

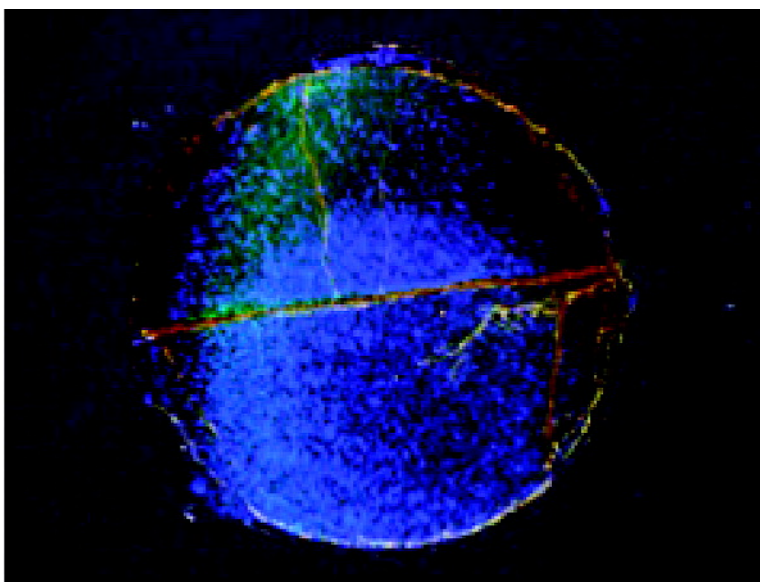
Communication

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## Self-Sustaining Peristaltic Motion on the Surface of a Porous Gel

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All living things reveal self-sustained oscillations of chemical and physical organizations for the maintenance of life. Some purely nonliving systems also exhibit analogous self-sustained oscillations through activator-inhibitor dynamics in a flask. The Belousov–Zhabotinsky (BZ) reaction is a well-known coupled-oscillator dissipative system that generates spatiotemporal dynamic patterns.<sup>1,2</sup> The BZ reaction in a thin layer of unstirred solutions is a prime example involving moving oscillating chemical waves.<sup>1a,b</sup> Concentric or spiral patterns of orange and faint green can be observed in the system containing a Ru-complex. The orange is due to the preponderance of the reduced state of the Ru-complex ion, while the faint green state is due to its oxidized state. This color variation is available to observe the appearance of the propagating BZ reaction.

Artificial materials exhibiting self-sustained oscillations coupled with the BZ reaction have been extensively studied during the past decades. These materials can change their periodic vibration depending on their environment, reacting to such factors as temperature,<sup>1c</sup> electric current,<sup>1d</sup> and light,<sup>1e</sup> and can recover their periodicity automatically. It is expected that these materials can alter their physical properties, including surface tension<sup>1f</sup> and volume,<sup>2</sup> during their oscillations. Such materials have been required in the development of a pulse generator, mechanical heart, and autonomous actuators. Because the BZ reaction involves the cyclic redox reaction, a gel membrane having a Ru-complex monomer spontaneously exhibits a cyclic swelling–deswelling change in a closed system under constant conditions requiring no external stimuli. Yoshida et al. demonstrated this phenomenon by measuring the change in the overall length of a rectangular gel membrane during the spatiotemporal BZ reaction.<sup>2</sup> This volume change is attributed to the variation in the inside osmotic pressure of the gel and to the hydrophilicity of the Ru-complex due to the change in the charge of the Ru-complex.<sup>3</sup> However, it was difficult to observe the mechanical oscillation on the surface of the gel, synchronized with the spatiotemporal patterns of the BZ reaction. In this paper, we present how to observe the self-sustained peristaltic motion on the surface of a gel membrane, which can be useful for the creation of actuators and self-cleaning surfaces.

