Polymer Gels

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A Thermally Adjustable Multicolor Photochromic Hydrogel**

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To create soft materials that undergo a reversible and rapid switching between two states found in living organisms, such as soft-bodied creatures, is a challenge for materials chemists.[1] Polymer gels can exhibit a discontinuous change in volume between the swollen state and the collapsed state. This bistable characteristic of gels, known as the volume phase transition, could be useful in the development of switching devices and biomimetic soft materials, such as artificial muscles.[2,3] Unfortunately, however, the slow response of gels, which is an inherent characteristic of the phase-transition phenomenon, has prevented them from being developed technologically.

Without the phase transition the change in the volume of the gel is drastic but continuous, and the characteristic duration of the volume change is often much shorter than it is in a discontinuous system.[4] However, as the swelling and shrinking processes of gels are determined by the collective diffusion of the polymer networks in a fluid, and the collective diffusion is associated with the bulk counterflow of the fluid through the polymer networks, the relaxation time of the volume change of gels (τ) can be expressed as the decay time in the single-exponential region.

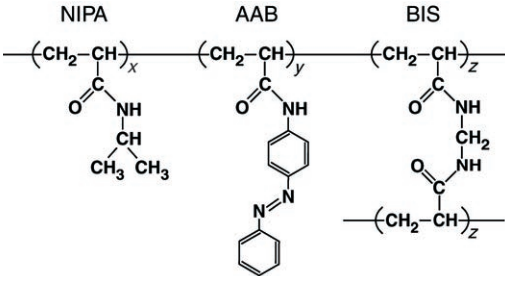
$$\tau = R^2/\pi^2 D \qquad (1)$$

In Equation (1), R is the characteristic length of a gel and D is the collective-diffusion coefficient. The characteristic time period that describes the volume changes is found to be approximately proportional to the square of the characteristic length of the gel.[5] Thus, the response speed can be improved predominantly by two methods: the downsize approach,[6] and the introduction of porosity into a gel.[7–9] The latter approach is preferable for the development of macroscopic gels.

Herein, we present a porous gel in which a light-triggered rapid two-state switching occurs between two arbitrary structural colors. The switching is attributed to the change between two volume states. This new smart soft material is prepared by introducing a periodically ordered interconnecting porous structure and incorporating azobenzene units into the gel. Multicolor photochromic behavior controlled by light is also observed in a temperature-controlled environment.

We introduced porosity into a gel by using a colloidal crystal as a template. The porous gel obtained demonstrated chromic phenomena as well as a rapid response. Azobenzene units were also incorporated into the polymer network in the expectation that the resulting gel would display photosensitivity. The presence of the azobenzene units made the coexistence of two volume states possible in the porous gel.

We chose two monomer types to prepare the polymer network of the gel, each of which plays a different role. The major monomer, *N*-isopropylacrylamide (NIPA), exhibits a change in its hydrophilicity in response to temperature, whereas the minor monomer, 4-acryloylaminoazobenzene (AAB), undergoes a change in the dipole moment upon the photoisomerization of the azobenzene group.



In water, this gel undergoes an abrupt volume change when the temperature is altered (Figure 1). The volume change is isotropic and shape independent. This behavior is the typical swelling change of bulk NIPA copolymer gels in water.[10] As the change in free energy becomes positive upon the mixing of the NIPA copolymer networks with water above a certain temperature,[11] the network shrinks. For this gel, the temperature at which we can observe the drastic change in volume, the lower critical solution temperature (LCST), is approximately 27 °C.

Azobenzene derivatives are well-known photochromic compounds that exist in two different states, the *trans* form and the *cis* form, which can be interconverted reversibly by means of a light stimulus. Each isomer of these derivatives has different properties, such as optical absorption, solubility, and steric structure. Azobenzene derivatives included in polymers can form the basis of a light-triggered molecular switch that induces conformational changes in the polymer, variations in viscosity and solubility, and changes in the mechanical strength of the polymer.[12–16] In this study, a reversible change in the dipole moment of the azobenzene moiety[17]

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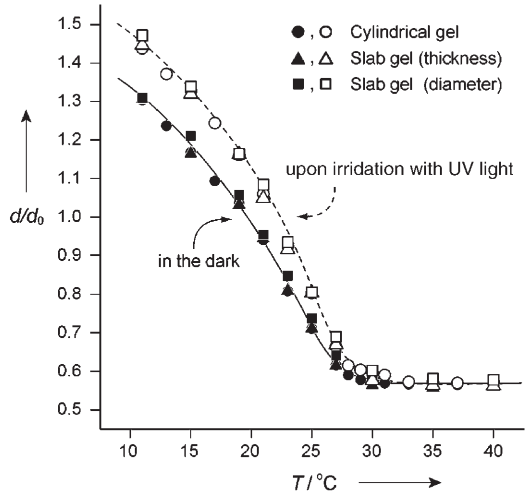

