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Oscillation of a Polymer Gel Entrained with a Periodic Force

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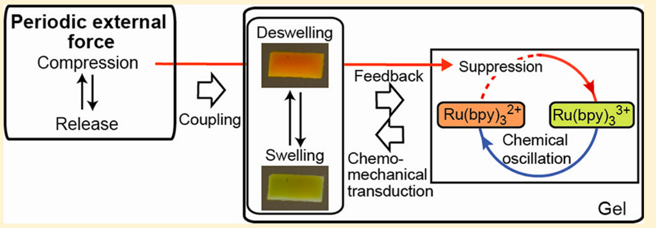
S *Supporting Information*

ABSTRACT: The oscillation of a polymer gel induced by the Belousov–Zhabotinsky (BZ) reaction was investigated under an external force composed of a square wave. The oscillation of the BZ reaction entrained to the periodic force and the features of this entrainment changed depending on the period and duty cycle of the square wave. The experimental results suggest that the change in the volume of the gel also gave feedback to the BZ reaction. The mechanism of entrainment is discussed in relation to the compression of the gel and the reaction–diffusion system in the BZ reaction.



■ INTRODUCTION

The development of autonomous actuators that can transport either a substance or themselves on a small scale and mimic sensation in living organisms has been studied in the fields of medicine and engineering.[1−3] Such actuators can not only control motion without the need for an external on/off switch but can also sense the physical and chemical environment, such as taxis in living organisms.

A self-oscillating polymer gel composed of *N*-isopropylacrylamide (NIPAAm) and $[Ru(bpy)_2(4\text{-vinyl-}4'\text{-methylbpy})]^{2+}$ ($Ru(bpy)_2(vmbpy)$) catalyst has been reported as a novel autonomous actuator.[4−12] This gel was shown to exhibit periodic alternation between swelling and deswelling in synchronization with the oxidation and reduction of the Ru catalyst in the Belousov–Zhabotinsky (BZ) reaction. Although many kinds of self-oscillating gels have been synthesized and several interesting systems (e.g., mass transfer and robots[7−9]) have been reported, feedback from gel oscillation to the BZ reaction has not yet been clarified experimentally.

In this study, the oscillation of a gel entrained with a periodic external force was investigated. The features of entrainment changed depending on the period and duty cycle of the forced oscillator. "Synchronization" refers to when the phases of two or more coupled oscillators are locked at a constant value, and is one of the most interesting phenomena in nonlinear systems.[13,14] Synchronization to an external force is called "entrainment".[15] The mechanism of entrainment in the present system is discussed in relation to the density of the polymer chain in the gel and the reaction–diffusion system in the BZ reaction.

■ EXPERIMENTAL SECTION

A NIPAAm gel was synthesized on the basis of a procedure reported by Yoshida et al.[9] Poly(NIPAAm-*co*-$Ru(bpy)_3$-*co*-AMPS) gels were prepared as follows: For a monomer solution, NIPAAm (623.7 mg), $Ru(bpy)_2(vmbpy)$ (16.2 mg), *N*,*N*′-methylenebisacrylamide (MBAAm, 11.2 mg, cross-linker), and 2,2′-azobis(isobutyronitrile) (AIBN, 26.6 mg, initiator) were dissolved in methanol (2 mL) and DMSO (0.4 mL). 2-Acrylamido-2-methylpropanesulfonic acid (AMPS, 22.0 mg) was dissolved in pure water (1.6 mL). These solutions were mixed together as a monomer solution, and O_2 molecules in the monomer solution were removed by nitrogen purging. The monomer solution without O_2 was then injected into the space between two glass plates gapped with a silicone sheet (thickness: 1.0 mm), as shown in Figure 1a. The injected solution was then polymerized at 333 K for 18 h. After polymerization, the gel was soaked in pure ethanol for 1 week, and then soaked in a graded series (75, 50, 25, and 0 vol %) of ethanol/water mixtures every day to remove unreacted monomers and hydrate carefully.

