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Self-Oscillation Mechanism of Hydrogel Coupled with Chemical Oscillations

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SUMMARY: A novel gel which undergoes an autonomic and periodical swelling-deswelling oscillation has been prepared by the copolymerization of N-isopropylacrylamide (NIPAAm) with ruthenium tris(2,2'-bipyridine) ($Ru(bpy)_3$) as a catalyst for the Belousov-Zhabotinsky (BZ) reaction. In order to enhance the amplitude of swelling-deswelling oscillations of the gel, we attempted to change the period and amplitude of the redox oscillation by varying the initial concentration of substrates of the BZ reaction. Both period and amplitude of chemical oscillation varied depending on the substrate concentration. This variation led to a change in the swelling-deswelling oscillation: i.e., the swelling-deswelling amplitude increased with an increase in the period and amplitude of the redox changes. The change in gel size with ca. 20% to the initial size was obtained as the maximum value. The swelling-deswelling amplitude of the gel is controllable by changing the initial concentration of substrates or the content of immobilized $Ru(bpy)_3$ catalyst within the gel.

Introduction

Many kinds of stimuli responsive gels have been extensively investigated and their ability to swell and deswell according to conditions makes them an interesting proposition for use in intelligent biomaterials. In contrast to these conventional stimuli-responsive gels, we developed a novel "self-oscillating" gel that undergoes an autonomic and periodical swelling-deswelling oscillation without reliance on an alteration in external conditions [1,2]. The mechanical oscillation in our gel system was produced via the Belousov-Zhabotinsky (BZ) reaction [3,4] that spontaneously generates rhythmical changes through its redox potential. We prepared gels composed of crosslinked N-isopropylacrylamide (NIPAAm) chain to which ruthenium tris(2,2'-bipyridine) ($Ru(bpy)_3$), as a catalyst for the BZ reaction, was covalently bonded. The BZ reaction occurring within the gel phase generates periodic redox changes of

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the catalyst moiety. Poly(NIPAAm) gel undergoes an abrupt volume-collapse when heated at around 32 °C. The oxidation of the $Ru(bpy)_3$ moiety caused not only an increase in the swelling degree, but also a rise in the transition temperature (T_v). Therefore, under constant temperature below T_v of oxidized state, the chemical oscillation is converted into the mechanical oscillation of the polymer network through the change in hydrophilicity of polymer chains with the cationic changes. As a result, the poly(NIPAAm-co-$Ru(bpy)_3$) gel underwent a periodical swelling-deswelling change.

For applications to new functional materials, it would be necessary to generate remarkable and powerful swelling-deswelling oscillations in gel volume. These considerations have lead to our present attempt to enhance swelling-deswelling amplitude of the gel through studies on the conditions of the BZ reaction. In this study, we varied the initial concentration of substrates to change the period and amplitude of redox oscillations in the BZ reaction. Effects of the concentration variations on the resulting swelling-deswelling oscillations were investigated through a comparison of oscillating behaviors between chemical and mechanical oscillations. Synchronization of chemical and mechanical oscillations in self-oscillating gels was discussed.

Experimental

Poly(NIPAAm-co-$Ru(bpy)_3$) gel was prepared in the same manner as used in the previous studies [1, 2)]. The gel membrane was cut into a miniature cube (each side lengths is about 0.5 mm); the cutting was then immersed into 1 ml of an aqueous solution containing malonic acid (MA), sodium bromate ($NaBrO_3$), and nitric acid (HNO_3) maintained at 20°C. The swelling-deswelling oscillations of the gel accompanying the redox oscillations were observed under a microscope equipped with a black-white CCD camera and a video. The swelling-deswelling profiles as a function of time was expressed as a track of the moving gel edge. The time-dependent change in the oxidized fraction of $Ru(bpy)_3$ at a fixed position of the gel was expressed as 8-bit grayscale changes by the image processing method.

Results and Discussion

In the miniature gel whose size is smaller enough than the wavelength of chemical wave (several mm under present conditions), the redox change of ruthenium catalyst can be regarded to occur homogeneously without pattern formation. The swelling-deswelling cycle of a miniature cubic poly(NIPAAm-co-Ru(bpy)$_3$) gel (each side length is ca. 500μm) was found to be synchronized with the chemical oscillation without a phase difference (Fig.1).

In order to enhance the amplitude of swelling-deswelling oscillations of the gel, we attempted to change the period and amplitude of the redox oscillation by varying the initial concentration of substrates of the BZ reaction. The oscillation period increases with the decrease in concentration of substrates. For the bulk solution system consisting of MA, $NaBrO_3$, HNO_3 and $Ru(bpy)_3Cl_2$, we obtained the following empirical relations between the period (T [s]) and initial molar concentration of substrates (Fig.2):

$$T = 2.97\,[MA]^{-0.414}[NaBrO_3]^{-0.796}[HNO_3]^{-0.743} \qquad (1)$$

T is most sensitive to $[BrO_3^-]$. This is due that the process A in the FKN mechanism[4], corresponding to the consumption of bromide ions (resting state), becomes a dominant factor in increasing the period. For the gel system, the oscillating profiles of the swelling-deswelling changes as well as the redox changes were studied as a function of the substrate concentrations by using an image-processing method. It was found that both period and amplitude of chemical oscillation varied depending on the substrate concentration. We obtained the following empirical relations for the gel system:

