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Polymer Gels

Photoregulated Wormlike Motion of a Gel**

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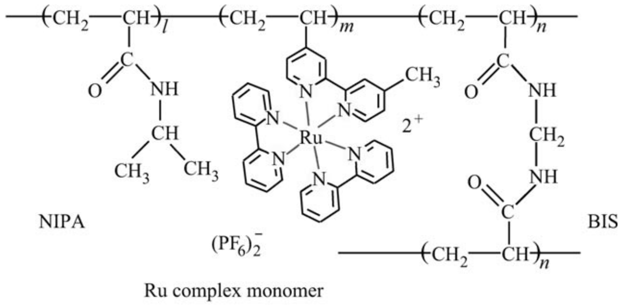
Many approaches to the development of artificial muscle actuators are currently being investigated.[1–11] To address the demand for these applications, many research groups have focused on soft materials capable of deforming their shapes by means of external stimuli such as electric fields and light irradiation. The deformation behavior of established systems, however, was mainly based on isotropic volume change or a bending motion; the movements of existing soft actuators are less complex than those of living organisms. New soft actuators that demonstrate unprecedented lithe motions are being developed so that the technology of biomimetic sensing and robotics can evolve to a high degree at a rapid pace. Herein we show that a self-sustaining peristaltic motion, completely synchronized with a nonlinear oscillatory reaction, is induced in a periodically ordered structured polymer gel with interconnecting pores and can be manipulated using visible light. The wavelike swelling–deswelling change of the porous gel is caused by the periodic redox change of a ruthenium complex, which is chemically bonded to the polymer network (Scheme 1), in the Belousov–Zhabotinsky (BZ) reaction—a well-known oscillating chemical reaction. The amplitude and the period of the peristaltic motion can be controlled by visible light because of the additional production of a BZ reaction inhibitor upon visible light irradiation.



Scheme 1. Chemical structure of the NIPA–Ru-complex polymer network.

The BZ reaction is a nonlinear oscillatory reaction that serves as a classical example of non-equilibrium thermodynamics.[12–19] This reaction is far from equilibrium and continues to oscillate over hours or days. As such, it provides an interesting chemical model of non-equilibrium biological phenomena. Indeed, the chemical traveling waves observed in the BZ reaction are very similar to the electromagnetic traveling waves in muscle tissue. In addition, analogues of this periodic behavior such as heartbeats and circadian rhythms exist in natural systems. Heart rate can be controlled by the concentrations of chemicals such as adrenaline and acetylcholine, which are produced in the bloodstream upon external stimuli. Similarly, in the BZ reaction, the concentrations of chemicals that play key roles in the reaction are also controlled by external stimuli.[14–19]

Although the shape variation of gels composed of *N*-isopropylacrylamide (NIPA), a Ru complex derivative monomer, and a cross-linker (namely poly(NIPA–Ru complex) gels) can be caused by the BZ reaction, the motion of the gel must show striking similarities to the characteristic motion of living organisms. As the Ru complex acts as a catalyst for the BZ reaction, and changes its redox state periodically during the BZ reaction, the polymer network of the gel, in which the Ru complex is embedded, exhibits cyclic expansion–contraction changes because of the change in the osmotic pressure inside the gel.[19–23] As the BZ reaction proceeds, the overall length of a rectangular poly(NIPA–Ru complex) gel (1 mm width, 20 mm length and 0.5 mm thickness) undergoes a cyclic expansion–contraction change.[20,21] However, an "antiphase mode" between the chemical and mechanical oscillations was observed in this system. The phase difference was due to the slow swelling–deswelling response of the gel compared to the cyclic redox changes. As the swelling–deswelling processes of gels are determined by the collective diffusion of the polymer networks in a fluid, which 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 [Eq. (1)],

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

where R is the characteristic length of gels and D_c is the collective diffusion coefficient. The characteristic time period that describes the volume changes is approximately proportional to the square of the characteristic length of the gels. Thus, the response speed can be improved predominantly by two methods—the downsize approach and the introduction of porosity into gels.