The synthesized gel was immersed in a BZ aqueous solution (4 mL) composed of 0.084 M $NaBrO_3$, 0.0625 M malonic acid, and 0.894 M nitric acid.[6,7,9−12] The experiments were carried out in a thermostat water bath at 291 ± 0.1 K.[7,9,11] A piece of the gel (3 mm × 1 mm × 1 mm) was placed on the flat bottom of the glass reactor and directly compressed with an acrylic plate (Acrylite, Mitsubishi Rayon, surface area: 7 mm × 20 mm) connected to a stepping motor (COMS Co. Ltd., PM80B-200K, Japan, minimum migration length: 14 μm) as a forced oscillator, as shown in Figure 1b. The external force was expressed as the relative change in the gel thickness, $\Delta h/h_0$ (h_0, initial thickness of the gel (∼1 mm); Δh, change in the thickness, which was equal to the compression length). The actual stress was applied within a range of 0−6 kPa (see Figure S1, Supporting Information). Thus, the experimental system was constructed to clarify the coupling between the BZ oscillatory reaction in the gel and the forced oscillator. The period of the applied force, T_p, was 6 min. The gel was monitored with a digital camera (Canon, EOS kiss Digital N) at

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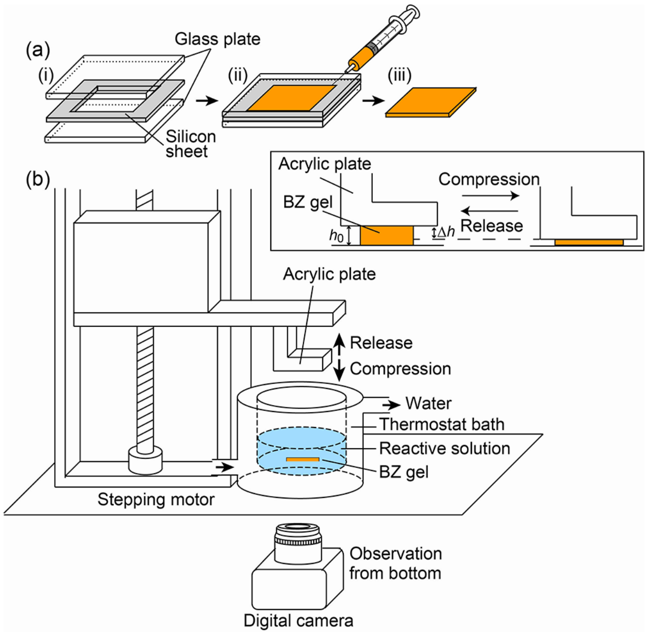

Figure 1. Schematic illustration of (a) the procedure for preparing a gel sheet with a definite thickness (i → ii → iii) and (b) the BZ gel system periodically compressed with a stepping motor.

a time interval of 15 s, and the images were analyzed by an image-processing system (National Institutes of Health, ImageJ). The green level was extracted from the RGB image of the gel to evaluate the BZ reaction of the gel, since the colors green and orange correspond to the oxidation and reduction states of the gel, respectively.

■ RESULTS

Figure 2 shows the response of a gel under a constant external force. The relationship between the external force and the volume of the BZ gel is also shown in Figure 2a. Here, the volume was measured for the BZ solution without $NaBrO_3$ in a reduced state. The gel did not collapse under the present conditions. The volume of the gel decreased with an increase in $\Delta h/h_0$. With regard to the features of oscillation, the period of the oscillation increased with an increase in $\Delta h/h_0$, as shown in Figure 2a. The duration of the reduced state at $\Delta h/h_0 = 0.7$ was longer than that at $\Delta h/h_0 = 0$, as shown in Figure 2b. We also confirmed that the period of BZ oscillation increased with an increase in the density of $Ru(bpy)_3^{2+}$ in the polymer gel, as shown in Figure S2 in the Supporting Information.