$$T = 60.3\,[MA]^{-0.155}[NaBrO_3]^{-0.436}[HNO_3]^{0.469} \qquad (2)$$

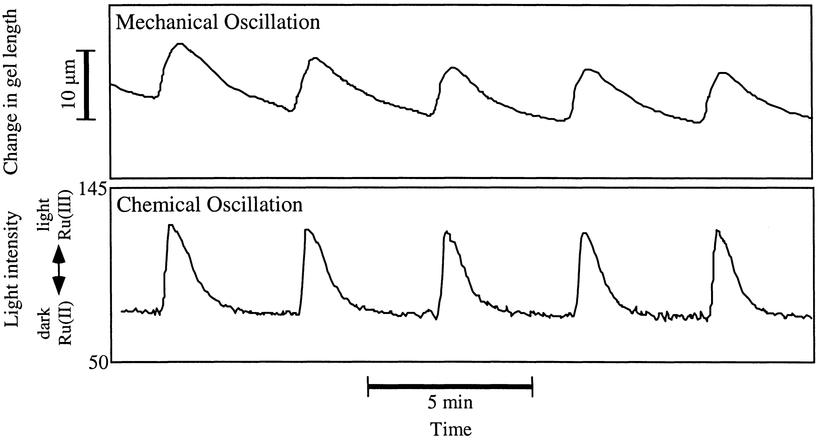

Fig. 1. Periodical redox changes of poly(NIPAAm-co-Ru(bpy)$_3$) gel (lower) and the swelling-deswelling oscillation (upper) at 20 °C. Transmitted light intensity is expressed as a 8-bit grayscale value. Outer solution: [MA] = 0.0625M; $[NaBrO_3]$ = 0.084M; $[HNO_3]$ =

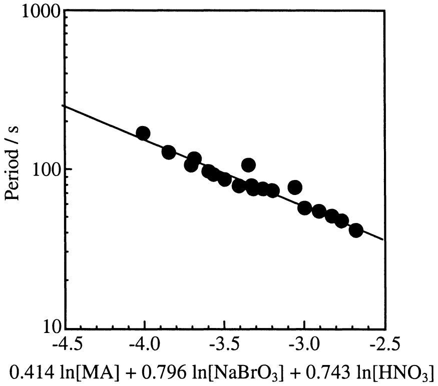

Fig. 2. Period as a function of the initial concentrations of malonic acid, sodium bromate and nitric acid for bulk solution system at 20 °C.

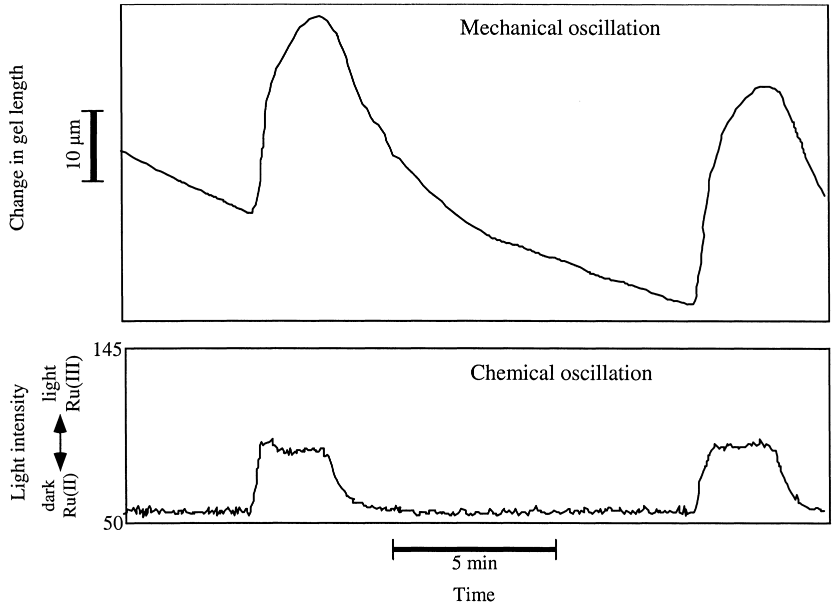

Fig. 3. Periodical redox changes of poly(NIPAAm-co-Ru(bpy)$_3$) gel (lower) and the swelling-deswelling oscillation (upper) at 20°C. Transmitted light intensity is expressed as a 8-bit grayscale value. Outer solution: [MA] = 0.0625M; [$NaBrO_3$] = 0.084M; [HNO_3] = 0.894M.

This concentration dependence is different from not only that for bulk solution system (eq. (1)), but also that for reaction-diffusion system using the same poly(NIPAAm-co-Ru(bpy)$_3$) gel with a rectangular shape [5]. The reason may be as follows. 1) In the case of the miniature gel, the dilution of intermediates from the gel into the surrounding aqueous phase must be more remarkable. The dilution effect, especially that for the activator ($HBrO_2$), leads to an increase in the period of chemical oscillations. 2) In addition, concentration change of substrates or products within the gel phase resulting from the swelling-deswelling oscillations may have some effects on the chemical oscillations (i.e., feedback effect).