Figure 1. Swelling behavior of the porous gel. The degree of swelling of the cylindrical and slab poly(NIPA-*co*-AAB) gel in water in the dark and upon irradiation with UV light (366 nm) was plotted as a function of temperature. The lines are drawn as guides for the eye.

was used to induce a volume change in the gel. Azobenzene is almost entirely in the *trans* configuration; it has no dipole moment at room temperature in the dark. Irradiation with UV light at about 366 nm leads to the production of a *cis* isomer with a dipole moment of 3 D. The back reaction to the *trans* form occurs upon irradiation with visible light at about 450 nm or thermal relaxation in the dark. It follows that the dipole moment of the azobenzene group can be switched reversibly by a light stimulus. The change in the dipole moment of the azobenzene group attached to the polymer network affects the free energy of the mixing process between the polymer network and water molecules. Hence, the network expansion of the gel in water can be controlled reversibly and independently by employing thermal and optical stimuli.[13]

A periodically ordered interconnecting porous structure was given to the NIPA-AAB gel. To obtain the porous gel, we used as a template a colloidal crystal with a face-centered-cubic (fcc) lattice composed of closest-packing monodispersed amorphous SiO_2 particles. The preparation of the porous gel is described in the Experimental Section.[18–20]

If the porous gel maintains the fine structure of the precursor colloidal crystal and the volume change is isotropic, the value of λ_{max} diffracted from the (111) planes in the porous gel with an fcc structure is expressed by Equation (2).

$$\lambda_{max} = 1.633(l/m)(d/d_0)\,(n_{av}^2 - \sin^2\theta)^{1/2} \qquad (2)$$

In Equation (2), l is the diameter of a colloidal particle, m is the order of the Bragg diffraction, d/d_0 is the equilibrium swelling degree of the gel (d and d_0 represent the thickness of the porous-gel membrane in the equilibrium state under certain conditions and in the prepared state, respectively), n_{av} is the average refractive index calculated by considering the indexes and the volume fractions of the gel portion and the water voids of the porous gel under certain conditions, and θ is the angle measured from normal to the gel surface. In our experiment, θ was fixed at 0°. Furthermore, we demonstrated experimentally that the variation in n_{av} for the porous gel was approximately 0.005 when the temperature was increased from 10 to 25 °C; this variation in n_{av} is negligible in comparison to the change in the swelling degree. We therefore used a constant value of 1.338 for n_{av}. The peak positions of the reflection spectra from the porous gels at all temperatures lower than the LCST coincide with the values of λ_{max} determined by Equation (2). This result indicates that the swelling degree has a dominant effect on the value of λ_{max}.

If the lattice spacing of the resulting porous gel is of the order of a subwavelength scale, the reflections can be observed visually as structural color. Figure 2 shows the observed temperature dependence of the changes in structural color and the reflection spectra for the porous gel in the dark. When the temperature was changed, structural-color variation of the porous gel was observed, accompanied by swelling behavior. The diffracted wavelength, λ_{max}, for the porous gel shifted towards shorter wavelengths with increasing temperature. This shift was due to the decrease in the lattice spacing of the porous structure with the shrinking of the gel.

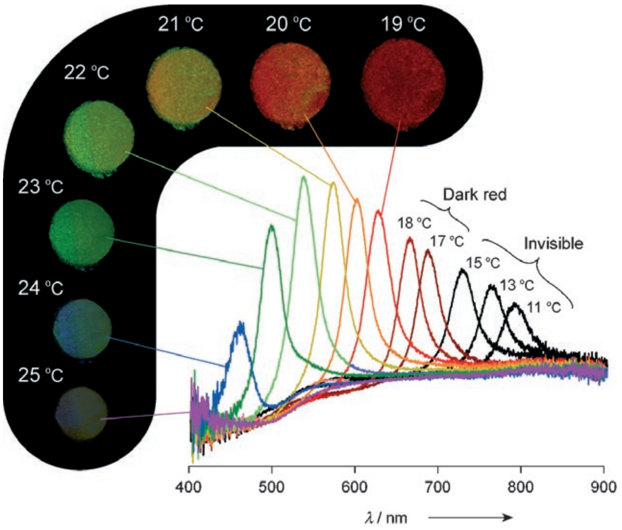

Figure 2. Spectroscopic characterization of the porous gel. Photographs and reflection spectra of the porous poly(NIPA-*co*-AAB) gel in the dark at various temperatures.