Figure 3 shows the experimental results regarding the BZ reaction in a gel under a periodic force at $T_h/T_p = 0.5$ (T_h: duration of higher $\Delta h/h_0$, T_p: period of one cycle of the forced oscillator). In this experiment, we selected $T_p = 6$ min since this value was close to the average period under the application of a constant force at $\Delta h/h_0 = 0.35$, which was equal to the average value of $\Delta h/h_0$ for one cycle. The period of the BZ oscillatory reaction in the gel was entrained to the period of the forced oscillator, i.e., 1 (gel): 1 (force) entrainment was observed, as shown in Figure 3a. To evaluate the nature of this entrainment, i.e., the phase difference between the periodic force and the BZ oscillation of the gel, a return map for $\Delta T_n/T_p$ vs $\Delta T_{n+1}/T_p$ (ΔT_n: nth phase difference between the BZ oscillatory reaction and the forced oscillator), was plotted as shown in Figure 3b. The points for $\Delta T_n/T_p$ vs $\Delta T_{n+1}/T_p$ were distributed around $(\Delta T_n/T_p, \Delta T_{n+1}/T_p) = (0.8, 0.8)$. As shown in Figure 3c and d, the gel began to oscillate from the reduced state when $\Delta h/h_0$ was low. In contrast, the gel remained in the reduced state when $\Delta h/h_0$ was high. The lateral amplitude of the swelling–deswelling change was ~20 μm under the compressed state (data not shown). The features of entrainment were independent of the initial phase difference between the BZ oscillation and the periodic force. As for the influence of the size of the gel, wave propagation was generated for a larger gel (e.g., 5 mm × 1 mm × 1 mm). On the other hand, a similar phenomenon was observed for a smaller gel (2 mm × 1 mm × 1 mm).

Figure 4 shows the experimental results regarding the BZ reaction of a gel depending on the amplitude of the periodic change in $\Delta h/h_0$ to investigate the coupling strength of entrainment. In this experiment, the minimum value of $\Delta h/h_0$ was constant at zero, but the maximum value changed. No entrainment was observed when the amplitude of $\Delta h/h_0$ was less than or equal to 0.20, as seen in Figure 4b.

Figure 5 shows the time variation of the green level for a gel under periodic forces with the same period but different duty cycles, T_h/T_p. At $T_h/T_p \geq 0.5$, 1:1 entrainment was observed, as seen in Figures 3 and 5a. At $T_h/T_p = 0.667$, the points for $\Delta T_n/T_p$ vs $\Delta T_{n+1}/T_p$ were distributed around $(\Delta T_n/T_p, \Delta T_{n+1}/T_p) = (0.9, 0.9)$, as shown in Figure 5a-2. With a further increase in T_h/T_p, the return map converged to $(\Delta T_n/T_p, \Delta T_{n+1}/T_p) = (1.0, 1.0)$ (data not shown). In contrast, 1:1 entrainment was broken at $T_h/T_p \leq 0.333$, as seen in Figure 5b and c. At $T_h/T_p = 0.333$, a quasi-periodic entrainment was observed, as shown