The polymer network of the gel consists of two species of monomers, each playing a different role. The majority monomer, *N*-isopropylacrylamide (NIPA), controls network expansion and makes the gel reversibly swell and collapse in response to temperature. The minority monomer, a Ru-complex monomer, catalyzes the BZ reaction. In this study, we prepared a periodically ordered mesoporous gel which reveals “structural color” depending on its swelling ratio.<sup>4a–d</sup> To obtain the gel, we used as a template the closest-packing colloidal crystal composed of silica sphere particles 210 nm in diameter. Details of the growth of the crystal

have already been reported elsewhere.<sup>4b</sup> The gel was prepared by free-radical polymerization as follows: First, NIPA (0.1560 g), ruthenium (4-vinyl-4'-methyl-2,2'-bipyridine)bis(2,2'-bipyridine)bis(hexafluorophosphate)(Ru(vm-bpy)(bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>) (0.0082 g), *N,N'*-methylene-bis-acrylamide as a cross-linker (0.0084 g), and *N,N'*-azobis(isobutyronitrile), the initiator (0.0066 g), were dissolved in 1 mL of degassed and nitrogen-saturated ethanol. The solution was then infiltrated into the colloidal crystal in a small Petri dish, and the polymerization was conducted at 60 °C for 18 h. Afterward, the sample was immersed in a 5 wt % HF aqueous solution to remove the SiO<sub>2</sub> component. The resulting porous gel was washed carefully with distilled water for 1 week.

The change of the structural color of the porous gel depending on temperature and oscillating reaction was photographed by a digital microscope (Keyence, VH-8000) and digital video (Sony, DCR-PC110). The reflection spectra were obtained using an Ocean Optics USB2000 fiber optic spectrometer. The temperature in the measurements was controlled by means of a circulating water temperature control system.

The porous gel obtained exhibits a bright color under white light and undergoes fast and drastic changes in color in response to water temperature. The color is caused by the Bragg diffraction of visible light from the ordered voids regarded as crystallites. Because this coloring is due primarily to the structures formed in the crystal-like structure, we call it “structural color”. The peak values of the reflection spectra,  $\lambda_{\max}$ , for the porous gel are obtained by:<sup>4,5</sup>

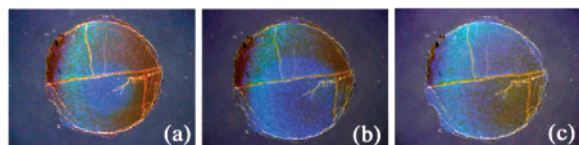
$$\lambda_{\max} = 1.633(d/m)(D/D_0)(n_a^2 - \sin^2 \theta)^{1/2} \quad (1)$$

where  $d$  is the diameter of a colloidal particle,  $m$  is the order of Bragg diffraction,  $D/D_0$  is the equilibrium swelling degree of the gel ( $D$  and  $D_0$  are diameters of the gel in the equilibrium state at a certain condition and in the reference state, respectively),  $n_a$  is the refractive index of the porous gel at a certain condition, and  $\theta$  is the angle measured from the normal to the plane of the gel. Although the change in  $n_a$  for the thermosensitive porous gel composed of NIPA is only 0.3% when the temperature is changed from 15 to 60 °C, the swelling ratio changes on the order of about a few times. Therefore, the swelling ratio is dominant over  $\lambda_{\max}$  of the observed reflection spectrum for the porous NIPA gel, when  $d$  and  $\theta$  are known. The templated periodical porous structure in the gel can reversibly change its spacing in response to temperature changes in impacting the volume of the gels and will signal these changes through iridescence. The structural color is visible even when the structural color overlaps with the pigmented color of the Ru-complex.

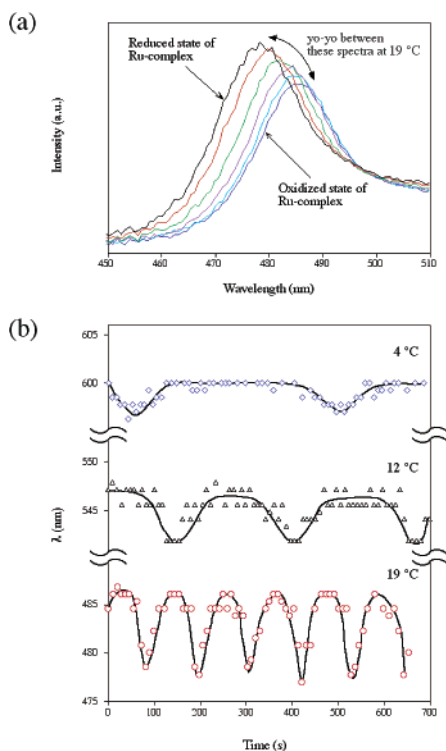
Considering these results, we are able to expect that the self-sustained peristaltic motion on the surface of a gel can be observed through the change in the structural color during the BZ reaction. To demonstrate this oscillating change in the structural color, the porous disk-shaped gel was immersed in a reaction solution