The intensity of the diffracted peaks increased as the temperature increased. It is well known that the intensity of the diffracted peaks is proportional to both the magnitude of the optical dielectric contrast and the number of lattice planes that result from the periodic arrangement.[21] The increase in the peak intensity is due primarily to increases in the contrast that result from the increase in the refractive index of the gel portion and the decrease in the refractive index of the water, as the number of lattice planes does not change at all in response to the deformation of the gel. The decay in the peak intensity at wavelengths below about 500 nm is attributed to the overlap between the diffracted spectra and the absorption band of AAB molecules. As shown above, this system exhibits thermally tunable structural color over a wide range of wavelengths.

A rapid and continuous shift in λ_{max} was induced by temperature jumps at temperatures lower than the LCST (Figure 3 a). This result indicates that the porous gel exhibits a fast and isotropic volume change that corresponds to the rapid temperature change. The porous gel undergoes changes in volume more than 1000 times faster than a conventional homogeneous gel.[18] This difference can be understood as follows: The relaxation time of the volume change of the gel can be defined by the collective-diffusion coefficient and the characteristic length of the gel, as described in Equation (1).[5] This equation shows that the smaller the gel is, the shorter its response time is. As we can regard intuitively this porous gel as an aggregate of many tiny gels, it is not surprising that the response time is drastically shorter than that of a homogeneous gel membrane of equal size. The interconnecting inner porous structure may also be a small factor in the rapid response, because the diffusion coefficient of water molecules in bulk water is larger than that of water molecules in a polymer network.[22] It follows that the interconnecting porous structure allows the solvent to diffuse smoothly into and out of the gel.[23] The fast volume change results from the ability of the structure to allow a sufficient amount of water to reach the internal tiny gels to produce the swelling, and its ability to expel water from the porous gel.

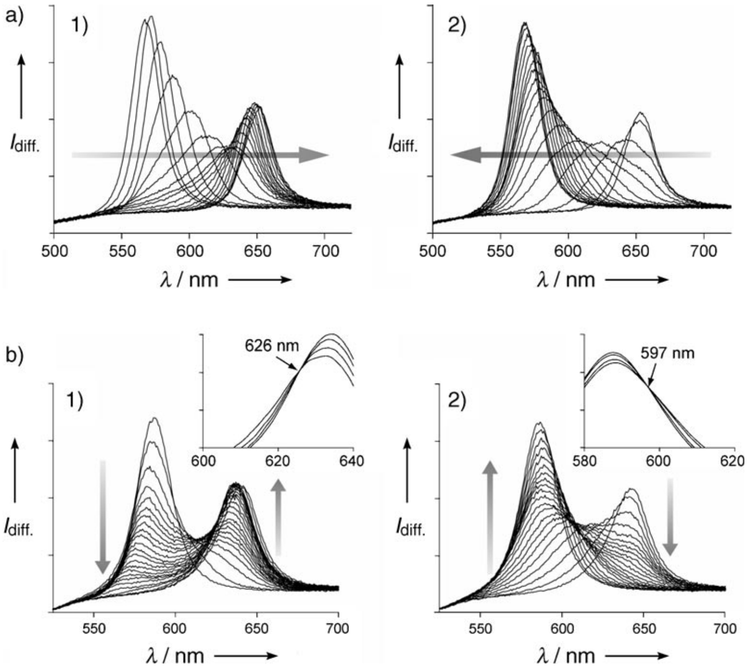

Figure 3. a) Changes in the reflection spectra with time for the porous poly(NIPA-*co*-AAB) gel in the dark upon a jump in temperature from 1) 22 to 19 °C and 2) 19 to 22 °C; b) changes in the reflection spectra with time for the porous poly(NIPA-*co*-AAB) gel at 21 °C upon irradiation with 1) light of wavelength 366 nm (8.0 mW cm^{-2}) and 2) light of wavelength 437 nm (4.0 mW cm^{-2}). Insets: An isosbestic point can be observed within a certain time range in both cases. As the position of the isosbestic point shifts gradually with the change in the volume, the presence of an isosbestic point becomes unclear during the total period of volume change.

