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Biform Structural Colored Hydrogel for Observation of Subchain Conformations

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ABSTRACT: We prepared a biform structural colored thermosensitive gel using both a close-packed colloidal crystal and a wing of a morpho butterfly. The porous portion of the gel obtained by the close-packed colloidal crystal as a template exhibits a change in "structural color" according to the volume when the water temperature is altered. Meanwhile, the portion where tiny scales of the wing are strewn on the surface of the gel (a morpho gel) also reveals "structural color", but irrespective of the volume change. The reflection spectrum from "the morpho gel" portion provides the standard value of the peak position, $\lambda_{\max,0}$, indicating that the subchains in the gel are Gaussian chains. Consequently, we can estimate the linear expansion factor α of the subchains by comparing the peak positions of the reflection spectra from the porous gel, $\lambda_{\max}$, and from the morpho gel, $\lambda_{\max,0}$: $\lambda_{\max}/\lambda_{\max,0} \sim \alpha$. We can detect the change in the conformation of subchains in the gel in response to the external perturbations surrounding the gel with the naked eye and/or spectroscopic methods through the comparison of the both structural colors.

Introduction

The development of polymer-based materials for electrical circuit-free sensing systems is an active area of research due to the need for simplified and rapid diagnostics to be used for medical and environmental purposes.[1−11] In the design of selective sensing systems, the materials must enable a transducer function that can convert external stimuli into observable signals as well as a recognition ability for certain stimuli.

Polymer gel composed of a three-dimensionally cross-linked polymer network and a large amount of solvent is applicable to the development of sensor systems because it undergoes volume changes in response to the changes in a wide variety of stimuli.[5−11] Stimuli-responsive gels that are sensitive to small changes in temperature,[12] pH,[13] ionic strength,[14] pressure,[15] and electric[16,17] or magnetic fields[18] have been already developed in the past few decades. The long-coveted tailor-made molecular recognition gels have also been produced as a result of researchers' extraordinary efforts.[11,19] The response speed that is essential for sensor systems can be improved by introducing porosity into gels.[20,21] Porous gels undergo changes in volume more than 10−1000 times faster than conventional homogeneous bulk gels. With ingenuity, we can develop unique polymer-gel-based sensing systems that have peculiarities not shared by the currently used sensing systems.

In existing sensing systems with an electrical circuit, e.g., a potentiometer used to determine some components of analyte solutions, a reference system is apparently more effectively utilized.[22] The purpose of setting a reference for sensing systems is to provide a stable and well-defined standard value against which observed values are evaluated. The introduction of an operational reference system for the polymer-based sensing systems may produce more convenient and unique methods of determining the value of diagnostic tests and environmental changes.

We have employed specific volumes of gels under various preparation conditions as a reference state to evaluate the swelling behavior.[6,7,19,23−26] We have done so for the following reasons: (1) it is easy to deal with the volumes of gels under certain preparation conditions because the sizes can be regarded as the inner sizes of the reaction vessels used; (2) the subchains in the polymer networks under the preparation conditions behave as unperturbed Gaussian coils, and thus we can make a molecular interpretation relating to the subchains in the gels, such as the linear expansion factor α of the subchains, just by measuring the lengths of the gels.[26] In the classical Flory theory,[27] the reference state is set in a dry state or the preparation conditions without diluents. However, we believe that the statics of the subchains in the polymer network under preparation conditions with a large amount of diluents are practically Gaussian-like, as some groups have pointed out.[12,28−33] The reference size of a cylindrical gel under preparation condition can be determined by the inner diameter of glass capillary used for making the cylindrical gel. In the case of a disk-shaped gel which is useful for sensor systems, though, the diameter of the disk-shaped gel may often lost in the course of some treatments such as a shape adjustment of the gel and removing of unreacted chemicals from the gel.

In this paper, we demonstrate a polymer-gel-based prototype-sensing system that exploits both observable and reference values in given situations. We chose thermosensitive *N*-isopropylacrylamide (NIPA) as a monomer with which to prepare the polymer network, because the use of NIPA gel, which is a well-known thermosensitive gel in water, will easily allow us to verify the availability of the newly introduced function, associated with the volume change, to the polymer-gel-based sensing system. A close-packed colloidal crystal (hereinafter called "colloidal crystal") and a wing of a morpho butterfly were used to introduce structural coloration to the gel. This system allows not only for the detection of simple temperature alterations surrounding the gel but also for the observation of the change in conformations of the subchains in the gel by megascopic or spectroscopic methods.