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If the whole size of the poly(NIPA–Ru complex) gel is smaller than the wavelength of the chemical wave of the BZ reaction, the redox change occurs homogeneously within the gel without pattern formation, and an in-phase mode coupling between volume and chemical oscillations of the gel is manifested.[21] For example, a tiny cubic (0.5 mm square) poly(NIPA–Ru complex) gel underwent periodic swelling–deswelling oscillations during the BZ reaction; the motion was very similar to the contraction of a single cardiomyocyte.

The incorporation of porosity into the gel (the second approach) is preferable for the development of macroscopic gels for artificial muscle actuators. Outward-moving 2D patterns of two different colors caused by the redox state of Ru complex are readily observed when the BZ reaction is run in a thin layer in a petri dish.[13] Accordingly, when the thickness of the poly(NIPA–Ru complex) gel membrane (Scheme 1) is smaller than the wavelength of the BZ reaction, a self-sustaining peristaltic motion can be produced in the gel (Figure 1). The introduction of the porosity into the thin poly(NIPA–Ru complex) gel membrane is likely to bring a rapid response in the swelling–deswelling oscillation during the BZ reaction. Furthermore, considering Equation (1), it is preferable to incorporate homogeneously dispersed pores into the gel membrane for the preparation of a soft actuator that displays motion. We used a closely packed colloidal silica crystal as a template to obtain the periodically ordered poly(NIPA–Ru complex) gel membrane with an interconnecting porous structure (Figure 2). If the porous gel precisely maintains the fine structure of the precursor colloidal crystal, we can observe the dynamic movement quantitatively through the structural color based on the reflection from the photonic bandgap in the gel (Figure 1).[24–28] The peak wavelength from the photonic bandgap of the porous gel can be estimated by Equation (2),

$$\lambda_{\max} = 1.633(d/m)(D/D_0)n_a \quad (2)$$

where d is the diameter of the colloidal particles used, m is the order of the Bragg reflection, D and D_0 are the characteristic sizes of the gel in the equilibrium state at a certain condition and in the preparative state, respectively, and n_a is the average refractive index of the porous gel. Hence, D/D_0 is defined as the degree of equilibrium swelling 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

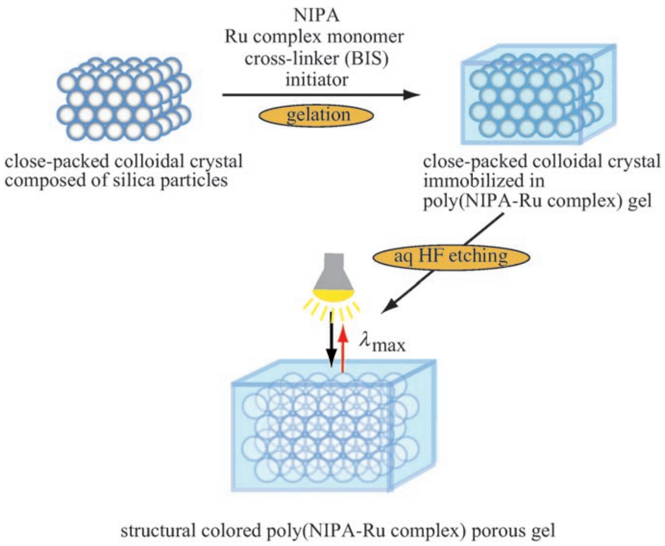

Figure 2. Preparation of a periodically ordered interconnecting porous poly(NIPA–Ru complex) gel using a closest-packing colloidal silica crystal as a template.