The decrease in intensity and the increase in width that occur at the half maximum of the peaks upon the abrupt volume change must be attributable to the distortion of the porous structure. The distortion may be induced by the difference in the size of various parts of the porous gel, because the relaxation time of the swelling and shrinking of a gel, as noted above, is proportional to the square of the characteristic size.

The most fascinating property of this porous gel is the rapid two-state switching between two arbitrary structural colors in synchrony with the *trans–cis* photoisomerization of the azobenzene moieties as a result of irradiation with light in a temperature-controlled environment. Figure 3 b shows the kinetic alteration in the reflection spectra upon irradiation with UV or visible light. An isosbestic point was observed in both cases en route to new equilibrium conditions (see insets in Figure 3 b). Isosbestic behavior indicates that there exist two distinct swelling states during the alterations.

Figure 4 contains simple sketches that explain this phenomenon. As described above, the continuous shifting of λ_{max} is attributed to the isotropic change in the volume of the gel upon a temperature jump (Figure 4 a). On the other hand, upon exposure to UV or visible light, part of the gel must swell first, and this swollen portion must then coexist with the remaining gel in its initial state (Figure 4 b). In the earliest state, the incident UV light is mostly absorbed by the azobenzene moiety in the vicinity of the surface of the gel on the side near the light source because of the strong absorption of light at about 366 nm by the azobenzene moiety: the π–π* absorption of azobenzene units in the *trans* configuration.[14] The photoisomerized *cis* form exhibits a low-intensity n–π* absorption in the visible region at around 450 nm. As a result, the incident UV light gradually reaches the azobenzene moieties in the *trans* form in the interior of the gel membrane: The *trans*--*cis* photoisomerization proceeds in the direction of light propagation. The portion in which the azobenzene moiety exists as the *cis* form will absorb water, and this portion swells to become bigger than the initial state. Consequently, there exist longitudinally two different degrees of swelling in a piece of gel membrane.

The coexistence of two different swollen states in a gel may cause the deformation of both portions at positions on the surface at which they are in contact. If we use a homogeneous gel consisting of NIPA and AAB, the gel can be bent away from the light source to reduce the elastic energy generated by the deformation. The total amount of elastic energy is proportional to the net volume of a gel.[24] Consequently, the amount of elastic energy induced by the coexistence of two different swollen states in the porous gel is much smaller than that in a homogeneous gel. As a result, the coexistence of different swollen states in the porous gel can be facilitated by irradiation with light in a temperature-con-

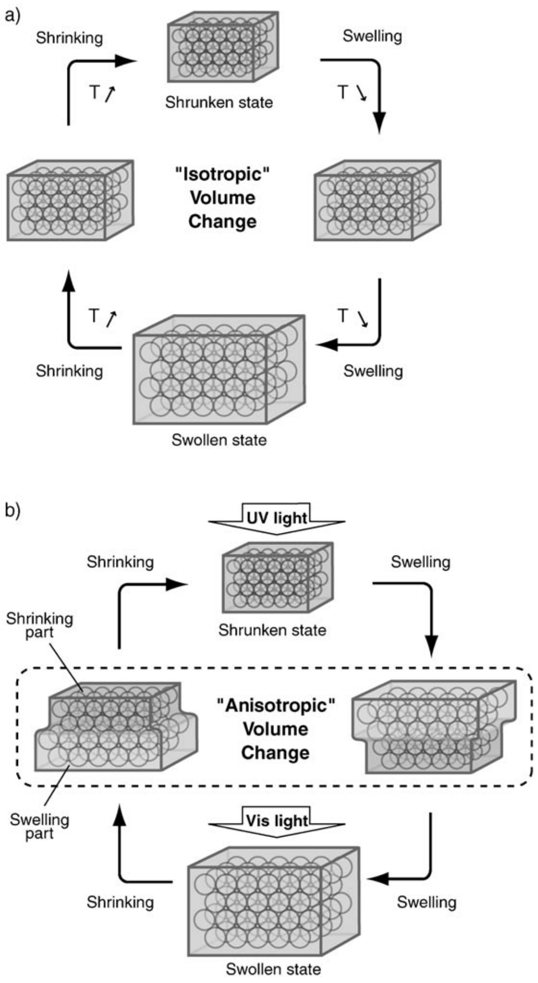

Figure 4. Models for the temporal volume-change mechanisms of the porous poly(NIPA-*co*-AAB) gel driven by a) a temperature jump and b) light irradiation.