Since T is most sensitive to [HNO_3] in eq. (2), we attempted to increase the amplitude of swelling-deswelling oscillations by changing the concentration of HNO_3. Figure 3 shows the time profiles of the swelling-deswelling oscillations of the gel as well as the periodical redox change when the initial concentration of nitric acid are increased from 0.6M to 0.894M. It was found that the period and amplitude of swelling-deswelling oscillations were increased with the increase in HNO_3 concentration. The waveform of redox changes showed a tendency to deform to rectangular shape with a plateau period when the amplitude of swelling-deswelling oscillation increased. From this result, it is supposed that not only energy transformation from chemical to mechanical change, but also feedback mechanism from mechanical to chemical change acts in the synchronization process.

We investigated the period of chemical oscillation under several initial conditions with different substrate concentrations. As a result, we can fit the relationship between the swelling-deswelling amplitude of the gel (i.e., the difference in gel size between the most swollen and shrunken states in the mechanical oscillation, Δd) and T by the following equation most well.

$$1 / \Delta d = 25.8 / (T - T_c) + 1 / \Delta d_{max} \qquad (3)$$

where Δd_{max} is the maximum value of Δd, and T_c is a critical period. The relationship means that Δd increases with an increase in T when T is longer than a critical value, T_c (= 94 s in this case). When T is shorter than T_c, the mechanical oscillation cannot be observed. It is suggested from the result that the swelling-deswelling response of the gel to the redox changes is rate-determining for the mechanical oscillations. T_c may correspond to the characteristic response time of swelling-deswelling for the gel.

The swelling-deswelling amplitude (Δd) also increased with an increase in the amplitude of the redox changes. Therefore, it is apparent that the swelling-deswelling amplitude of the gel is controllable by changing the initial concentration of substrates or the content of immobilized $Ru(bpy)_3$ catalyst within the gel. So far, the change in gel size with ca. 20% to the initial gel size was obtained as a maximum value (unpublished data). This swelling-deswelling ratio is comparable to that of typical stimuli-responsive gels which have been studied for the application to actuators, etc. Empirically, the relation between Δd [μm] and the substrate concentrations can be expressed as follows (Fig. 4):

$$\Delta d = 2.38\ [MA]^{-0.392}[NaBrO_3]^{0.059}[HNO_3]^{0.764} \qquad (4)$$

We also studied the swelling-deswelling behavior of the rectangular poly(NIPAAm-co-Ru(bpy)$_3$) gel membrane under the conditions that a train of excited pulses of the oxidized catalyst spontaneously evolves and propagates along the length by the reaction-diffusion mechanism [2)]. In the case of a large rectangular gel, the total length of the gel periodically changes with the propagation of chemical waves. It is demonstrated by the mathematical model simulations that the change in the overall gel length is equivalent to that in the remainder of gel length divided by the wavelength of the chemical wave, because the swelling and the deswelling cancel each other per one period of oscillations under steady oscillating conditions [2)]. The dynamic behavior that locally shrunken (or swollen) parts propagate is similar to the peristaltic motion observed in worms.

These self-oscillating gels may be useful in a number of important applications to intelligent biomaterials such as pulse generator or chemical pacemaker, self-walking (auto-mobile) actuators or micropumps with peristaltic motion, device for signal transmission, etc.

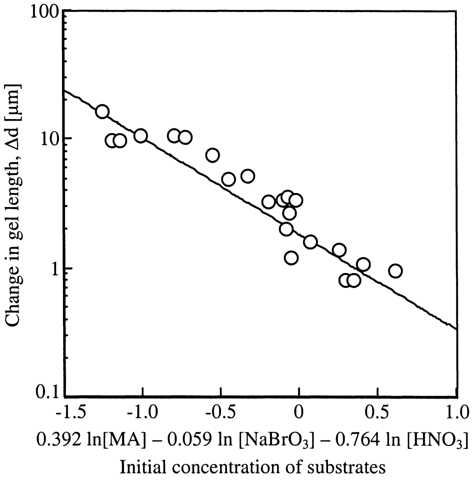

Fig. 4. Dependence of the swelling-deswelling amplitude (Δd) on the initial concentration of substrates.

Conclusions

A novel polymer gel that undergoes autonomous swelling-deswelling oscillations has been prepared by coupling with the BZ reaction. Sufficiently small bead-like gels demonstrate isotropic beating without pattern formation. The chemical and mechanical oscillations synchronize without a phase difference. The period of redox oscillation depends on the initial concentration of substrates. In the gel system accompanied with mechanical oscillations, the concentration dependence of period was different from that for the bulk solution system and for the gel system without mechanical changes (i.e., reaction-diffusion system). It was suggested that feedback mechanism from mechanical to chemical oscillation acts in the synchronization process. Swelling-deswelling amplitude of the gel is controllable by changing the initial concentration of substrates or the content of immobilized catalyst within the gel. The change in gel size with ca. 20% to the initial size was obtained as the maximum value.

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