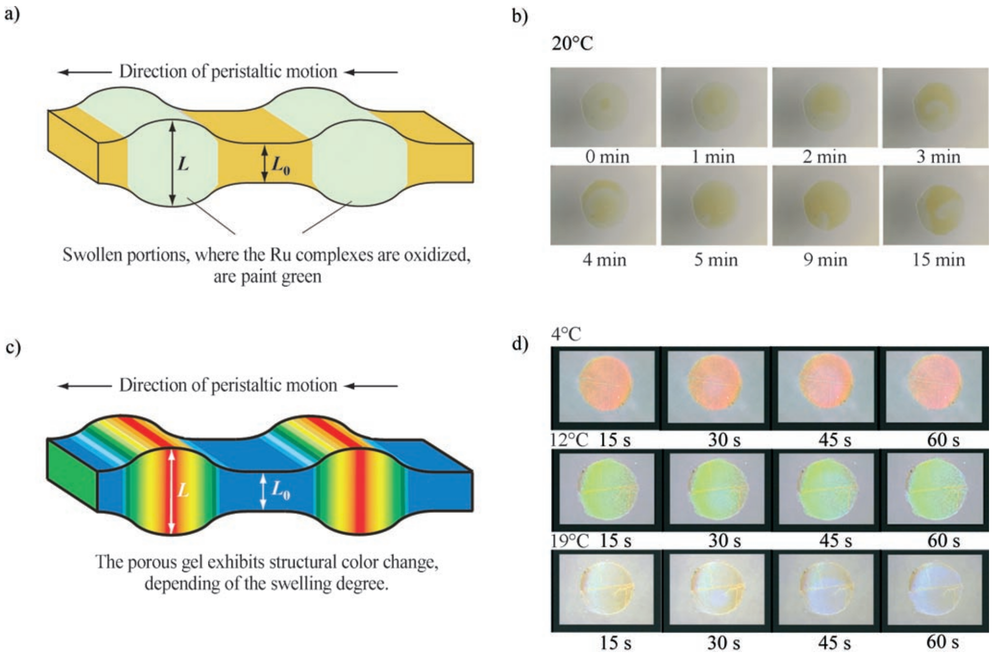

Figure 1. Models and pictures of peristaltic motion of the surface of poly(NIPA–Ru complex) gel membranes. a) and b) Spatiotemporal color patterns of oscillating behavior for a rectangular (a: model) and a disk (b: pictures) bulk poly(NIPA–Ru complex) gel can be observed because of the difference in color between the reduced state and the oxidized state of the Ru complex (see below). c) and d) Spatiotemporal structural color changes of a rectangular-shaped (c: model) and a disk (d: pictures) porous poly (NIPA–Ru complex) gel during the BZ reaction shows that the gel moves like an earthworm. The pictures show the time change in the pigment color of the bulk gel and the structural color of the porous gel during the BZ reaction at several temperatures. Both disk-shaped gels (4 mm diameter and 0.5 mm thickness) were immersed in an aqueous solution (20 mL) containing malonic acid (0.0625 M), sodium bromate (0.084 M), and nitric acid (0.890 M) in a temperature-controlled glass cell. Because the thickness of the gel is smaller than the wavelength of the chemical wave, a 2D pattern of the concentric chemical waves was produced in the gels.

portion [Eq. (3)]:

$$n_{\mathrm{a}}^2 = \Sigma n_i^2 \phi_i \tag{3}$$

where ϕ_i is the volume fraction of each portion (i). For the closely packed structure, ϕ of the sphere portion is 0.74. According to these equations, the changes in the average refractive index that occur upon changes in swelling must be evaluated in order to calculate the theoretical value of λ_{max} of the porous gel in a certain environment, because these parameters seem to be independent. It is important to note, however, that the change in the equilibrium swelling degree of the gel can be up to a factor of ten, while the change in n_{a} for the inverse opal-type periodical porous gel was found to be vanishingly small when the volume undergoes drastic changes; the value of n_{a} can therefore be treated as a constant under varying degrees of D/D_0. Thus, the value of D/D_0 during the BZ reaction can be estimated by using the spectroscopically observed value of λ_{max}. It follows that the variable thickness L of the gel membrane can be calculated by using the spatiotemporally determined value of λ_{max}, the preparative thickness L_0 of the gel membrane, the diameter d of the colloidal particles used, and the invariable average refractive index n_{a} of the porous gel according to Equation (4):

$$L = L_0(D/D_0) = L_0\, m\lambda_{\mathrm{max}}/1.633\, d\, n_{\mathrm{a}} \tag{4}$$

Figure 3a shows the absorption spectra of the bulk gel membrane with the oxidized and the reduced Ru complexes. The peak at 460 nm in the absorption spectra arises from the metal–ligand charge-transfer transition in the reduced form of the Ru complex. A new absorption band at 670 nm appeared in the UV/Vis spectra of the oxidized Ru complex, while the absorbance at 460 nm was dramatically decreased compared to that of the reduced state. As the reduced and the oxidized Ru complexes exhibit different UV/Vis spectra, the oscillating redox reaction could easily be followed spectrophotometrically. The oscillatory redox reaction during the BZ reaction was observed by measuring the optical transmittance of light at 670 nm. The time variation of the structural color during the BZ reaction was observed by reflectance spectrophotometry of a rectangular piece of the porous gel membrane (Figure 3b). To record the spectra, a reflection probe was fixed in a determined position above the porous gel. A periodic swinging of the reflection spectra was observed during the BZ reaction, which indicates that the swollen portions of the gel pass by the probe in regular sequence.