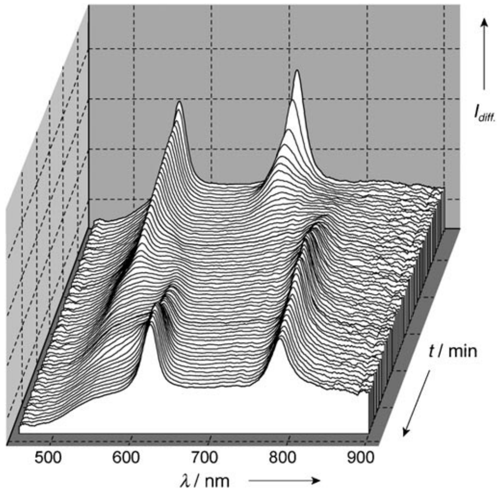

Figure 5. Changes in the reflection spectra with time for the double porous poly(NIPA-*co*-AAB) gel, prepared with a bilayer colloidal crystal, at 15 °C upon irradiation with UV light (8.0 mW cm^{-2}).

trolled environment. The back reaction can be explained by a similar mechanism.

To confirm our above hypothesis, we prepared a double porous gel that reflected two notably different wavelengths of light by using a bilayer colloidal crystal; the upper layer was composed of SiO_2 particles of 280 nm diameter, and the lower layer consisted of SiO_2 particles of 220 nm diameter (Figure 5). We observed two peaks, at 560 and 710 nm, in the reflection spectrum of the porous gel kept at 15 °C in the dark. Upon irradiation of the double porous gel with UV light from above, the peak at 710 nm that arose from the upper porous structure was replaced by a new peak at a higher wavelength. Further two-state switching was observed upon continued irradiation with UV light, as the peak produced by the lower porous structure then disappeared to be replaced by a new peak. In the reverse reaction promoted by irradiation with visible light, the disappearance of the new peaks, one after the other, and the reappearance of the original peaks indicated similar double two-state switching. Thus, these observations verify our prediction shown in Figure 4b.

The coexistence of different degrees of swelling of the porous gel in a longitudinal direction can be applied in a lateral direction. If the porous gel is stored in darkness for a certain time and then exposed to UV light through a photomask, the irradiated portion will increase in volume and undergo a change in color (Figure 6a). As the swollen portion has little influence on the nonirradiated portion in terms of volume, patterns of color can be generated on the gel membrane (Figure 6b). These patterns can be erased and reproduced easily.

Figure 7 shows the photoinduced change in the multistructural color of the porous gel in water at 19, 21, and 24 °C.

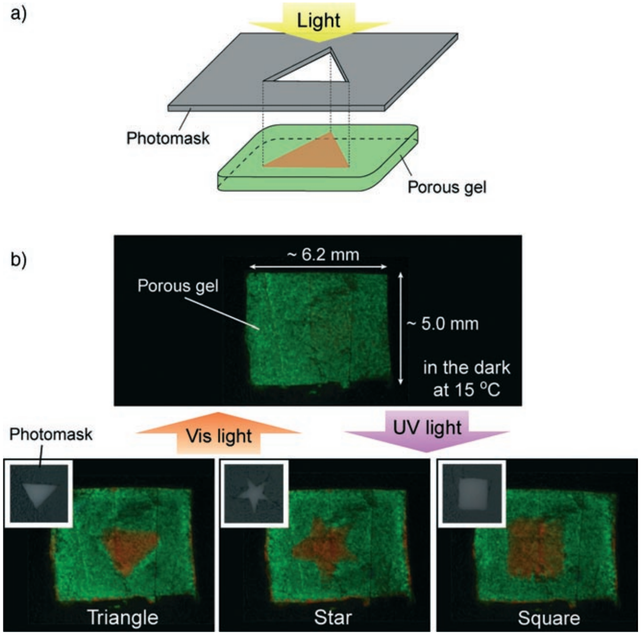

Figure 6. Multicolor photochromic behavior of the porous gel. a) Schematic view of structural-color patterning of the porous gel by irradiation with UV light through a photomask; b) photographs of the porous poly(NIPA-*co*-AAB) gel marked with a triangle, a star, and a square; these images result from the structural-color change caused by irradiation with UV light through the corresponding photomasks.

