

## Chromic Slide-Ring Gel Based on Reflection from Photonic Bandgap

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**ABSTRACT:** Here we report on a chromic slide-ring gel consisting of polyrotaxane by using a close-packed colloidal crystal as a template. In the slide-ring gel, the polymer chains with bulky end groups are not covalently cross-linked like chemical gels nor do they interact attractively like physical gels, but are topologically interlocked by figure-of-eight cross-links. The slide-ring gel has freely movable cross-links, which have a pulley effect on tensile deformation. This effect improves the mechanical properties of polymer gels. In this work, this physically and mechanically optimized polymer gel was used to make stimuli-responsive photonic band gap materials. Our gel exhibits solvatochromic behavior based on the change in structural color.

## Introduction

Photonic band gap materials are the subject of intense research interest because of their potential use as sensors to detect chemical and biological species, active photonic crystals to control light propagation in response to various external perturbations, and dynamic optical switches for displays and smart windows.<sup>1,2</sup> It is becoming increasingly clear that novel approaches to these applications demand smart soft materials with high-performance stimuli-responsivity. Polymer gels have the remarkable ability to respond to stimuli in a large variety of ways.<sup>3</sup> Moreover, it is apparent that polymer gels have the distinction of being able to memorize or immobilize submicrometer-sized periodical fine structures in the network and hold the potential to be used as photonic band gap materials.<sup>4</sup> Indeed, there have been a number of reports on the preparation of periodical structured polymer gels exhibiting a photonic band gap using templating techniques and self-organizing methods.<sup>4–14</sup> As a result, research on active photonic band gap materials composed of polymer gels has recently increased, and this is attracting attention in a variety of fields.

However, because traditional synthesis of polymer gels relies upon a free radical chain reaction between monomers and cross-linkers, these polymer gels have permanent and fixed spatial inhomogeneities<sup>15</sup> and topological constraint on the subchains.<sup>16</sup> This results in low deformability, low swellability, and low mechanical strength of the polymer gels, and these properties can be drawbacks for use in stimuli-responsive materials. For example, the polymer chains in the chemical cross-linked polymer gels will be cleaved gradually with repetitive alteration in the volume, due to the unequal stress exerted on the polymer chains.<sup>17</sup> For this reason, it would be highly desirable to develop active photonic band gap materials for the above applications by using physically and mechanically optimized polymer gels. Various approaches to avoiding these problems are currently under trial. One of them is based on a nanocomposite hydrogel

composed of water-soluble polymer and water-swelling inorganic clay.<sup>18</sup> This gel can deform to a large extent without any damage under bending, compression, torsion, and elongation. This mechanically improved property is attributed to the organic/inorganic network structure in which exfoliated clay platelets act as multifunctional cross-linking units. Another hydrogel system is based on interpenetrating polymer networks that exhibit amazingly strong and tough mechanical behavior.<sup>19</sup> The hydrogel cannot be sliced with a cutter nor broken down by a high compression. However, these hydrogels are inappropriate for making the intended polymer gels that show a photonic band gap, because the preparative conditions for obtaining structural colored porous gels are unfavorable.

In devising a new strategy to address this issue, our attention was drawn to the utilization of “slide-ring gels” for making stimuli-responsive photonic band gap materials. Slide-ring gels can be prepared using polyrotaxane molecules consisting of terminal capped linear polymer chains that are threaded through ringlike molecules.<sup>20–22</sup> The network structure of the slide-ring gels can be obtained by the cross-linking reaction among the ringlike molecules on different polyrotaxane molecules. As the ringlike molecules can rotate and slide along the polymer chains, the length of the polymer chains in the network will be averaged, and the tension of the polymer chains can be equalized. This effect leads to improvement in the drawbacks that are observed in the traditional chemical cross-linked polymer gels. The application of the slide-ring gels for the fabrication of stimuli-responsive photonic band gap materials could drive innovation in this field. In this paper we describe a new stimuli-responsive photonic band gap materials that is made of appropriate slide-ring gels using a close-packed colloidal crystal as a template (Scheme 1).

