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Chemical Robot–Design of Peristaltic Polymer Gel Actuator-

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Abstract— **In this proceeding, we introduce peristaltic gel actuators as a chemical robot. The polymer gels prepared here have a cyclic reaction network like metabolic process in itself. With a cyclic reaction, the polymer gel swells-shrinks autonomously. The periodic self-oscillating motion of the gel is produced by the dissipating chemical energy of the oscillatory Belouzov-Zhabotinsky (BZ) reaction. We have succeeded in convey the object automatically by utilizing the synthetic polymer gel. This experimental fact represents the great possibility of the chemical robot.**

I. INTRODUCTION

Recently, many kinds of soft materials have been researched. In particular, stimuli-sensitive polymers and gels that swell or shrink by the molecular interactions have been studied fundamentally [1]-[5]. And also, in application, many kinds of soft and wet system such as a drug delivery system, robotic actuators and mass transporting devices, have been developed in various fields [6]-[12]. By changing the external physicochemical condition, these devices can drive. For example, bending motion of the polymer gel actuator was made of bi-gel [6]. The bi-gel was made by the interpenetrating N-isopropylacrylamide (NIPAAm) gel, which is a thermo sensitive polymer, into a fraction of the poly-acrylamide (PAAM) gel network. This gel could bend in water in response to temperature as a result of the characteristic of the thermosensitive NIPAAm component. Recently, the ionic polymer-metal composite (IPMC) actuator that bends quickly using a low voltage was reported. The actuator forms the electrode by the chemical plating. The bending mechanism is the unidirectional electro-osmosis by the positive ion with their polar solvent toward the cathode. As a result of the solvent enrichment at the cathode and depletion at the anode, the actuator cause bending motion due to the differential degree of swelling and shrinking. A micro robotic arm made from a conducting polymer that can grip and carry objects for single-cell manipulation was developed from a fabricated circuit of conducting polymers upon oxidation and reduction [8].

However, these systems require the complex and fabricated circuit or external control devices because the function of the polymer gel is driven by on-off switching of external signals. On the other hands, in biological systems, there are several autonomous phenomena such as peristaltic motion, self-oscillation, etc. without any on-off switching of external stimuli. If materials cause the self-motion, a novel device that does not depend on the external control would be realized. But actually, there are few reports to realize autonomous systems. As attempts to use cardiac muscle cells and synthetic polymers, Whitesides and co-workers have demonstrated the self-walking bioactuator [13]. Although the utilization of biopolymer or cell system is one method, our strategy is to use only completely artificial system without relying on biomolecules, biopolymer, cardiac muscle, etc. which are originated from living organism.

Previously, active oscillating polymer and gel systems that exhibit the small volume oscillation of polymer gel autonomously without any external stimuli have been reported [14], [15]. The volume change oscillation is induced by the oscillatory Belousov-Zhabotinsky (BZ) reaction [16], [17]. The BZ reaction is well known as a nonequilibrium dissipative system and generates autonomous oscillations in changing its redox potential. Generally, the importance of the BZ reaction has been recognized in the similarities of life phenomena. In an unstirred solution, the BZ reaction generates chemical waves and spatial pattern formations as a reaction-diffusion system. The overall process of the BZ reaction is the oxidation of an organic substrate by an oxidizing agent in the presence of the catalyst under acidic conditions. In the reaction process, there are periodic concentration oscillations of some reactants such as the metal catalyst moiety: $Ru(bpy)_3^{2+} \leftrightarrow Ru(bpy)_3^{3+}$. Yoshida et al have synthesized an ionic polymer gel which consists of the cross-linked PNIPAAm and ruthenium catalyst of the BZ reaction. When the gel is immersed in the aqueous solution containing the substrates of the BZ reaction except for the catalyst, the substrates penetrate into the polymer network and the BZ reaction occurs in the gel. When the redox state of the Ru moiety into the gel changed, the solubility of the polymer chain changed as well. As a result, the change in the osmotic pressure inside the gel causes the swelling or shrinking of the polymer gel. The displacement of the self-oscillating gel is several dozen micrometers [15] as shown in Figure 1.