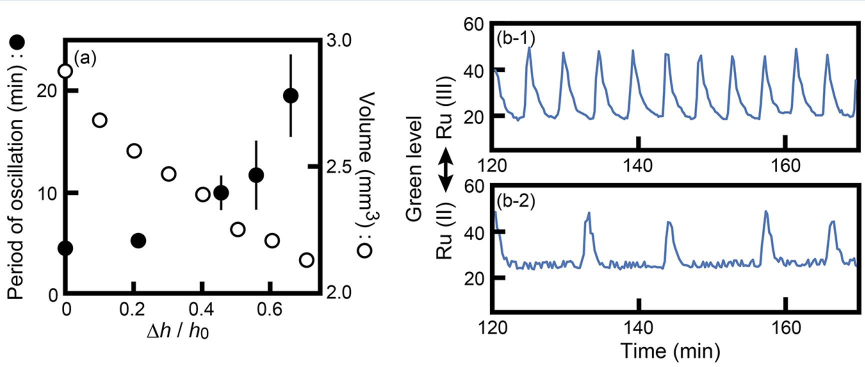

Figure 2. Experimental results regarding (a) the period of oscillation (filled circles) and the volume of a gel (empty circles) under a constant value of $\Delta h/h_0$ and (b) the time variation of the green level of the gel under a constant value of $\Delta h/h_0$ = (1) 0 and (2) 0.7.

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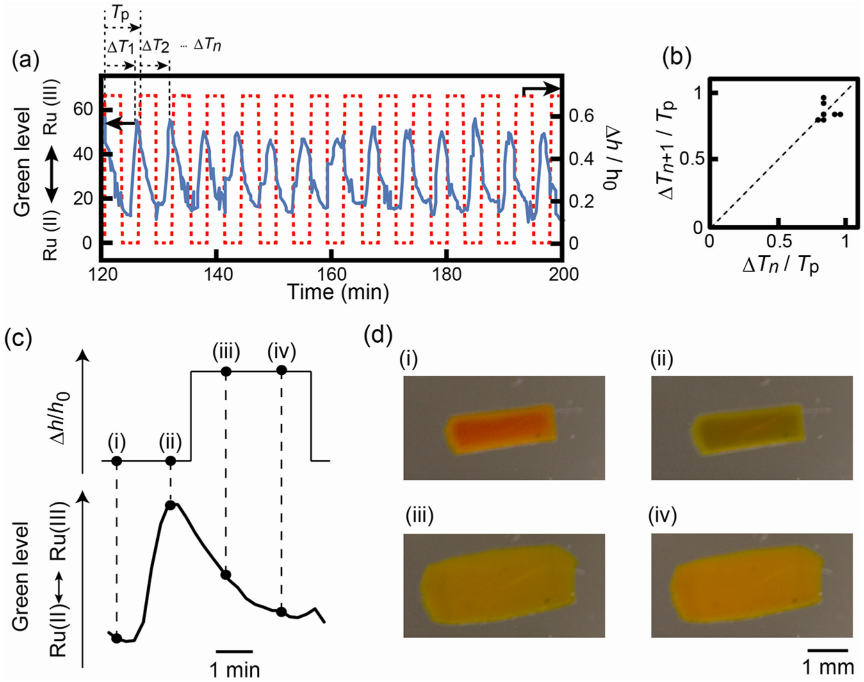

Figure 3. Experimental results regarding (a) the time variation of the green level and $\Delta h/h_0$ under a periodic force (T_h/T_p = 0.5), (b) a return map of the phase difference between the periodic force and BZ oscillation for part a, (c) the extracted time variation in part a, and (d) snapshots of the gel (bottom view, time interval: 90 s). The amplitude of the periodic change in $\Delta h/h_0$ was 0.35. (i), (ii), (iii), and (iv) in part c correspond to those in part d, respectively.