## Experimental Section

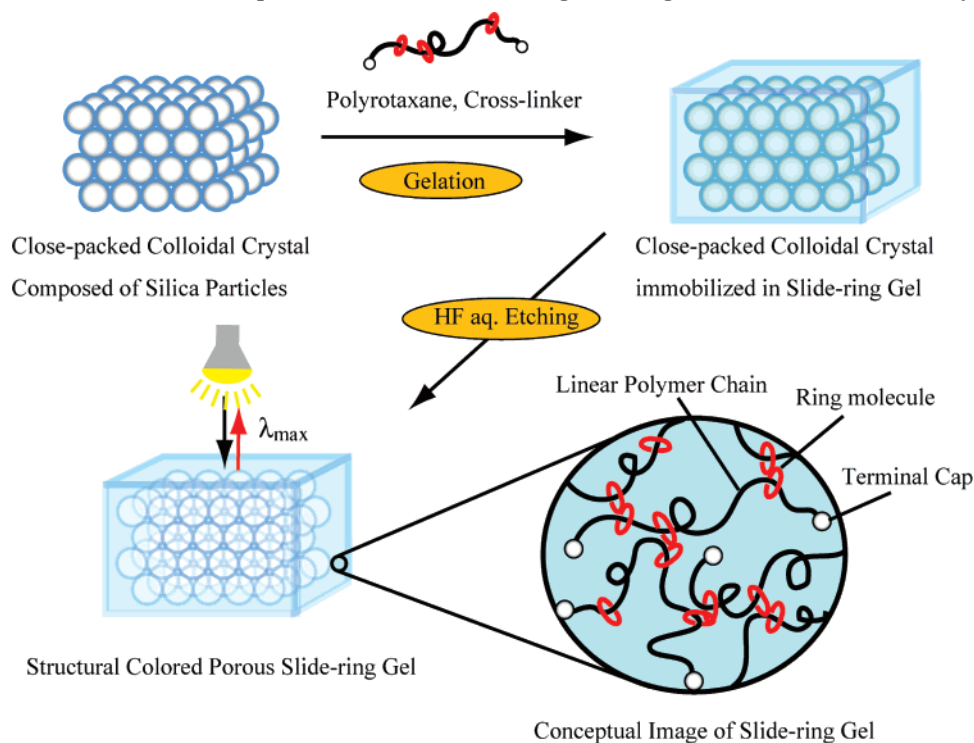
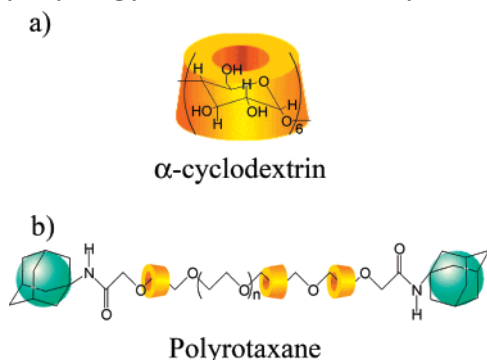
**Materials.** An aqueous suspension of submicrometer-sized silica particles (silica particles with a narrow particle size distribution, dispersed in water, Nippon Shokubai) was obtained and used to prepare close-packed colloidal crystals. The mean diameter of the particles used in this study was 300 nm.  $\alpha$ -Cyclodextrin ( $\alpha$ -CD), which was used for the ringlike molecule (Scheme 2a), was purchased from Nihon Shokuhin Kako Co. Ltd. ( $\alpha$ -CD content

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**Scheme 1. Schematic Procedure of the Preparation of a Porous Slide-Ring Gel Using a Close-Packed Colloidal Crystal as a Template****Scheme 2. Chemical Structures of  $\alpha$ -Cyclodextrin ( $\alpha$ -CD) and a Polyrotaxane Composed of  $\alpha$ -CDs as Ring Molecules and a Poly(ethylene glycol) as an Axile Linear Polymer Chain**

>99%). Poly(ethylene glycol) 35000 (PEG 35000), having a hydroxyl content of  $7.00 \times 10^{-5}$  mol/g, corresponding to a number-average molecular weight of 28600 (determined by titration of phthalic anhydride bound to OH groups), was purchased from Fluka. This macromolecule is used as an axis molecule for preparing a polyrotaxane. The free base form of 1-adamantanamine as a terminal cap was from ICN Biomedicals, Inc. The polyrotaxane, composed of a single chain of the PEG molecule, about 90–100  $\alpha$ -CDs (28% coverage of the PEG chain), and two terminal adamantane moieties (Scheme 2b), was synthesized. The detailed preparation of the polyrotaxane has previously been reported.<sup>23,24</sup> A polyrotaxane that was essentially similar to the one we prepared in this study was also supplied by Advanced Softmaterials, Inc. (Tokyo, Japan) and was used to prepare slide-ring gels. 1,1'-Carbonyldiimidazole was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Ethylene glycol diglycidyl ether, cyanuric chloride, tolylene 2,4-diisocyanate, dibutyltin dilaurate, and anhydrous dimethyl sulfoxide (DMSO) were obtained from Sigma-Aldrich Co. and used as received. *N*-Isopropylacrylamide (NIPA, Kohjin Co.) was purified by recrystallization from toluene/*n*-hexane. *N,N'*-Methylenebis(acrylamide) (BIS, Acros Organics) and  $\alpha,\alpha'$ -azoisobutyronitrile (AIBN, Kanto Chemical Co.) were reagent grade and used as received unless otherwise noted. Other chemicals were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification.

Milli-Q deionized water (Millipore) was used for all experiments. For the preparation of the close-packed colloidal crystals, the surface of a slide glass (76 mm  $\times$  26 mm, Matsunami glass) was cleaned by ultrasonic treatment in a concentrated KOH ethanol solution. The slide glass was removed from the solution and was thoroughly rinsed with clean ethanol and Milli-Q deionized water.

**Preparation of a Colloidal Crystal.** A thick colloidal crystal was prepared by a solvent evaporation method using the silica colloidal suspension that was relatively concentrated compared with those used in earlier methods.<sup>25,26</sup> The suspension of 20 wt % of the silica component was spread out on the surface-cleaned slide glass, which was placed in a thermostatic chamber at 90 °C. The water was gradually evaporated over 6 h. High-quality colloidal crystal was obtained with a thickness of about 0.5 mm. The evaluation of this thick colloidal crystal has previously been reported.<sup>14</sup>