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Experimental Section

Materials. An aqueous suspension of monodisperse SiO_2 particles was purchased from Nippon Shokubai Co., Ltd. The mean diameter of the particles used in this study was 260 nm. Scanning electron microscopy (JEOL JSM-5600) was used to determine the size of the particles. NIPA was kindly supplied from Kohjin Co., Ltd., and was purified by recrystallization from a toluene (Wako Pure Chemical Industries, Ltd: WPCI) and hexane (WPCI) mixed solvent prior to use. *N*,*N*′-Methylenebis(acrylamide) (BIS) (WPCI) as a cross-linker, benzoyl peroxide (BPO) (WPCI) as an initiator, 1,4-dioxane (DOX) (WPCI) as a polymerization solvent, and sodium hydroxide (WPCI) to obtain an alkaline etching solution were purchased and used as received. Milli-Q deionized water (Millipore) was used for all experiments. A wing of a morpho butterfly was obtained from Mushi-sha Ltd.

Synthesis. NIPA gels used in this project were synthesized by free-radical polymerization of NIPA (11.30 g), and BIS (0.51 g) solubilized in DOX (50 mL) at 60 °C for 12 h using BPO (0.07 g including 30 wt % water). A cylindrical gel for the swelling measurement was prepared in a glass capillary with an internal diameter of 100 μm. The resulting cylindrical gel was washed in water to remove unreacted chemicals from the polymer network. The structural colored gels were made by a flat glass cell created by two glass plates and a Teflon spacer attached with Teflon grease (Daikin Industries, Ltd.). The detailed fabrication technique to prepare the colloidal crystal has previously been reported.[26] The colloidal crystal and/or the wing of the morpho butterfly were attached to one or both internal sides of the glass plates. The gels were left in 0.05 M NaOH aqueous solution for 30 days to remove the silica component and to peel the tiny scales from the wing before the swelling and spectroscopic experiments were carried out.

Characterization. The swelling measurement was carried out by monitoring the diameter of the cylindrical gels in water under a microscope with a circulating water temperature control system. The reflection spectra of the structural colored gels were obtained using an Ocean Optics USB2000 fiber optic spectrometer. All spectra were monitored at normal incidence to the plane of the samples. Photographs of the gels were taken using a digital microscope (KEYENCE VHX-500).

Results and Discussion

In recent studies, we have demonstrated that stimuli-responsive gels having a periodically ordered interconnecting porous structure can be prepared by using the colloidal crystal as a template.[21,23−26] The built-in porosity provides a periodical refractive index to the stimuli-responsive gels. The porous gels exhibit structural color and show a change in color in synchronization with the volume change. The basic optical properties can be quantitatively described by Bragg's law combined with Snell's law:

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

where $\lambda_{\max}$ is the peak wavelength of the reflection spectra determined by means of diffraction properties, d is the diameter of the colloidal particles used for the colloidal crystal, m is the order of the Bragg reflection, and D and D_0 are the characteristic sizes of the gel in the equilibrium states at a given condition and in the reference state, respectively. Thus, D/D_0 is defined as the equilibrium linear swelling degree of the gel. The value of n_a is calculated as a weighted sum of the refractive indices of the sphere portion and the gap portion

$$n_a^{\,2} = \Sigma n_i^{\,2}\,\phi_i \tag{2}$$

where ϕ_i is the volume fraction of each i portion. For the closed-packed structure, the volume fraction of the sphere portion is 0.74. If we fabricate this type of porous gel by means of a polymer network that is sensitive to the intended stimuli, the resultant system can be applicable for use in a desired indicator or sensor that changes color in response to the stimuli.[6,7]

Figure 1a shows typical reflection spectra of the porous NIPA gel at various temperatures in water. As the temperature increased, the reflection spectrum from the porous NIPA gel shifted toward the shorter wavelength. NIPA gel exhibits a gradual decrease in volume with the increase in temperature and undergoes an abrupt volume change at the lower critical solution temperature (LCST), at about 32−34 °C.[12] This structural-color variation of the porous gel was accompanied by swelling behavior; this shift was due to the decrease in the lattice spacing of the porous structure with the shrinking of the gel. The position of the peak wavelength from the porous gel can be estimated by eq 1 at temperatures lower than the LCST. However, the peak positions at temperatures higher than the LCST do not coincide with the theoretical values of $\lambda_{\max}$, because of the deformation of the porous structure. The change in n_a for the porous gel is vanishingly small when the volume is changed; the swelling degree is dominant over $\lambda_{\max}$ of the observed reflection spectrum for the porous gel.