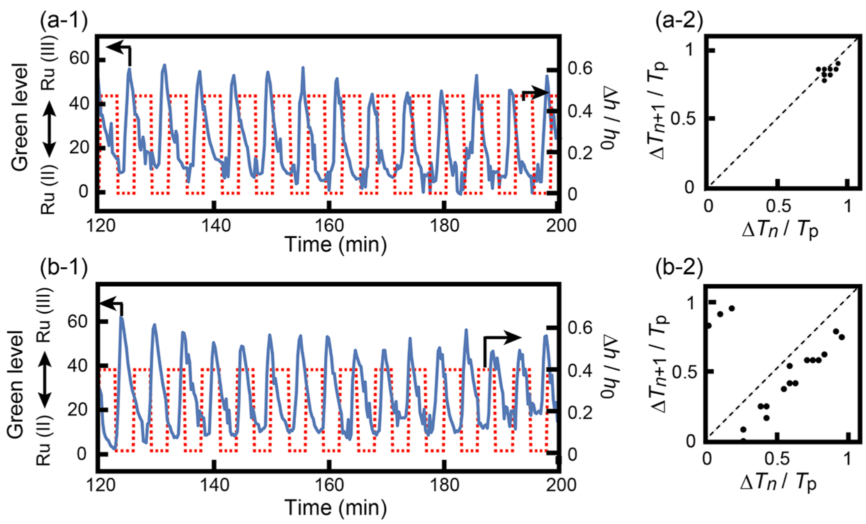

Figure 4. Experimental results regarding (1) the time variation of the green level of a BZ gel under a periodic force (T_h/T_p = 0.5) and (2) a return map of the phase difference between the periodic force and BZ oscillation for (1) depending on the amplitude of the periodic change in $\Delta h/h_0$ ((a) 0.25, (b) 0.20).

in Figure 5b. That is, one cycle was repeated every four oscillations (see downward arrows in Figure 5b-1), while the phase difference, $\Delta T_n/T_p$, decreased from 1.0 to 0.4, as shown in Figure 5b-2. At T_h/T_p = 0.167, the BZ reaction of the gel oscillated independently of the forced oscillator, as shown in Figure 5c. The points in the return map were almost on a line to $\Delta T_{n+1}/T_p = \Delta T_n/T_p$, as shown in Figure 5c-2.

To investigate the influence of the period of the external force, we examined the system at T_p = 4 min and the lower duty cycle (=0.167), since the period of gel oscillation was ca. 4 min at a constant $\Delta h/h_0$ (=0.117) (see Figure 2a), which was equal to the average value of $\Delta h/h_0$ for one cycle (6 min) in Figure 5c. No entrainment was observed under these conditions (see Figure S3, Supporting Information).

■ DISCUSSION

On the basis of the experimental results and those in related works,[7,16] we discuss entrainment between the BZ reaction and a periodic compressive force. Figure 2 suggests that the volume of a gel is changed by the external force and the compressed gel inhibits the oscillatory BZ reaction by keeping it in a reduced state ($Ru(bpy)_3^{2+}$). Here, the decrease in the volume of the gel due to the compression corresponds to the increase in the density of the polymer chain in the gel. The increase in the