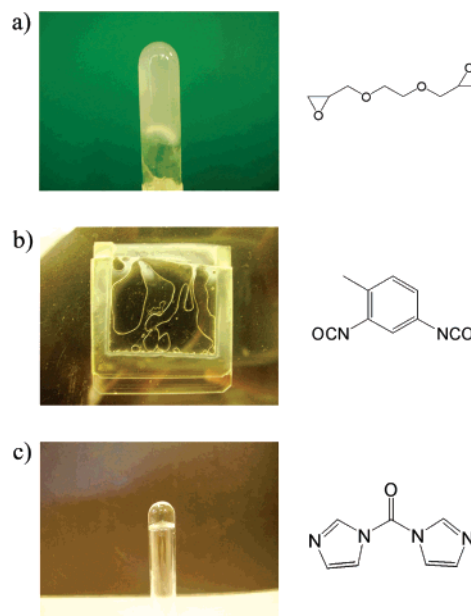
**Preparation of Gels.** We examined the following chemicals as cross-linkers, having multiple reactive groups with hydroxyl groups of  $\alpha$ -CD, to obtain the slide-ring gels under suitable conditions: ethylene glycol diglycidyl ether, tolylene 2,4-diisocyanate, cyanuric chloride, and 1,1'-carbonyldiimidazole. The polyrotaxane (25 mg) and an arbitrary amount of each candidate cross-linking agent were dissolved in 0.3 mL of anhydrous DMSO. In designing a controlled swelling degree of the gel, the amount of cross-linker was changed while that of the polyrotaxane was fixed. When tolylene 2,4-diisocyanate was used as a cross-linking agent, a slight amount of dibutyltin dilaurate was added as a catalyst in the reaction solution. The viscosities of all the pregel solutions were of the right consistency to be infiltrated into a close-packed colloidal crystal. To check the physical appearance of the gels obtained, the slab gels or rodlike gels were obtained in a flat cell composed of two glass plates and a Teflon spacer or a glass tube, respectively. To examine the swelling behaviors of the gels, tiny cylindrical-shaped gels were prepared in glass micropipettes with an internal diameter of 270  $\mu$ m. The pregel solutions in these cells were polymerized at various temperatures for 24 to 120 h. The gels obtained were washed with DMSO to remove unreacted chemicals.

The pregel solutions that turn into gels under the appropriate conditions for making structural colored porous gels were infiltrated into the interstitial regions of the colloidal crystal in a Petri dish, and the polymerizations were conducted under suitable conditions.

Afterward, the resulting gels with involvement of the silica component were immersed in a 10 wt % HF aqueous solution for 1 week to remove the silica component. The porous gels obtained were washed carefully with a large amount of distilled water and DMSO to remove HF and other impurities. We confirmed that the polymer networks were chemically stable during the etching procedure by  $^1\text{H}$  NMR and by checking the degree of swelling of the gels. When the silica component is etched away, the remaining structures are porous gels consisting of a close-packed array of solvent spheres. Because of the direct templating of the close-packed colloidal crystal, the porous gels maintain the high crystalline quality of the colloidal crystal and exhibit structural color attributed to a photonic band.

A series of poly(NIPA) gel was prepared by free radical polymerization in which the concentration of NIPA monomer was kept constant at 2 M and that of the cross-linker, BIS, was varied from 20 to 100 mM. The NIPA, BIS, and 8.125 mM AIBN (initiator) were dissolved in anhydrous DMSO, and  $\text{N}_2$  bubbling was passed through the pregel solution for 30 min. The pre gel solution infused to glass slides separated by Teflon spacers for the preparation of slab gels. Cylindrical gels were prepared using a microcapillary tube with an inner diameter of 270  $\mu\text{m}$ . The gelation was carried out at 60  $^\circ\text{C}$  for 24 h. To remove the unreacted monomer and reaction residues, the gels were thoroughly washed with DMSO for 2 weeks.

**Sample Characterization.** Photographs of the colloidal crystal and the gels were taken using a digital microscope (KEYENCE VH-8000). The sphere size of the silica particle and the extent of ordering in the colloidal crystal were determined using a JEOL JSM-5600 scanning electron microscope (SEM) operating at 20 kV. The conductive coating on the surface of the colloidal crystal was applied by Au prior to the SEM observation. The reflection spectra of the colloidal crystal and the porous gels were obtained using an Ocean Optics USB2000 fiber optic spectrometer. All spectra were monitored at normal incidence to the plane of the samples. The swelling measurements of gels were carried out by monitoring the diameter of the cylindrical gels in a glass cell. The temperature in the cell was controlled by using a circulating water temperature control system. The cylindrical gels were cut into small pieces and put into various solvents. The equilibration time for swelling and shrinking depends on the solvent composition. The equilibrated swelling degree of each gel was measured under the various conditions. The kinetics of the swelling of gels when the solvent composition was changed were observed as follows. A cylindrical gel immersed in water was dropped into another glass cell filled with a large amount of DMSO. This time-point was taken to be zero, and the change in the diameter of the cylindrical gel was observed with time. The refractive index of the bulk gels and solvents was measured using a digital refractometer (ATAGO RX-7000 $\alpha$ ). The viscoelastic properties of the gels were measured with a Rheometric solids analyzer (RSA III of Rheometric Scientific, Inc.) equipped with one normal force transducer (1kFRT) that can detect normal forces up to 35 N (3500 g) and a motor having a frequency range from  $6.28 \times 10^{-6}$  to 502  $\text{rad s}^{-1}$ , an amplitude range of  $\pm 1.5$  mm, response time  $< 5$  ms to 90% of the final value, and strain resolution of 0.00005 mm. For the purpose of measurement, 10  $\text{mm}^2$  gel samples were cut after the gels reached equilibrium at room temperature, where the gels were 4 mm thick in the preparative state. Only the bulk-type slide-ring gels and the NIPA gels were used for this measurement, because structural colored porous gels cannot be obtained at that size. The swelling and deswelling of gels were maintained throughout the experiments by immersing the gels in the solvent used. To ensure that the sample was always under compression, 5% pre-strain was applied to the samples during the experiments. The data of storage ( $E'$ ) and loss ( $E''$ ) moduli and  $\tan \delta$  were analyzed in the frequency range of 0.05 to 50  $\text{rad/s}$  with a 3% strain amplitude. The strain-controlled dynamic frequency sweep test was used as a test setup, and the selected 3% strain was in the region of the linear viscoelastic region of the sample. The temperatures in the sample chamber were controlled by an air oven equipped with an  $\text{N}_2$  cooling unit.