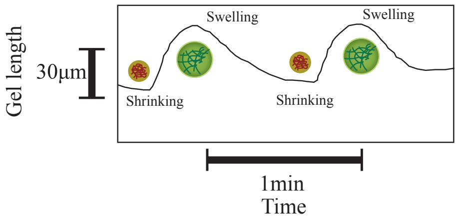

Fig. 1. Conventional self-oscillating gel.

In our previous works, we have designed the ciliary typed gel actuator [18], [19] by fabrication and molding of the self-oscillating gel. The ciliary motion was generated by the chemical waves due to the reaction diffusion dynamics. Since the mechanical displacement of the actuator was very small, the motility of the gel actuator was small. For the purpose of improvement of the motility for the gel, we have realized the large deformation of the gel with gradient structure. For making the gradient structure in the gel, we utilized the hydrophobic interaction during the polymerization. As a result, the large deformation of the self-oscillating gel has been achieved [20]. Furthermore, by coupling with ratchet mechanism, the gel walked with repeated bending and stretching motion by itself like a looper [21].

However, it was difficult to observe the peristaltic motion of synchronized with the chemical wave directly because the mechanical oscillation was too small in comparison with the gel size. Theoretical studies have predicted the occurrence of peristaltic motion within the gel [22]. In previous report, the peristaltic motion of the gel has been indirectly evaluated from its color tones [23]. And also, by using the structural color of the gel, the peristaltic motion was evaluated indirectly.[15] However, there is no repot for the direct observation of the macroscopic peristaltic motion of the gel. Recently, we have succeeded in observing the peristaltic motion of the gel [24] directly by utilizing a novel gel with a porous structure.

In this proceeding, we introduce a novel peristaltic motion, mass transport and annihilation phenomena of the polymer gel at the macroscopic scale. We focus on the kinetics of the polymer gel. The network motion of the gel as given by Tanaka, Hocker and Benedek [25] is

$$\frac{\partial \vec{u}}{\partial t} = \frac{K + \mu/3}{f} grad(div\vec{u}) + \frac{\mu}{f}\Delta\vec{u} \qquad (1)$$

where Δ denotes the Laplacian and $\vec{u}(\vec{r},t)$ is the displacement vector that represents the displacement of a point in the network. K, μ and f are the osmotic bulk modulus, shear modulus of polymer gel and friction coefficient between network and fluid medium, respectively. In the case of a radial deformation (1) becomes

$$\frac{\partial u}{\partial t} = D_c \frac{\partial}{\partial r}\left(\frac{\partial u}{\partial r} + 2\frac{u}{r}\right) \qquad (2)$$

With

$$D_c = \frac{K + 4/3\mu}{f} \qquad (3)$$

D_c is the diffusion coefficient of the polymer gel. If the D_c is high value, the response of the gel is fast as shown in Eq. (2). In general, the degree of the response of hydro gels composed of chemically cross-linked polymer networks is low because the polymer chains are molecularly restricted by a large number of cross-links. There are remarkable difference of swelling ratio between the reduced Ru(II) state and oxidized Ru(III) state in the poly(NIPAAm-co-Ru(bpy)$_3$) gel at the equilibrium swelling state. But actually, the volume oscillation coupled with the redox oscillation of the ruthenium catalyst moiety due to the BZ reaction is very small. The rate of the redox reaction of the Ru moiety is significantly faster than that of swelling-deswelling of the gel in the equilibrium condition such as above mentioned. Therefore, the poly(NIPAAm-*co*-Ru(bpy)$_3$) self-oscillating gel generated the small mechanical oscillation. To produce the large mechanical oscillation in comparison with the gel size, the self-oscillating gel has to response firstly to the change in the charge density of the metal catalyst. For realizing this purpose, we prepared the microphase-separated self-oscillating gel. In the previous work, we reported that the NIPAAm gel with micro scale phase separation underwent quick response [26]. By preparing NIPAAm gel above the lower critical temperature (LCST), the network structure becomes inhomogeneity due to the LCST nature of the NIPAAm component. As a result, the NIPAAm gel forms a porous structure with polymer rich domains and aggregations in the matrix of loosely tied network structure. Consequently, rich domains inside the gel clump or loose rapidly because of an effluent pathway of water due to the porous structure as shown in Figure 2. However, the micro phase separation in the gel strongly depends on the methods and ways of gel preparation. Therefore, the control of the phase separation was too difficult by utilizing this method.