As the value of λ_{max} can be related to the thickness L of the gel by Equation (4), the temporal change in the thickness of the gel can be observed spectrophotometrically. Figure 4 shows the periodic changes in the thickness of the gel

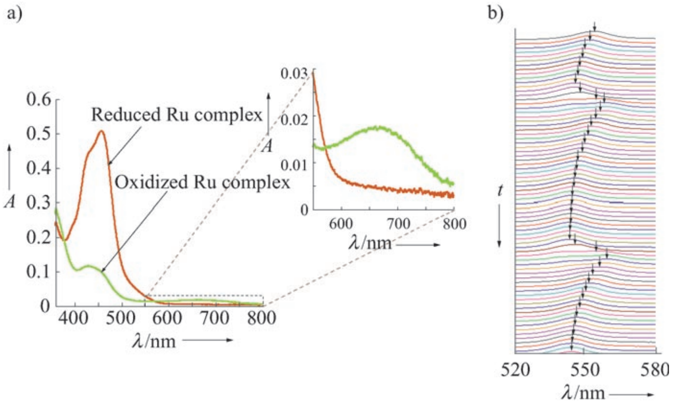

Figure 3. Characteristic optical properties of bulk-type and porous-structured poly(NIPA–Ru complex) gels. a) UV/Vis spectra of Ru(III) (oxidized state, aqueous solution of $Ce(SO_4)_2$ (5 mM) of HNO_3 (916 mM)) and Ru(II) (reduced state, aqueous solution of $Ce_2(SO_4)_3$ (5 mM) and of HNO_3 (906 mM)) of bulk poly(NIPA–Ru complex) gel membrane. The thickness of the gel membrane was ca. 0.5 mm. b) Changes in the reflection spectra of the porous poly(NIPA–Ru complex) gel membrane were monitored during the BZ reaction. The porous gel was immersed in an aqueous solution (20 mL) containing malonic acid (0.0625 M), sodium bromate (0.042 M), and nitric acid (0.890 M) in a temperature-controlled container at 13 °C. Each arrow shows the position of λ_{max} in the reflection spectra.

