a monomer precursor for the outer gel matrix. Transmittance spectra of the light modulator were measured with a Hitachi U-4000 UV-vis spectrometer.

### Measurement of the response time

The light modulator was held at a fixed temperature (25°C) for more than 30 min to reach thermal equilibrium. Then, the light modulator was immediately immersed into a large bath of hot water (70°C). The color change of the light modulator was recorded with a digital camera (FinePix F700, Fuji Photo Film, Tokyo, Japan) with continuous shooting.

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