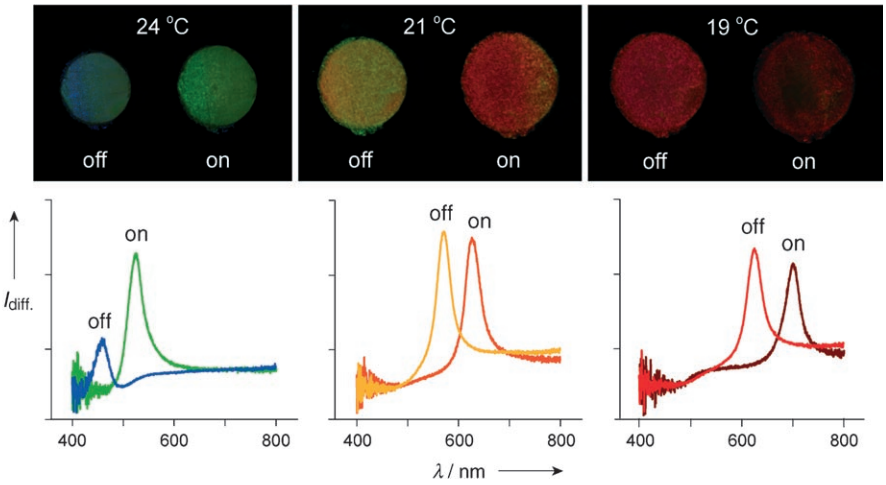

Figure 7. Multicolor photochromic behavior of the porous gel. Photographs and reflection spectra of the porous poly(NIPA-co-AAB) gel in water at 19, 21, and 24 °C before UV irradiation and after the equilibrium degree of swelling had been reached in response to the UV irradiation (366 nm, 8.0 mW cm^{-2}).

Upon irradiation with UV light, a new spectral peak appeared at a higher wavelength than the corresponding peak observed in the dark at each temperature. The observed change in the peak position could be reversed by exposure of the gel to visible light.

Our results show that it is possible to tune the structural color of a porous gel rapidly between two arbitrary states by using photostimuli at a controlled temperature, in a way that mimics the iridophores of fishes and chameleons.[25] We believe that this approach may be applicable to other smart gels that are sensitive to electric and magnetic fields.

Experimental Section

A close-packing silica colloidal crystal consisting of monodispersed amorphous spherical silica particles with diameters of 280 nm and/or 220 nm was used as a template. The template was obtained by a solvent-evaporation method in which a colloidal suspension casting on a slide glass is gradually evaporated at a high temperature. The detailed fabrication technique for the template has been reported previously.[18–20] The colloidal crystal composed of particles of 280 nm diameter was placed on the crystal consisting of particles of 220 nm diameter to give the bilayer crystal.

The thermo- and photoresponsive gel was prepared by free-radical copolymerization. First, the thermosensitive monomer NIPA (0.077 mol), the photoresponsive monomer AAB (2.4 mmol), the crosslinker *N*,*N*′-methylenebisacrylamide (BIS, 1.6 mmol), and the initiator 2,2′-azobis(isobutyronitrile) (0.7 mmol) were dissolved in oxygen-free 1,4-dioxane (50 mL). This pre-gel solution was infiltrated into the colloidal crystals and then polymerized at 60 °C for 48 h. The samples were then immersed in an aqueous solution of HF (3 wt %) at 4 °C for a week to etch away the silica component. The cylindrical bulk gel for the swelling measurements was also prepared in a micropipette with an inner diameter of 280 μm by the protocol used for the porous gels. The resulting porous and cylindrical poly(NIPA-*co*-AAB, 97:3) gels were washed carefully with a large amount of distilled water during 1 week at 4 °C in a refrigerator.

The equilibrium cylindrical-gel diameter and the equilibrium thickness of the porous gel were measured under a microscope. The reflection spectra were obtained by using an Ocean Optics USB2000 optical-fiber spectrometer. The structural color changes of the porous gels upon exposure to thermo- and photostimuli were monitored by using a digital microscope (Keyence, VH-8000). The temperature during the measurements was controlled by means of a circulating-water temperature-control system. Two temperature controllers were connected to the cell so that it was possible to switch quickly from one temperature to another for the kinetic experiments. Irradiation with light was performed with a 500-W high-pressure mercury lamp (Ushio USH-500D). The wavelengths of irradiated light (UV light: $\lambda \approx 366$ nm, visible light: $\lambda \approx 437$ nm) were selected with the aid of color filters (Toshiba; for $\lambda \approx 366$ nm, the pair UV-D35 and UV-35 were used; for $\lambda \approx 437$ nm, V-40 and Y-43). A heat-absorbing filter (HOYA HA50) was used to eliminate the heat from the mercury lamp.

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