Here, we show the theoretical treatment of the swelling degree of NIPA gel to explain the correlation between the equilibrium linear swelling degree D/D_0 and the linear expansion factor α. According to the Flory−Rehner theory of gels, the equilibrium swelling degree is controlled by the competition between the rubberlike elasticity and the polymer/solvent mixing.[27] We identify these two contributions to the free energy of nonionic gels such as NIPA gel and assume they are additive:

$$\Delta F = \Delta F_M + \Delta F_{el} \tag{3}$$

where ΔF_M and ΔF_{el} represent the mixing and elastic contributions to the free energy, respectively. On the basis of the Flory−Huggins lattice theory, the free energy of mixing between the polymer network and solvent molecules can be written as

$$\Delta F_M = N_s kT[\ln(1-\phi) + \chi\phi] \tag{4}$$

where N_s is the number of solvent molecules, k is the Boltzmann's constant, T is the absolute temperature, ϕ is the polymer volume fraction, and χ is the polymer−solvent interaction parameter, the so-called Flory parameter. Since the parameter χ is defined as the change in the free energy per solvent molecule induced when a solvent−solvent contact is changed into a solvent−polymer contact, and depends not only on temperature but also on the volume fraction of the polymers, χ can be written as follows:

$$\chi = \chi_1 + \phi\chi_2 = \frac{\Delta H - T\Delta S}{kT} + \phi\chi_2 \tag{5}$$

Here χ_1 is the parameter depending on temperature, χ_2 is the constant that must be appreciably larger than $^1/_3$ for a discontinuous volume change to occur, and ΔH and ΔS are the enthalpy and entropy of polymer−solvent mixing.[32] The elastic contribution to the free energy of gels can be expressed as

$$\Delta F_{el} = \frac{3\nu T}{2}\left[\left(\frac{\phi_0}{\phi}\right)^2 - 1 - \ln\left(\frac{\phi_0}{\phi}\right)\right] \tag{6}$$

where ν is the total number of subchains per unit volume of the gels, and ϕ_0 is the polymer volume fraction in the reference state. In general, the reference state for the polymer networks