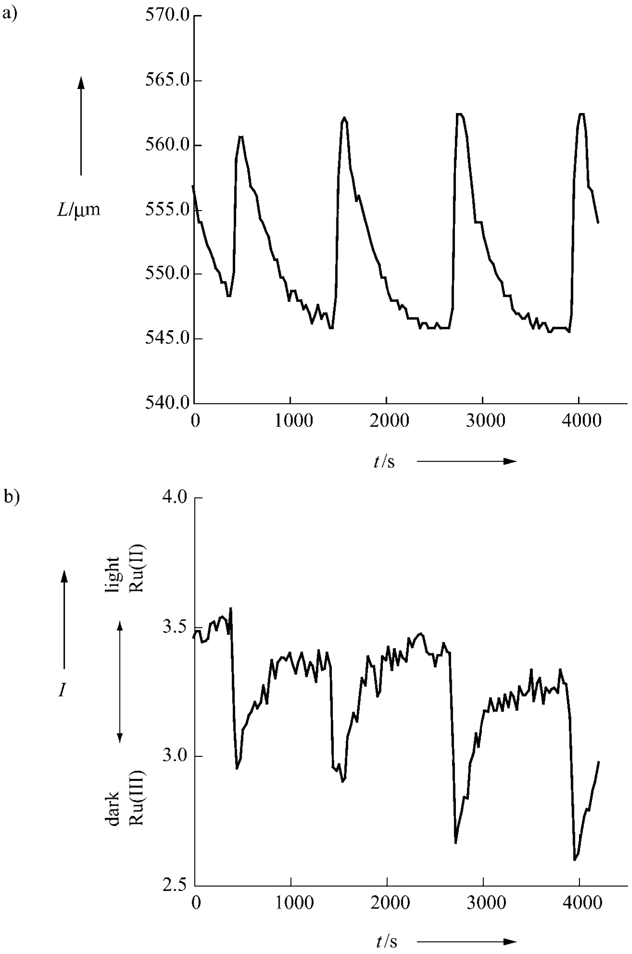

Figure 4. Oscillating behavior of the structural colored porous gel membrane, synchronized with the BZ reaction. a) Time change of the thickness of the porous gel membrane during the BZ reaction at 13 °C. A rectangular piece of the porous gel membrane was immersed in the reaction solution (20 mL) in a temperature-controlled glass cell. The initial compositions of the reaction solution were $[NaBrO_3] = 0.042$ M, [malonic acid] = 0.0625 M, and $[HNO_3] = 0.890$ M. The periodic change in L was estimated using the value of λ_{max} observed from the porous gel membrane. b) The intensity of transmissive weak light through the porous gel membrane with time was observed at 13 °C.

membrane and in the optical transmittance of light at 670 nm from the porous gel at 13 °C during the BZ reaction. The mechanical oscillation of the gel autonomously occurs with the same period as that of the redox oscillations—the chemical and mechanical oscillations are synchronized without a phase difference. The periodically ordered structure with interconnecting pores induces a rapid change in the volume as well as a chromic phenomenon based on the reflection from the photonic bandgap in the gel. As a result, the wavelike swelling–deswelling change of the porous gel was caused by the BZ reaction without a phase difference, and the change in the thickness of the porous gel could be observed both by eye (Figure 1 d) and spectroscopically (Figure 3 b). We found that the maximum wave height of the peristaltic motion of the gel membrane caused by the BZ reaction was about 16 μm. As the thickness of the porous gel was smaller than the wavelength of the chemical wave of the BZ reaction, a 2D pattern of the spatiotemporal BZ reaction was produced in the gel; a self-sustaining peristaltic motion of the gel coupled with the BZ reaction could be quantitatively observed.

Similar to non-equilibrium biological phenomena, the perturbation of the oscillatory chemical reaction can be provoked by external stimuli. The BZ reaction, which incorporates the Ru complex as a catalyst, is particularly interesting because of its unusual and complex photochemical properties. Illumination with visible light produces bromide ions, which can act as inhibitors of the oscillatory chemical reaction, which itself occurs by photochemical reaction of the Ru complex. The effective rate of bromide ion production is readily controlled by selecting the wavelength and/or the intensity of the exciting light. Hence, the self-sustaining peristaltic motion of the poly(NIPA–Ru complex) gel coupled with the ruthenium-complex-catalyzed BZ reaction can be manipulated by light irradiation.

Figure 5 a shows the effect of light irradiation on the self-sustaining peristaltic motion of the porous gel at 13 °C. As light absorption by the reduced form of the Ru complex, rather than the oxidized form, is a primary step in the oscillating reaction, the gel was illuminated at 436 nm. The amplitude and the periodicity of the peristaltic motion decreased as the intensity of the light increased. The peristaltic motion could be stopped completely at a sufficiently high light intensity (6.45 mW). Once irradiation was stopped, the periodical motion quickly recovered entirely. Figure 5 b shows the on–off photoregulation of self-sustaining peristaltic motion on the surface of the porous gel at 13 °C. Thus, an on–off system of light-induced pumping action can be developed by using the present system.

We have shown that the amplitude and the period of the ruthenium-complex-catalyzed BZ system can be controlled by visible light. Using this phenomenon, the in-phase self-sustaining peristaltic motion on the porous gel can also be influenced by visible light irradiation. This photoregulative peristaltic motion might be useful in developing new micromachines capable of imitating biological functions, future lab-on-a-chip systems,[29,30] and functional surfaces that transport fluids. Research into the use of this system with lab-on-a-chip systems and microactuators is currently underway.