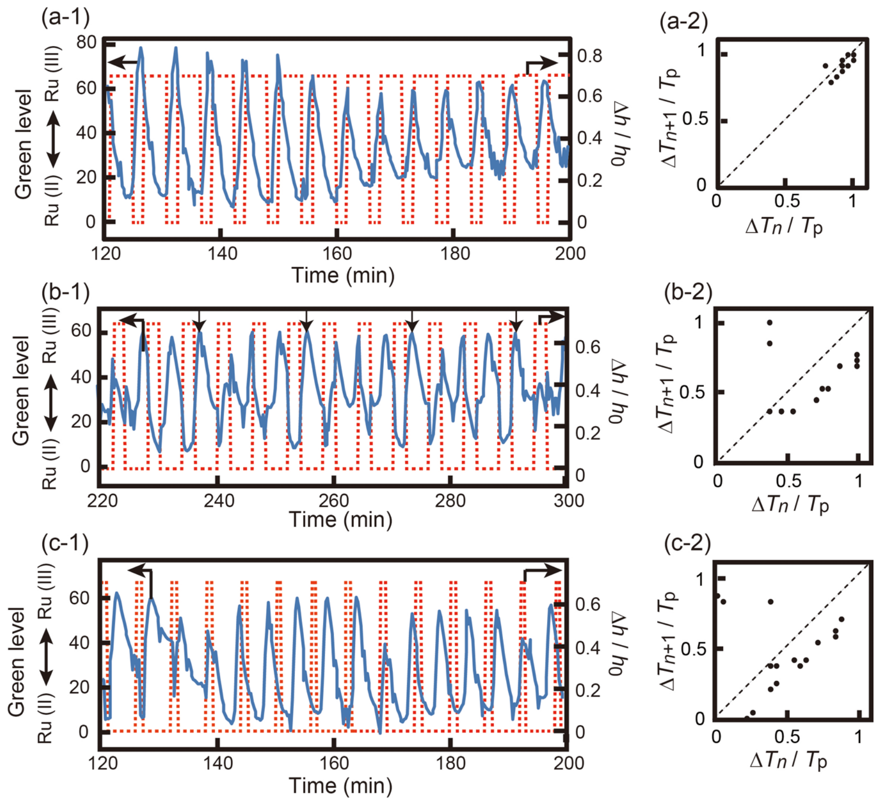

Figure 5. Experimental results regarding (1) the time variation of the green level for a gel under a periodic force and (2) a return map of the phase difference between the periodic force and BZ oscillation for (1) depending on the duty cycle, T_h/T_p (= (a) 0.667, (b) 0.333, and (c) 0.167). The amplitude of the periodic change in $\Delta h/h_0$ was 0.35. Downward arrows in (b-1) denote entrainment between the periodic force and BZ oscillator.

period of the BZ reaction with an increase in the compression (Figure 2) and with an increase in the density of $Ru(bpy)_3^{2+}$ (Figure S2, Supporting Information) agrees with the experimental findings reported by Miyakawa et al. that the period of the BZ reaction increases with an increase in the density of $Ru(bpy)_3^{2+}$ in the polymer gel.[12] Figure 3 suggests that the phase of the BZ oscillation is regulated by the external periodic force while the Ru catalyst is oxidized without compression and the catalyst is maintained in the reduced state with compression. Figure 4 suggests that the amplitude of $\Delta h/h_0$ plays a role in the coupling strength of entrainment but the phase difference between two oscillators is not sensitive to the amplitude of $\Delta h/h_0$ under the condition of entrainment. Figure 5 suggests that the features of entrainment are sensitive to the duty cycle, even in the same period. In addition, the phase difference between two oscillators depends on the duty cycle, since oxidation in the BZ reaction occurs as soon as the compression is released.

Figure 6 shows a schematic representation of the mechanism of entrainment between the BZ reaction of the gel and the external periodic force. The density of the polymer chain in the gel under compression is greater than that without compression. When the gel is compressed, the chemicals are extruded from the gel into the bulk phase, and the diffusion rates of the chemicals that remain in gel may decrease, as shown in state I in Figure 6.[16] Thus, it is difficult for fresh chemicals to diffuse into the gel. In state I, the autocatalytic reaction of the activator, $HBrO_2$, is suppressed due to the greater density of the polymer chain. It may be difficult to decrease the concentration of inhibitor, Br^-, in the gel because of the suppression of the reaction with $NaBrO_3$ or $HBrO_2$,[17−19] and therefore, the

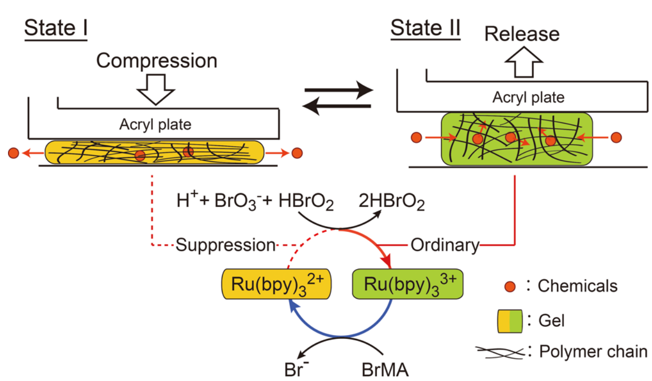

Figure 6. Schematic representation of the mechanism of entrainment between the BZ reaction of the gel and the external periodic force with (state I) and without (state II) compression of the gel. The reaction rate of the oxidation of $Ru(bpy)_3^{2+}$ is slow and normal in states I and II, respectively.