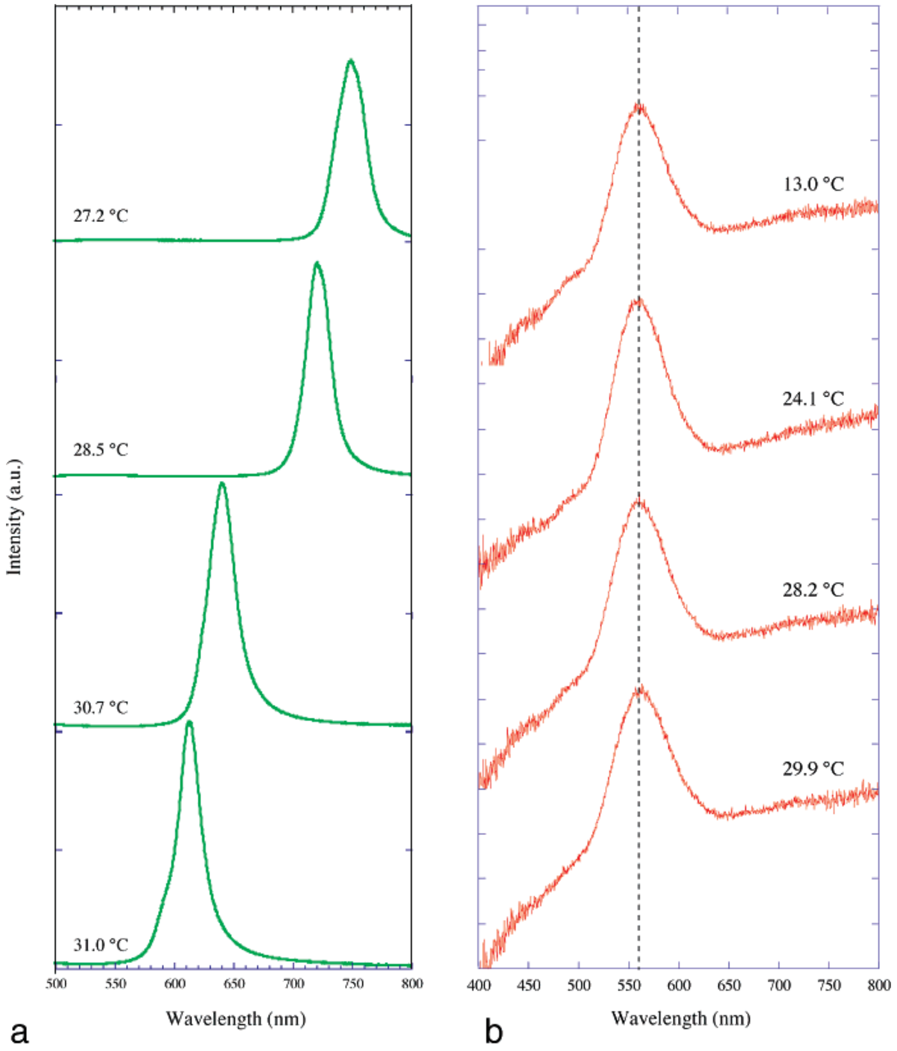

Figure 1. (a) Reflection spectra of the porous NIPA gel at various temperatures. (b) Reflection spectra of the morpho gel at various temperatures.

is chosen near the Θ temperature where the subchains behave as unperturbed Gaussian coils. In this study, we believe that the statics of the subchains in the polymer network under preparation conditions are practically Gaussian-like.

The thermodynamic equilibrium of gels is attained when the chemical potential of the solvent is equal inside and outside of the gels. In this case, the condition of zero osmotic pressure applies:

$$\Pi = -\frac{N_a}{\upsilon_1}\left(\frac{\partial \Delta F}{\partial N_s}\right) = 0 \qquad (7)$$

Here N_a is Avogadro's number, and υ_1 is the molar volume of the solvent. Equating the gels and the bath solvent chemical potentials using eqs 3−7 gives us the swelling equilibrium condition as follows:

$$\frac{1}{T} = \frac{\Delta S}{\Delta H} + \frac{k}{\Delta H}\left\{\frac{\upsilon_1 \nu}{N_a \phi^2}\left[\left(\frac{\phi}{2\phi_0}\right) - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] - \frac{1}{\phi} - \frac{\ln(1-\phi)}{\phi^2} - \chi_2 \phi\right\} \qquad (8)$$

We have been able to fit the experimental curve well for the swollen state of the NIPA gel by using eq 8 with appropriate values of each parameter.[26]

If the subchains in the polymer networks under the preparation conditions behave like Gaussian chains, as some groups believe and have pointed out,[12,29−31] we can quantitatively estimate the static conditions of the subchains in the equilibrium state of the gels just by measuring the swelling degree of the gels. In this condition, the swelling degree of the gels (ϕ_0/ϕ) and the size of the subchain coils in the polymer networks are related through

$$\phi_0/\phi = \alpha^3 \qquad (9)$$

The quantity of α directly specifies the role of the excluded volume interactions of the subchains.[27] The value of α, which is larger than 1, means that the coil of the subchains is swollen in comparison with its Gaussian size, whereas the coil with $\alpha < 1$ is a compressed state. As α is the linear expansion factor, it is equivalent to the one-dimensional swelling degree D/D_0:[33]

$$\alpha = D/D_0 \qquad (10)$$

Thus, when $D/D_0 = 1$, the reflection spectrum of the porous gel provides the reference value of the peak maxima $\lambda_{\max,0}$, indicating that the subchains in the gel behave as Gaussian chains.[26] It follows that we can estimate the linear expansion factor α of the subchains by comparing the position of the peak