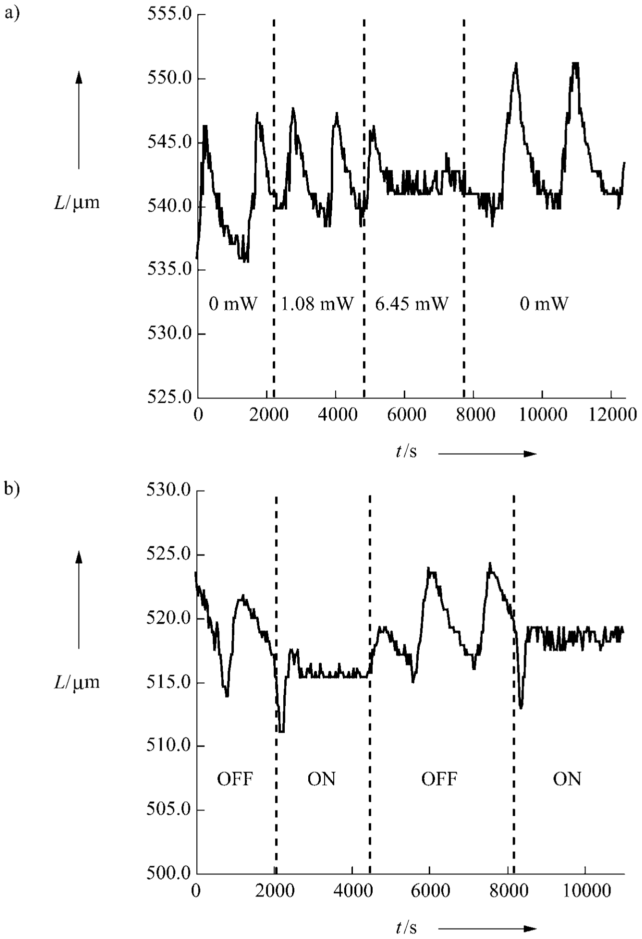

Figure 5. Effect of light irradiation on the peristaltic motion of the porous gel membrane generated by the BZ reaction. a) Effect of light intensity on the peristaltic motion. b) On–off switching of the peristaltic motion. The light intensity was 6.45 mW. The initial compositions of the reaction solution were [$NaBrO_3$] = 0.028 M, [malonic acid] = 0.0625 M, and [HNO_3] = 0.890 M.

Experimental Section

Colloidal crystal preparation: A thick colloidal crystal was prepared by a solvent evaporation method using a silica colloidal suspension in water that was relatively concentrated compared to those used in earlier methods.[27] The diameter of the colloidal silica particles was 230 nm. The silica colloidal suspension (20 wt %) was spread onto a surface-cleaned glass slide, which was placed in a thermostatic chamber at 90 °C. Water was gradually evaporated over 6 h. A high-quality colloidal crystal with a thickness of about 0.5 mm was obtained.

Gel preparation: A solution of NIPA (1.56 g), (4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine) bis-(hexafluorophosphate) ([Ru(vm-bpy)(bpy)$_2$](PF$_6$)$_2$, Ru complex monomer, 0.082 g), and BIS (0.084 g) in methanol (10 mL) was infiltrated into the colloidal crystal in a flat glass cell created from two glass plates and a teflon spacer attached with teflon grease (Daikin Industries, Ltd.). The thickness of the teflon spacer was about 0.5 mm. The polymerization was conducted at 60 °C for 18 h. Afterwards, the sample was immersed in HF (5 wt % aqueous solution) to remove the silica component. The resulting gel was washed in water to remove unreacted chemicals and HF from the polymer network, to leave the porous gel membrane.

Measurements: UV/Vis and reflection spectra of the bulk gel and the porous gel were obtained using an Ocean Optics USB2000 fiber optic spectrometer with a low-power light source. All spectra were recorded at a normal incidence to the plane of the samples. The intensity of transmitted light through the porous gel during the BZ reaction was monitored by an optical power meter (ADVANTEST TQ8210). Photoirradiation was performed with a Xe–Hg lamp (SAN-EI Electric, SuperCure-203S) through color glass filters, bandpass filter, and an IR cut filter. Photographs of the gels were taken using a digital microscope (KEYENCE VHX-500). The temperature of all measurements was controlled by using a circulating water temperature control system.