**Figure 1.** Photographs of slide-ring gels prepared by different cross-linkers. (a) A squashy and opaque gel was prepared by using ethylene glycol diglycidyl ether as a cross-linker; (b) A clear gel could be obtained by using tolylene 2,4-diisocyanate as a cross-linker, but bubble formation was observed; (c) A clear gel was synthesized by using 1,1'-carbonyldiimidazol as a cross-linker.

## Results and Discussion

**Preparation of Slide-Ring Gels.** Several requirements must be met when using a colloidal crystal to prepare polymer gels having a photonic band gap. First, pregel solutions must be infiltrated into the interstitial regions of the colloidal crystal without structural collapse of the crystal. The pregel solutions revealing extreme viscosity and low wettability upon the surface of the colloidal crystal are not adequate for preparing the polymer gels. Second, it is vital that the crystal structure remains stable during the gelation. A chemical reaction under an appropriate condition is preferred, such that the colloidal crystal can maintain its original structure. Finally, it is imperative that the polymer network is chemically stable for the etching liquids used. Cleavage of chemical bonds and hydrolysis of functional groups will affect the swelling behavior and mechanical properties of the polymer gel. In this work, the polyrotaxane comprised of a long chain PEG as an axis molecule and  $\alpha$ -CD as a ringlike molecule was selected as the main structural component for the slide-ring gel. The presence of hydroxyl groups on  $\alpha$ -CD allows for not only the formation of cross-linkage but also the incorporation of various functional groups to the polyrotaxane, leading to chemical tailoring of stimuli-responsive gels. We examined the following four chemicals as cross-linkers to obtain the slide-ring gels: ethylene glycol diglycidyl ether, tolylene 2,4-diisocyanate, cyanuric chloride; and 1,1'-carbonyldiimidazol. In terms of the results, however, we could not identify the appropriate conditions for preparing structural colored porous gels except when using 1,1'-carbonyldiimidazol. Only squashy and opaque gels could be obtained when ethylene glycol diglycidyl ether was used as a cross-linker (Figure 1a). The opacity of the gels interferes with the structural color from the porous gels. Clear gels could be prepared by the reaction between tolylene 2,4-diisocyanate and the polyrotaxane, but bubble formation was observed (Figure 1b). As the emergence of the bubble from the pregel solution in the colloidal crystal may cause destruction of the crystal structure, the reaction solution is an undesirable candidate for preparing the porous

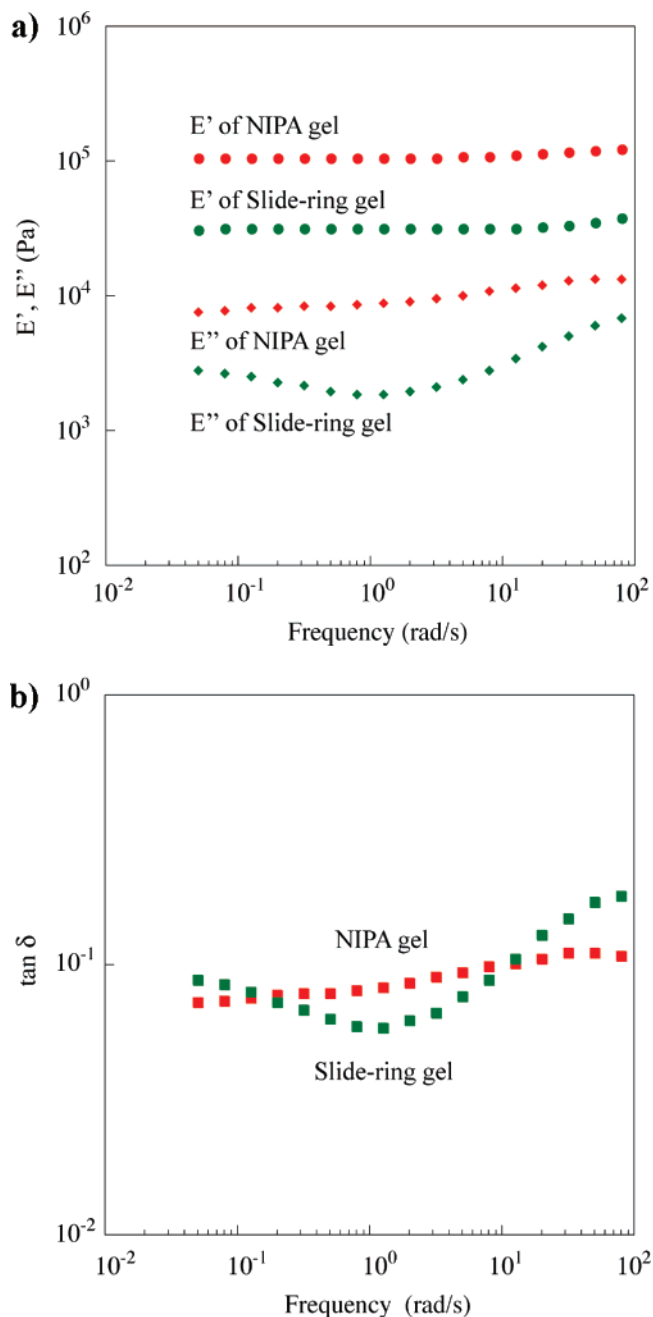


gels. The addition of cyanuric chloride into DMSO solution containing the polyrotaxane results in a risk of bumping and bubble formation;<sup>20</sup> the use of cyanuric chloride was rejected as unsuitable for the preparation of the slide-ring gel. In contrast, we could prepare a clear and homogeneous gel using 1,1'-carbonyldiimidazol under appropriate conditions for making the porous gels (Figure 1c).