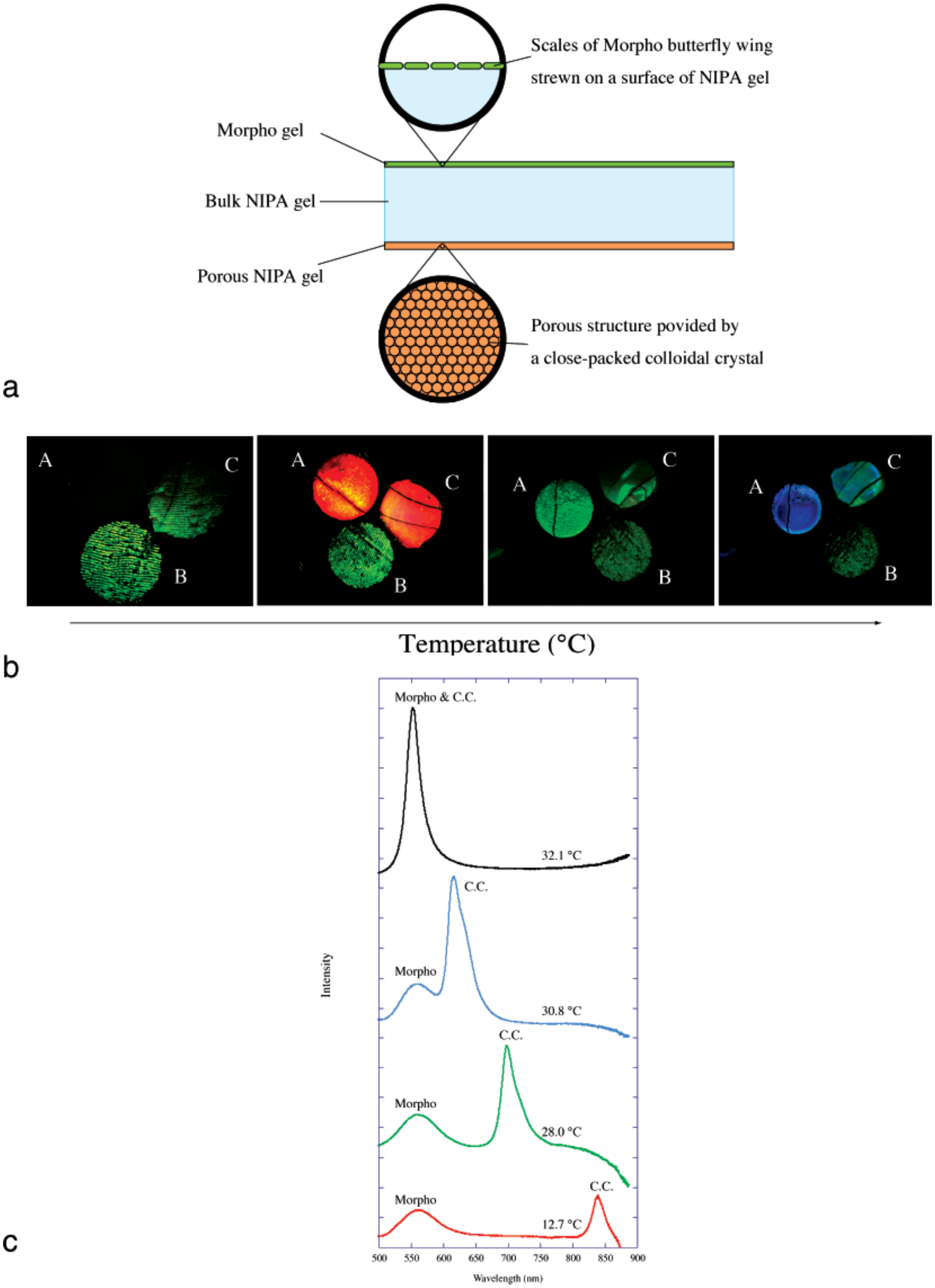

Figure 2. (a) Schematic representation of the cross section of the biform structural colored gel. (b) Photographs of (A) the porous NIPA gel, (B) the morpho gel, and (C) the biform structural colored gel at various temperatures. (c) Reflection spectra of the biform structural colored gel at various temperatures.