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[1] J. Livage, *Nat. Mater.* **2003**, *2*, 297–299.
[2] Y. Osada, *Adv. Mater.* **1991**, *3*, 107–108.
[3] Z. Liu, P. Calvert, *Adv. Mater.* **2000**, *12*, 288–291.
[4] R. Pelrine, R. Kornbluh, Q. Pei, J. Joseph, *Science* **2000**, *287*, 836–839.
[5] W. Lu, A. G. Fadeev, B. Qi, E. Smela, B. R. Mattes, J. Ding, G. M. Spinks, J. Mazurkiewicz, D. Zhou, G. G. Wallace, D. MacFarlane, S. A. Forsyth, M. Forsyth, *Science* **2002**, *297*, 983–987.
[6] T. Fukushima, K. Asaka, A. Kosaka, T. Aida, *Angew. Chem.* **2005**, *117*, 2462–2465; *Angew. Chem. Int. Ed.* **2005**, *44*, 2410–2413.
[7] Y. Yu, T. Ikeda, *Angew. Chem.* **2006**, *118*, 5542–5544; *Angew. Chem. Int. Ed.* **2006**, *45*, 5416–5418.
[8] A. Sidorenko, T. Krupenkin, A. Taylor, P. Fratzl, J. Aizenberg, *Science* **2007**, *315*, 487–490.
[9] H. Finkelmann, E. Nishikawa, *Phys. Rev. Lett.* **2001**, *87*, 015501.
[10] S. J. Kim, G. M. Spinks, S. Prosser, P. G. Whitten, G. G. Wallace, S. I. Kim, *Nat. Mater.* **2006**, *5*, 48–51.
[11] S. Hara, T. Zama, S. Sewa, W. Takashima, K. Kaneto, *Chem. Lett.* **2003**, *32*, 576–577.
[12] R. J. Field, I. Koros, R. M. Noyes, *J. Am. Chem. Soc.* **1972**, *94*, 8649–8664.
[13] A. N. Zaikin, A. M. Zhabotinsky, *Biological and Biochemical Oscillators* (Eds.: B. Chance, E. K. Pye, A. K. Ghosh, B. Hess), Academic Press, New York, **1973**.
[14] L. Kuhnert, *Nature* **1986**, *319*, 393–394.
[15] M. Jinguji, M. Ishihara, T. Nakazawa, *J. Phys. Chem.* **1992**, *96*, 4279–4281.
[16] S. Kádár, T. Amemiya, K. Showalter, *J. Phys. Chem. A* **1997**, *101*, 8200–8206.
[17] P. K. Srivastava, Y. Mori, I. Hanazaki, *Chem. Phys. Lett.* **1991**, *177*, 213–218.
[18] K. Agladze, R. R. Aliev, T. Yamaguchi, K. Yoshikawa, *J. Phys. Chem.* **1996**, *100*, 13895–13897.
[19] J. Wang, *Chem. Phys. Lett.* **2001**, *335*, 123–126.
[20] R. Yoshida, T. Takahashi, T. Yamaguchi, H. Ichijo, *J. Am. Chem. Soc.* **1996**, *118*, 5134–5135.
[21] R. Yoshida, M. Tanaka, S. Onodera, T. Yamaguchi, E. Kokufuta, *J. Phys. Chem. A* **2000**, *104*, 7549–7555.
[22] R. Yoshida, E. Kokufuta, T. Yamaguchi, *CHAOS* **1999**, *9*, 260–266.
[23] S. Maeda, Y. Hara, T. Sakai, R. Yoshida, S. Hashimoto, *Adv. Mater.* **2007**, *19*, 3480–3484.
[24] Y. Takeoka, M. Watanabe, *Langmuir* **2002**, *18*, 5977–5980.
[25] Y. Takeoka, M. Watanabe, *Langmuir* **2003**, *19*, 9104–9106.
[26] Y. Takeoka, M. Watanabe, R. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 13320–13321.
[27] Y. Takeoka, T. Seki, *Langmuir* **2006**, *22*, 10223–10232.
[28] K. Matsubara, M. Watanabe, Y. Takeoka, *Angew. Chem.* **2007**, *119*, 1718; *Angew. Chem. Int. Ed.* **2007**, *46*, 1688–1692.
[29] D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, *Nature* **2000**, *404*, 588–590.
[30] D. J. Beebe, J. S. Moore, Q. Yu, R. H. Liu, M. L. Kraft, B.-H. Jo, C. Devadoss, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 13488–13493.