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**Figure 1.** Time change in structural color during the BZ reaction in a porous poly(NIPA-co-Ru(bpy)<sub>3</sub>) gel at 19 °C. The porous disk-shaped gel, which was 4 mm in diameter and 0.5 mm in thickness, was immersed in 20 mL of an aqueous solution containing malonic acid (0.0625 M), sodium bromate (0.084 M), and nitric acid (0.890 M) in a temperature-controlled glass cell: (a) 15 s, (b) 30 s, (c) 45 s, after the blue portion appeared in the center of the gel. 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 gel.



**Figure 2.** (a) Change in reflection spectra was monitored during the BZ reaction. (b) Periodical  $\lambda_{\max}$  changes of the reflection spectra from the porous gel at several temperatures.

containing nitric acid, malonic acid, and sodium bromate at certain temperatures. The gel revealed an orange-tinged color when the Ru-complex is in a reduced state at 19 °C in the reaction solution. Because the swelling ratio of the gel became smaller in the reaction solution than that in water at the same temperature, the structural color of the gel shifted into the ultraviolet region.

Concentric brilliant blue rings caused by the swelling of the gel due to the oxidation of the Ru-complex spread out from the center with the BZ reaction can be observed on the surface of the gel (Figure 1).<sup>6</sup> The period of the oscillation is about 2 min, and the waves propagate with a velocity of approximately 0.05 mm/s at 19 °C. The faint red structural colored concentric rings are developed and spread out on the porous gel at 4 °C, whereas the green concentric waves which are also indistinct from the surrounding color were observed at 12 °C. Although the change in the swelling ratio is relatively small during the BZ reaction, this observed phenomenon indicates that the swollen portion moves on the surface of the gel. The change in the reflection spectra during the BZ reaction was monitored at several temperatures. A reflection

probe to observe the spectra was fixed in the prescribed position above the porous gel. A periodically swinging of the reflection spectra was observed during the BZ reaction (Figure 2a). Figure 2b demonstrates the periodic changes in the peak values of the reflection spectra for the porous gel at 4, 12, and 19 °C, respectively. The change in the vibrational amplitude became more pronounced as the solution temperature was increased. This result explains why the structural colored concentric rings caused by the BZ reaction are faint at lower temperature. As the temperature decreases, the period of the oscillation lengthens (Figure 2b). It is a general tendency that the oscillation period of the BZ reaction increases as the temperature increases, following the Arrhenius equation.

This change in structural color with the chemical waves indicates a peristaltic motion, resembling intestinal motility and the motion of an earthworm, occurring on the surface of the gel. This is the first evidence that a self-sustaining peristaltic motion of a gel coupled with the BZ reaction. This peristaltic motion can be useful in developing new micromachines capable of imitating biological functions, such as self-beating/locomotion actuators. We intend to fabricate the artificial materials which reveal peristaltic locomotion and enhance fluid stirring, based on propagating waves on the moving surface of the device. Furthermore, our results demonstrate a clear example of the dynamic conversion of a chemical reaction to an optical signal through a gel membrane. The signal from the gel can be easily tuned by adjusting temperature. Because we can prepare gels whose optical properties can be precisely tuned by the recipe for the gel synthesis,<sup>4c</sup> it is technically possible to obtain gel membranes generating a specific colored signal at a certain temperature. These gels have a potential for use in the displays of devices intended to search for invisible oscillations and spatial pattern formations in nonlinear chemical reactions.

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**Supporting Information Available:** Experimental details for the preparation and the chemical structure of the gel (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) Spontaneous initiation of the waves tends to appear from the corner at the end of a rectangular gel having the Ru-complex because the oscillation takes place earliest there after the gel is soaked into the solution. However, the waves do not always appear from the corner and the edge of the gel. Any heterogeneous portion in the gel can be the start point of the BZ reaction.

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