**Properties of Slide-Ring Gels. Rheometric Analysis.** Dynamic mechanical analysis provides information on the gel strength expressed as viscosity or elasticity. For the ease of comparing the mechanical spectra between the slide-ring gels and chemically cross-linked poly(NIPA) gels, we used the slide-ring gel obtained using 1,1'-carbonyldiimidazol and NIPA gel, which exhibit similar swelling ratios in DMSO. Figure 2a represents the frequency dependencies of  $E'$  and  $E''$  in the strain-controlled dynamic frequency sweep test of the NIPA gel and the slide-ring gel, respectively, in DMSO. For the NIPA gel,  $E'$  is considerably higher than  $E''$  and both moduli do not depend on the test frequency, in the range between 0.05 and 50 rad/s. This result indicates that this NIPA gel represents typical characteristics of well-developed polymer networks. NIPA gels inherently have a large inhomogeneous structure due to the irregular distribution of the cross-links in the gel network. The cross-links fix the polymer chain and the gel cannot adjust its cross-link distribution or polymer length in the network structure under deformation. As a result, all of the stress is localized to short polymer chains, and gel networks cannot spread out the experienced tension. For this reason, the gel can only elastically respond to the mechanical spectra and gives higher modulus values under applied frequency.

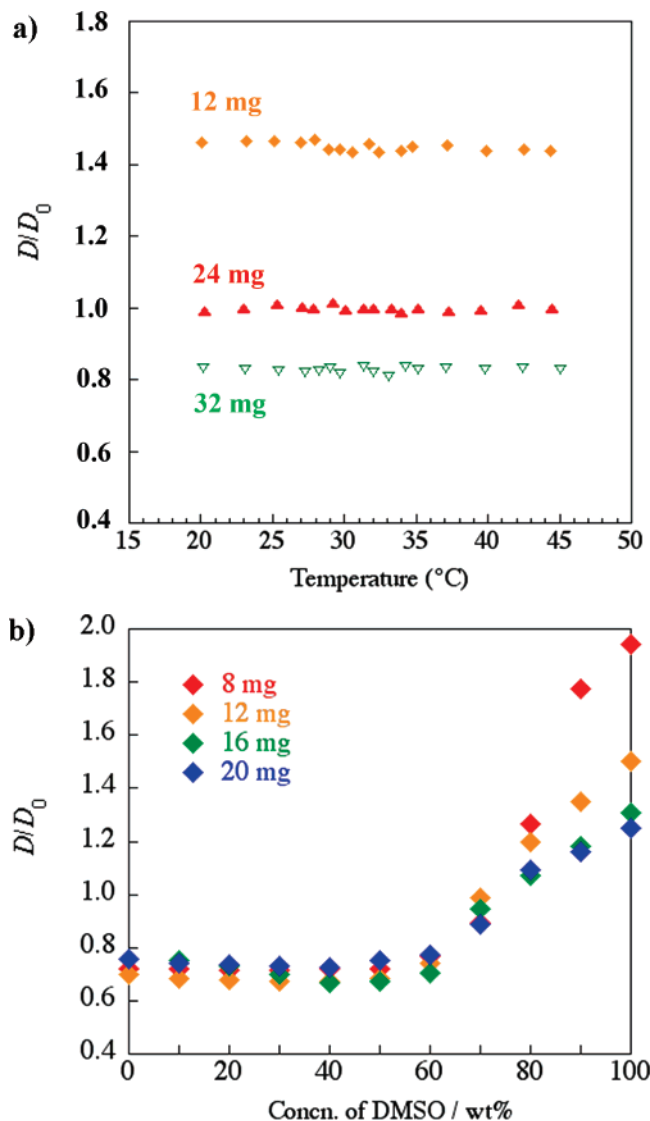
The slide-ring gel obtained by using 1,1'-carbonyldiimidazol as a cross-linker displays high tensibility and softness. The values of both  $E'$  and  $E''$  for the slide-ring gel are considerably smaller than those for the NIPA gel. This finding indicates that this slide-ring gel is softer than the NIPA gel. Figure 2b depicts the change of  $\tan \delta$  ( $\tan \delta = E''/E'$ ) values in the strain-controlled dynamic frequency sweep test for the NIPA gel and the slide-ring gel in DMSO. Judging from the values of  $\tan \delta \approx 0.1$ , these gels are considered to exhibit elastic behavior. For the NIPA gel, the loss angle  $\delta$  gradually decreases with decreases in frequency. On the other hand, the slide-ring gel shows a distinctive alteration of the loss tangent result due to the change in  $E''$  in the frequency range. The relaxation of the sliding cross-links points occurs with ease at low frequencies but after some extent it again starts to increase. The excellent reproducibility of the results of the viscoelastic measurements of the slide-ring gel indicates that differences in the viscoelastic behavior from high to low frequencies do not correspond to damage of the gel networks. This viscoelastic behavior implies that the slide-ring gel is more liquid-like than the NIPA gel.<sup>27</sup> The softness must result from the inherent pulley effect of the slide-ring gel network. Additionally, as the two-dimensional small-angle neutron scattering patterns for uniaxially stretched slide-ring gel showed a normal butterfly pattern,<sup>21</sup> we are convinced that the slide-ring gel is more liquid-like and that there exists a pulley effect in the gel. Thus, the use of this slide-ring gel to prepare structural colored gel will be highly mechanically advantageous over chemically cross-linked poly(NIPA) gel.