wavelength in a given situation $\lambda_{\max}$, and in the reference state, $\lambda_{\max,0}$:

$$\lambda_{\max}/\lambda_{\max,0} \sim \alpha \tag{11}$$

De Gennes's scaling theory explains that gels and semidilute polymer solutions are equivalent except in terms of the lifetime of the contact points.[34] Consequently, the linear expansion factor can be represented by

$$\alpha = R/R_0 \tag{12}$$

where R is the radius of gyration of a subchain of polymer networks in a given condition, and R_0 is the same radius in a Θ condition. R_0 can be defined as

$$R_0 = N^{1/2}b \tag{13}$$

where N is the total number of segments and b is the effective segment length contained in the subchain.[27] Here, b is expressed as $b = ma$, where m is the number of monomers involved in the effective segment length and a is the length of the monomer. For a stiff polymer chain such as NIPA polymer we expect b

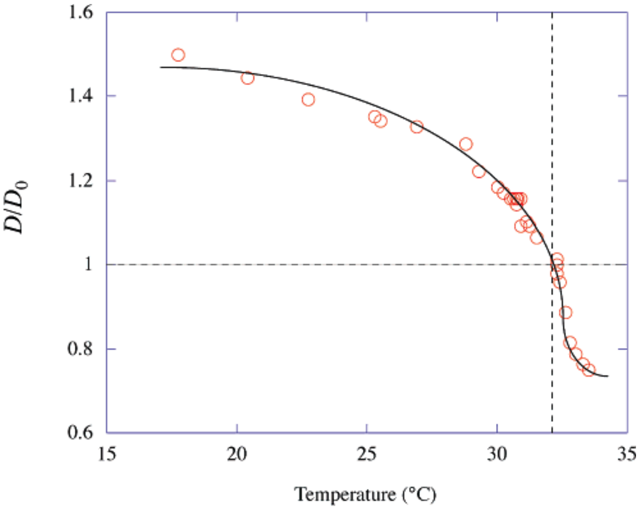

Figure 3. Degree of swelling of the cylindrical NIPA gel in water plotted as a function of temperature. The line is drawn as guide for the eye.

$> a$.[35] The value of b was approximately 3 nm for NIPA polymer chain.[36] As the length of NIPA monomer can be predicted to be around a few angstroms, the value of m can be predicted to be around 10. If the total number of the rigid segments N can be determined for a target NIPA gel,[32] the radius of gyration of the subchain in a given condition is known; we can make a molecular interpretation relating to the subchain in the NIPA gel just by observing the reflection spectra of the porous gel. It is shown that the conformation of the subchain in the gels can be translated into spectroscopic information.

In the present study, we used the wing of a morpho butterfly to observe the reference value of the peak maxima $\lambda_{\max,0}$ from the structural colored gel at the given conditions. The wing of the male didius morpho butterfly shows a metallic blue structural color caused by the complex microscopic structure of tiny scales that cover the upper side of the wing.[37−39] The size of the scale is about 200 μm long and 70 μm wide. The scales overlap like roof tiles and completely cover the wing. Its coloration hardly changes with the viewing angle, as it is due to normal organic pigments rather than to the physical structure. The scales can be strewn on the surface of NIPA gel; hereinafter the NIPA gel with the scales strewn on the surface is known as the "morpho gel". The morpho gel diffracts visible light at 565 nm at any temperature, irrespective of the swelling degree of the gel (Figure 1b). If we can obtain a gel that displays the properties of both the porous structure and the scales of the male didius morpho butterfly and that exhibits the peak wavelength from the porous portion corresponding with that from the scales at the preparative state, the linear expansion factor α of the subchains in the gel can be estimated by a direct comparison of the positions of the two peaks.

Here, we explain the methodology for the preparation of the biform structural colored gel. Judging from eq 1, the diameter of the colloidal particles used (d), the swelling degree of the gel (D/D_0) and the average refractive index (n_a) must be considered in order to obtain the desired value of $\lambda_{\max}$. The size of the colloidal particle can be precisely chosen in advance for the preparation of the porous gel. The target swelling degree, here, is unity. As the change in n_a for the porous gel is a negligible factor coming from the change in the swelling degree, the constant value of n_a can be used to estimate the value of $\lambda_{\max}$. We used the value 1.34 as the average refractive index of the porous gel.[26] Hence, we require colloidal particles of 258 nm in diameter are required to fabricate the desired system. In this experiment, we used SiO_2 particles of 260 nm in diameter. The preparation procedure of the gel was explained in the experimental part. The schematic representation of the cross section of the biform structural colored gel is shown in Figure 2a.