compressed gel may maintain a reduced state. In contrast, the reactants easily diffuse in the gel without compression, as shown in state II in Figure 6. As a result, the oxidation of BZ reaction occurs when the compressed gel is released. Volume change in the gel under the periodic compression was similar to that for the swelling−deswelling oscillation without external force in the present condition. On the other hand, the swelling is difficult at the compressed state. Thus, the swelling is easy to occur when the gel is not compressed. We focus on the production process of activator, $HBrO_2$, and inhibitor, Br^-. Yashin et al. reported the influence of the volume fraction of a polymer, ϕ ($1 - \phi$: volume fraction of solvent in the gel).[20]

Here, $\phi = V_p/(V_p + V_s(t))$, where V_p and $V_s(t)$ are the volumes of the polymer network and solvent in the gel; i.e., the density of the Ru catalyst is decreased, but its amount is not changed when the polymer gel is swollen, i.e., $V_s(t)$ is increased. They modified five essential steps in the BZ reaction rate equations. The following three reactions in the five steps are strongly suppressed when ϕ is increased.

The production of $HBrO_2$ from BrO_3^- and Br^-:

$$k_a[H]^2[A] \rightarrow k_a(1-\phi)^3[H]^2[A]$$

The autocatalytic reaction:

$$k_b[H][A] \rightarrow k_b(1-\phi)^2[H][A]$$

The production of Br^- from bromomalonic acid and malonic acid:

$$k_c[B] \rightarrow k_c(1-\phi)[B]$$

where [H] is the concentration of H^+, [A] is the concentration of BrO_3^-, and [B] is the total concentration of malonic acid and bromomalonic acid. These descriptions suggest that the production of activator, $HBrO_2$, is suppressed rather than the production of the inhibitor due to the decrease in $(1-\phi)$ by the compression. Therefore, the production of the activator may progress in the released gel rather than the compressed gel. Thus, the oscillation of the BZ reaction is entrained to the periodic force due to the oxidation of the gel at the change from the compressed state to the released state.

Chen et al. reported that the BZ gel begins to oscillate when a constant pressure is applied to the gel in a reduced state and the frequency of oscillation increases with an increase in the pressure.[21] The pressure-dependent frequency in our results under a constant pressure was different from that in their results. These different dependencies of the frequency on the pressure may be due to the different states; i.e., our system and theirs were examined in oscillatory and non-oscillatory states without stress, respectively. In addition, the homogeneity of the density of the polymer chain used in their system was greater than that in our system. These different dependencies should be clarified in a future study in relation to the state of the reaction field and the chemical compositions in the experimental system.

■ CONCLUSION

Entrainment between the BZ reaction of a gel and a periodic compressive force occurred at a higher amplitude ($\Delta h/h_0$) and a higher duty cycle for the force even if the period of the force (T_p) was ca. 30% longer than that of the BZ reaction of the gel without compression. The duty cycle and $\Delta h/h_0$ influenced the coupling strength between them, and in particular, the duty cycle could change the phase difference between them. We suggested that the features of entrainment are determined by the change in density of the polymer chain and the diffusion rate of chemicals in the gel. We discussed the mechanism that entrainment is generated by the oxidation of the gel when the compressed state is released. The features of entrainment may be changed depending on the frequency of the BZ oscillation due to the change in the rate balance between the diffusion and chemical reaction. The effect of the frequency of the BZ oscillation will be separately reported in the future study. Thus, the present study suggests that not only does the BZ reaction induce a periodic change in the volume of the gel, but also the change in the volume of the gel provides feedback to the BZ reaction.

■ ASSOCIATED CONTENT

Supporting Information

Additional information on the effect of oscillation of the BZ gel under the external force. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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