**Equilibrium Swelling Degree of Slide-Ring Gel.** In DMSO, the swelling ratios of the gels decreased with the increase in the amount of cross-linker, but these gels did not exhibit a dependence of volume on temperature from 20 to 45 °C (Figure 3a).  $D$  and  $D_0$  are the diameters of the cylindrical gels in



**Figure 2.** Dynamic frequency sweep test for a slide-ring gel and a chemical gel (NIPA gel). (a) Frequency dependence of storage moduli and loss moduli of NIPA gel and the slide-ring gel by using 1,1'-carbonyldiimidazol as a cross-linker, in DMSO at 25 °C. (b) Frequency dependence of  $\tan \delta$  of NIPA gel and the slide-ring gel by using 1,1'-carbonyldiimidazol as a cross-linker, in DMSO at 25 °C.

equilibrium states under certain conditions and in the reference state, respectively. Therefore,  $D/D_0$  is defined as the equilibrium swelling degree of the gels. In this study, we used  $D_0$  as the inner diameter of the glass micropipette used for the gel preparation. The volumes of these gels were found to be influenced by the solvent composition. Figure 3b shows the degrees of swelling of the gels plotted as a function of DMSO concentration in DMSO/water mixtures. The gels immersed in the mixtures of DMSO composition above 75% were swollen compared to the preparative states, but the swelling ratio gradually decreased with the increase in water content. At above a 40% H<sub>2</sub>O composition, there was a reentrant phenomenon as the H<sub>2</sub>O composition changed; the gel shrank and then swelled slightly again as the water kept being added. This reentrant

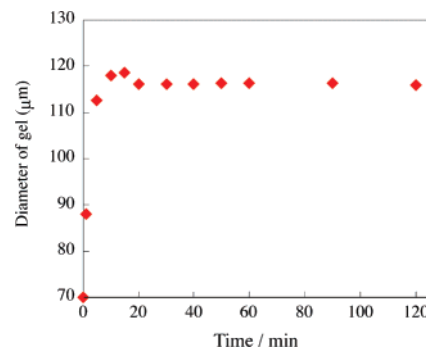


**Figure 3.** Degree of swelling of slide-ring gels prepared with different amounts of 1,1'-carbonyldiimidazol: (a) in DMSO at several temperatures; (b) in DMSO aqueous solutions of various compositions at 25 °C.

phenomenon was observed in several gels and was considered to reflect the strong attractive interaction between water and the DMSO molecules that exclude the polymers.

**Kinetics of Swelling Degree of Slide-Ring Gel.** The kinetics of the swelling of the gel were observed with the abrupt environmental change. The swelling of the gel started immediately after the gel was taken from water and immersed in DMSO at room temperature. A typical time course of the swelling change is plotted in Figure 4. The gel exhibited rapid swelling at an early stage, followed by gradual shrinkage. This phenomenon is known to be a characteristic behavior of slide-ring gels.<sup>29,30</sup> We can interpret this phenomenon in the following ways. The change in the solvent compositions from water to DMSO expands the polymer network due to an attractive interaction between DMSO molecules and PEG chains.  $\alpha$ -CD molecules then begin to aggregate,<sup>31</sup> causing the repositioning of  $\alpha$ -CD in the gel and slight gel shrinkage. This particular dynamic behavior of the swelling and shrinking processes seems to be closely related to the pulley effect.

**Properties of Colloidal Crystal.** An SEM image of the surface of the colloidal crystal composed of 300 nm silica particles is shown in Figure 5a. The silica spheres are organized



**Figure 4.** Typical time course of the diameter increase of the cylindrical slide-ring gel (this gel was prepared with 12 mg of 1,1'-carbonyldiimidazol) in response to a sudden change in solvent is plotted as a function of time at 25 °C.

into a close-packed arrangement with a long-range order in the lateral direction. This colloidal crystal exhibits monochromatic color caused by an interferential effect (Figure 5b). The appearance of the sample was observed when it was illuminated with white light at an angle normal to the planar surface of the crystal. The visual appearance of the crystal is a testament to the high crystalline quality. The reflection spectrum for the crystal is shown in Figure 5c. The intensity maximum of the photonic-band  $\lambda_{\max}$  of the crystal is located at 593 nm. We have reported that a face-centered cubic fcc structure is the most energetically stable, and this colloidal crystal is oriented with its (111) axis parallel to the glass substrate.<sup>14</sup> Thus, the peak shown represents the selective reflection of a narrow band of wavelengths due to Bragg diffraction from the fcc (111) crystal. It follows that the silica spheres are organized into a close-packed arrangement with a long-range order in both the lateral and normal directions in this crystal.