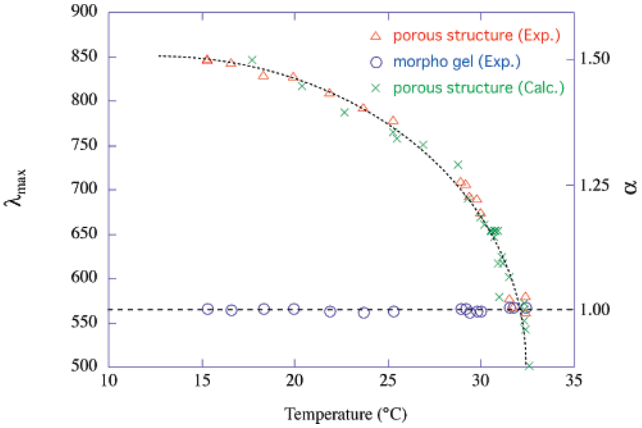

Figure 4. Values of $\lambda_{\max}$ of the reflection spectra and α of the subchains for the biform structural colored gel in water were plotted as a function of temperature.

Figure 2b shows the photographs of the following structural colored gels: (A) the periodically ordered interconnecting porous NIPA gel; (B) the morpho gel; (C) the biform structural colored gel. The porous gel undergoes a change in color according to the water temperature, whereas the structural color from the morpho gel remains unchanged. The biform structural colored gel displays the combined properties of both gels. Figure 2c shows the reflection spectra of the biform structural colored gel at different temperatures. As the swelling degree of the NIPA gel used becomes unity at 32.1 °C (Figure 3), a single sharp peak is observed at 32.1 °C. Since the peak arising from the porous structure appears and shifts toward the longer wavelength with decreasing temperature, double peaks in the spectra can be observed at temperatures lower than 32.1 °C. The peak values of both peaks are plotted as a function of temperature (Figure 4). The temperature dependence of the calculated values of $\lambda_{\max}$ as determined using the swelling degrees is shown in comparison with the experimental values. It can be seen that the experimental data are in excellent agreement with the calculated values; the presence of the scales in the gel does not affect the free swelling of the gel. The biform structural colored gel by which we can simultaneously observe the varying $\lambda_{\max}$ and the reference value $\lambda_{\max,0}$ provide us with the linear expansion factor α of the subchains in the gel from the ratio between the two peaks. This system can be applied to various stimuli-responsive gels, because it is technically possible to prepare this type of porous gel reflecting 565 nm as $\lambda_{\max}$ at the given conditions by controlling the compositions of monomers and cross-linker in pregel solutions, and the size of colloidal particles.[26]

Conclusions

In conclusion, we have succeeded in fabricating a biform structural colored gel that enables us to observe conformations of the subchains in the gel just by measuring reflection spectra at given circumstances. The quantity of α is referred to as the swelling parameter of subchains in a gel;[35] the experimentally measured value of α will provide information on the solvent qualities depending on both the temperature and the solvent compositions. If the polymer network is composed of molecular recognizable subchains, the presence of target molecules will be reflected in the quantity of α. Moreover, we can detect the presence and the approximate amount of the target molecules with the naked eye through the comparison of the both structural colors. In the future, our newly developed system may be useful in applications such as simplified and rapid biochemical sensors and visible indicators.[40,41]