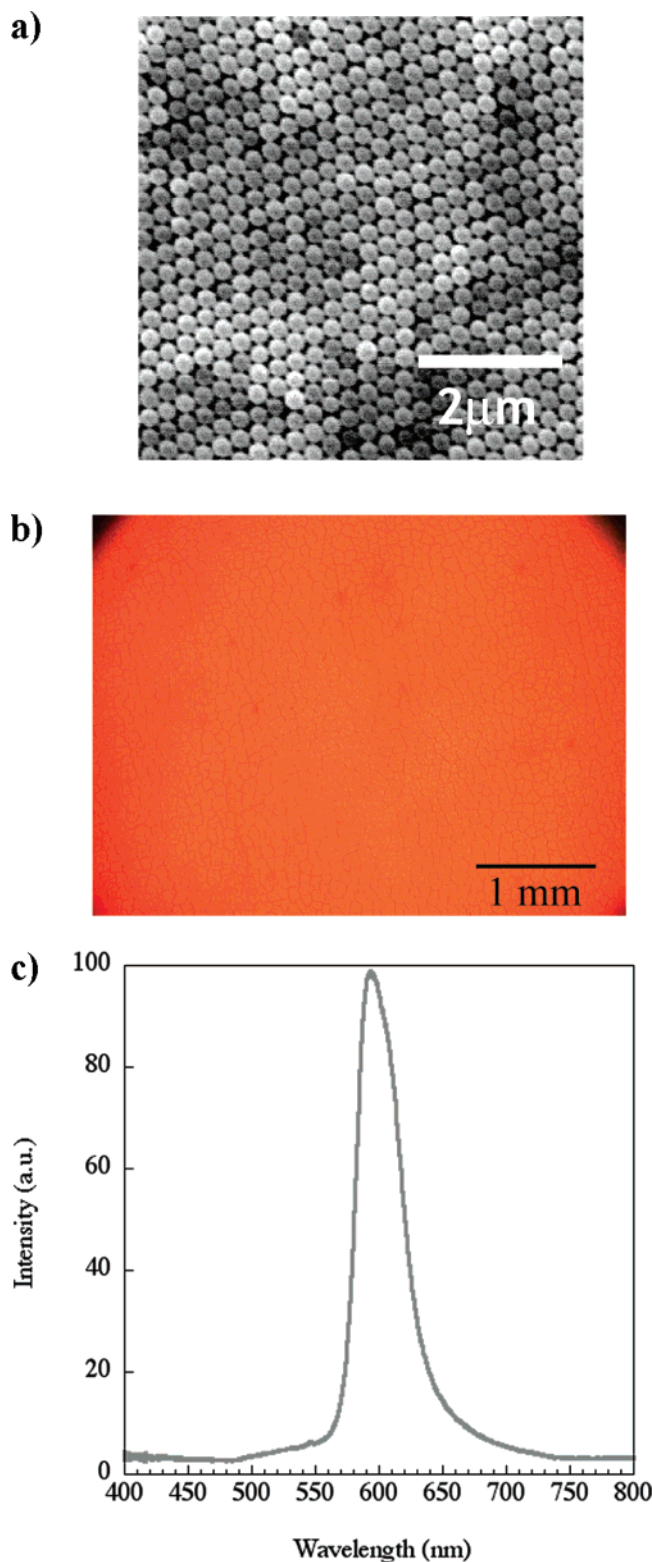
**Properties of Structural Colored Slide-Ring Gel.** Figure 6a shows a photograph of a rectangular piece of the structural colored porous gel. The porous gel, obtained by the close-packed colloidal crystal as a template, also exhibits brilliant structural color. Figure 6b shows the reflection spectra of the porous gel in a DMSO/water mixed solvent with different compositions. As the water composition was increased, the reflected peak wavelength shifted toward the shorter wavelength until the water composition reached 60%, but the peak position returned to the slightly higher wavelength when the water composition rose above 60% (Figure 6c). If the porous gel maintains the fine structure of the precursor colloidal crystal and the volume change is isotropic, the peak wavelength ( $\lambda_{\max}$ ) can be estimated by the following eq.<sup>12,14</sup>

$$\lambda_{\max} = 1.633 \{d(D/D_0)/m\} n_a \quad (1)$$

where  $d$  is the diameter of the silica spheres, and  $m$  is the order of the Bragg reflection. The value of  $n_a$  is calculated as a weighted sum of the refractive indices of the sphere portion and the gap portion:

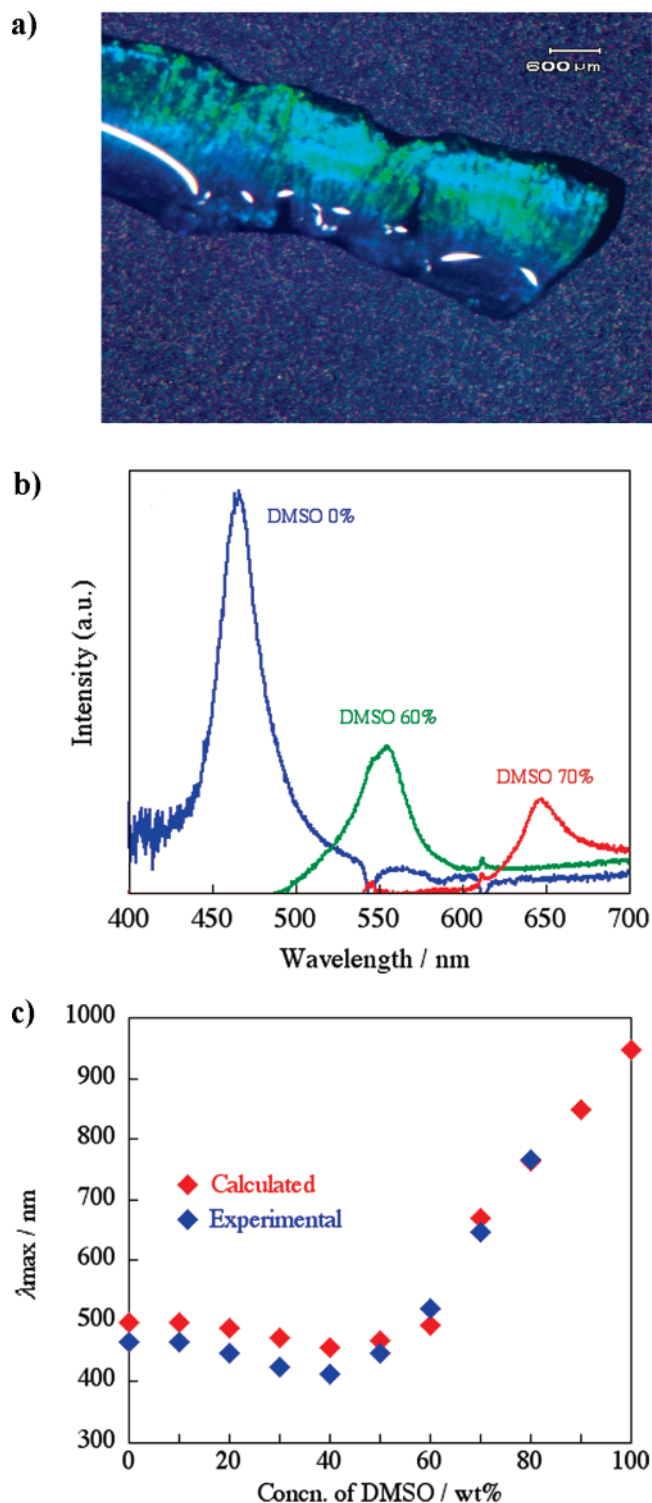
$$n_a^2 = \sum n_i^2 \phi_i \quad (2)$$

Here  $\phi_i$  is the volume fraction of each  $i$  portion. For the close-packed structure, the  $\phi$  values of the sphere portion and the intersphere portion are 0.74 and 0.26, respectively. It follows that this shift is due to a decrease in the lattice spacing of the crystal ( $d(D/D_0)$ ) and/or to a change in the value of  $n_a$ . Thus, both the change in the lattice spacing and the value of  $n_a$  of the porous gel have to be considered to calculate the theoretical value of  $\lambda_{\max}$  when the solvent composition is varied. The



**Figure 5.** SEM image, optical microscope image, and reflection spectrum of a close-packed silica colloidal crystal composed of 300 nm-diameter silica particles.

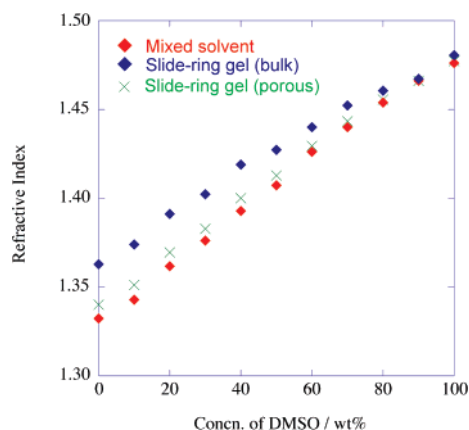
refractive indices of the DMSO–water mixed solvents and the slide-ring gel in these mixed solvents are plotted as a function of the solvent compositions (Figure 7). Both refractive indices increase almost linearly with the DMSO content. The solvent composition dependence of  $n_a$  of the porous slide-ring gel can be calculated by eq 2, assuming that the volume fraction of the gel portion is constant during the volume change. As shown in Figure 7, the change in  $n_a$  also increased linearly with the DMSO



**Figure 6.** (a) Photograph of a porous slide-ring gel swollen with water; (b) Solvent composition dependence of reflection spectra for the porous slide-ring gel made by using colloidal crystals composed of silica particles with radii of 300 nm, at 25  $^{\circ}\text{C}$ ; (c) Change in the position of  $\lambda_{\text{max}}$  of the reflection spectrum for the porous slide-ring gel with varying solvent compositions.

content. The amount of change in  $n_a$  for the porous gel was about 0.13 when the solvent composition was changed, while the change in the value of  $D/D_0$  was almost a dozen times that of  $n_a$ . Therefore, the swelling ratio is dominant over  $\lambda_{\text{max}}$  of the observed reflection spectrum for the porous gel. The positions of the peak wavelength, estimated by eq 1 using the experimentally obtained values of  $d$ ,  $D/D_0$ , and  $n_a$ , coincide with the spectroscopically determined values of  $\lambda_{\text{max}}$  (Figure 6c). This





**Figure 7.** Refractive indices of DMSO–water mixed solvents, a bulk slide-ring gel, and a porous slide-ring gel in these solvents are plotted as a function of solvent composition.

result provides evidence that the gel effectively templates against the colloidal crystal and preserves this imprinted fine structure even with the changes in volume and in the location of the cross-link-points.

In addition, as the structure of the polymer network can be modified by the incorporation of various functional groups, this system can shed light on the development of stimuli-responsive photonic band gap materials for use in future optical devices. Work is underway to promote such worthwhile applications of the gels.

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