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Supporting Information Available: Text describing the butterfly used in the experiment and figures showing the schematic procedure used. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Piletsky, S. A.; Piletskaya, E. V.; Panasyuk, T. L.; El'skaya, A. V.; Levi, R.; Karube, I.; Wulff, G. *Macromolecules* **1998**, *31*, 2137.
(2) Haupt, K.; Mosbach, K. *Chem. Rev.* **2000**, *100*, 2495.
(3) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
(4) Liu, Y.; Mills, R. C.; Boncella, J. M.; Schanze, K. S. *Langmuir* **2001**, *17*, 7452.
(5) Bashir, R.; Hilt, J. Z.; Elibol, O.; Gupta, A.; Peppas, N. A. *Appl. Phys. Lett.* **2002**, *81*, 3091.
(6) Nakayama, D.; Takeoka, Y.; Watanabe, M.; Kataoka, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 4197.
(7) Saito, H.; Takeoka, Y.; Watanabe, M. *Chem. Commun.* **2003**, 2126.
(8) Marshall, A. J.; Blyth, J.; Davidson, C. A. B.; Lowe, C. R. *Anal. Chem.* **2003**, *75*, 4423.
(9) Ben-Moshe, M.; Alexeev, V. L.; Asher, S. A. *Anal. Chem.* **2006**, *78*, 5149.
(10) Mao, J.; McShane, M. J. *Adv. Mater.* **2006**, *18*, 2289.
(11) Miyata, T.; Jige, M.; Nakaminami, T.; Uragami, T. *PNAS* **2006**, *103*, 1190.
(12) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379.
(13) Annaka, M.; Tanaka, T. *Nature (London)* **1992**, *355*, 430.
(14) Ohmine, I.; Tanaka, T. *J. Chem. Phys.* **1982**, *77*, 5725.
(15) Kato, E. *J. Chem. Phys.* **1997**, *106*, 3792.
(16) Tanaka, T.; Nishio, I.; Sun, S.-T.; Ueno-Nishio, S. *Science* **1982**, *218*, 467.
(17) Osada, Y.; Okuzaki, H.; Hori, H. *Nature (London)* **1992**, *355*, 242.
(18) Szabo, D.; Szeghy, G.; Zrinyi, M. *Macromolecules* **1998**, *31*, 6541.
(19) Alvarez-Lorenzo, C.; Guney, O.; Oya, T.; Sakai, Y.; Kobayashi, M.; Enoki, T.; Takeoka, Y.; Ishibashi, T.; Kuroda, K.; Tanaka, K.; Wang, G.; Grosberg, A. Y.; Masamune, S.; Tanaka, T. *Macromolecules* **2000**, *33*, 8693.
(20) Yoshida, R.; Uchida, K.; Kaneko, Y.; Sakai, K.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Nature (London)* **1995**, *374*, 240.
(21) Takeoka, Y.; Watanabe, M. *Langmuir* **2002**, *18*, 5977.
(22) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons, New York, 1980.
(23) Takeoka, Y.; Watanabe, M. *Adv. Mater.* **2003**, *15*, 199.
(24) Takeoka, Y.; Watanabe, M. *Langmuir* **2003**, *19*, 9104.
(25) Takeoka, Y.; Watanabe, M. *Langmuir* **2003**, *19*, 9554.
(26) Takeoka, Y.; Seki, T. *Langmuir* **2006**, *22*, 10223.
(27) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(28) Grosberg, A. Y.; Nechaev, S. K. N. *Macromolecules* **1991**, *24*, 2789.
(29) Khokhlov, A. R. *Polymer* **1980**, *21*, 376.
(30) Baker, J. P.; Blanch, H. W.; Prausnitz, J. M. *Polymer* **1995**, *36*, 1061.
(31) Marchetti, M.; Prager, S.; Cussler, E. L. *Macromolecules* **1990**, *23*, 1760.
(32) Hirotsu, S. *J. Chem. Phys.* **1991**, *94* 3949.
(33) Bromberg, L.; Grosberg, A. Y.; Matsuo, E. S.; Suzuki, Y.; Tanaka, T. *J. Chem. Phys.* **1997**, *106*, 2906.
(34) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(35) Grosberg, A. Y.; Khokhlov, A. R. *Statistical Physics of Macromolecules*; AIP Press: Melville, NY, 1994.
(36) Ito, K.; Chuang, J.; Alvarez-Lorenzo, C.; Watanabe, T.; Ando, N.; Grosberg, A. Y. *Prog. Polym. Sci.* **2003**, *28*, 1489−1515.
(37) Tabata, H.; Kumazawa, K.; Funakawa, M.; Takimoto, J.; Akimoto, M. *Opt. Rev.* **1996**, *3*, 139.
(38) Vukusic, P.; Sambles, J. R.; Ghiradella, H. *Photonics Sci. News* **2000**, *6*, 61.
(39) Kinoshita, S.; Yoshioka, S.; Kawagoe, K. *Proc. R. Soc. London B* **2002**, *269*, 1417.
(40) Matsubara, K.; Watanabe, M.; Takeoka, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 1688.
(41) Ueno, K.; Matsubara, K.; Watanabe, M.; Takeoka, Y. *Adv. Mater.*, in press.

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