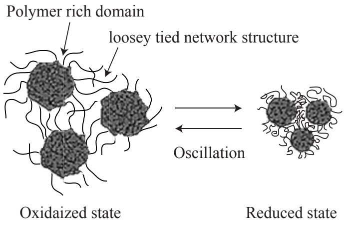

Fig. 2. Illustration of the porous gel.

In order to control the micro scale phase separation into the self-oscillating gel, we synthesized the gel under the water-methanol mixture solution by utilizing the hydrophobic casting mold. Furthermore, we added the hydrophilic 2-acrylamido-2-methylpropanesulfonic acid (AMPS) to the tied network structure in the gel to form clear rich domains in order to pretend the aggregation of the ruthenium moieties originating in the hydrophobic interaction.

II. EXPERIMENTAL SECTION

A. *Synthesis of the polymer gel.*

The poly(NIPAAm-co-Ru(bpy)$_3$-co-AMPS) gels were prepared as follows. 0.156 g of N-isopropylacrylamide (NIPAAm), 16.2mg ofruthenium(4-vinyl-4'-methyl-2,2'-bipylridine)bis(2,2'-bipyridine)bis(hexafluorophosphate) (Ru(bpy)$_3$) as a metal catalyst for the BZ reaction, 2.8mg of N,N'-methylenebisacrylamide (MBAAm) as a cross-linker, and 6.6mg of 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator were dissolved in O_2-free methanol (0.5ml). 5.5mg of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was dissolved in O_2-free pure water (0.5ml). Then the two solutions were mixed together. The monomer solution was injected into the casting mold. In this study, we designed a cylindrical hole (diameter: 0.8mm) in the hydrophobic wax plate (The Kindt-Collins Company) as the casting mold by using PC software (MiniCAD7) and then dig a hole in the wax plate by using the CAM machine (MIMAKI, NC-5). And then the monomer solution was polymerized at 60°C for 18 hours. After polymerization, the gel was soaked in pure methanol for a week to remove unreacted monomers. The gel was carefully hydrated through dipping it in a graded series of methanol-water mixtures, for 1 day each in 75, 50, 25 and 0%.

B. *Measurement of the swelling kinetics of the gel*

The swelling kinetics of the polymer gel was measured under reduced and oxidized states, by using $Ce(SO_4)_2$ as an oxidizing agent and $Ce_2(SO_4)_3$ as a reducing agent, respectively. The experiment was conducted in a water-jacketed cell made of acrylic plates. The temperature was controlled by circulating thermostated water through the water-jacket around the cell. Shape changes of the gel strip was observed and recorded by using a microscope (Fortissimo Corp. WAT-250D), a LED light (LEDR-74/40 W) and a HDD recorder (Victor, SR-DVM700) as shown in Figure 2.

C. *Measurement of the oscillating behavior of the cubic gel*

The cubic poly(NIPAAm-co-Ru(bpy)$_3$-co-AMPS) gel was in the mixture solution of the BZ substrates (62.5 mM malonic acid, 84mM sodium bromate, 0.894M nitric acid) at constant temperature.

D. *Measurement of the peristaltic motion of gel*

The cylindrical poly(NIPAAm-co-Ru(bpy)$_3$-co-AMPS) cubic gel was in the mixture solution of the BZ substrates (62.5 mM malonic acid, 84mM sodium bromate, 0.894M nitric acid) at constant temperature.

E. *Measurement of the mass transport by using peristaltic motion of gel*

The cylindrical polyacrylamide gel as the object was set on the rectangular poly(NIPAAm-co-Ru(bpy)$_3$-co-AMPS) gel in the aqueous solution containing the three reactants of the BZ reaction (62.5 mM malonic acid, 84mM sodium bromate, 0.894M nitric acid) at constant temperature.

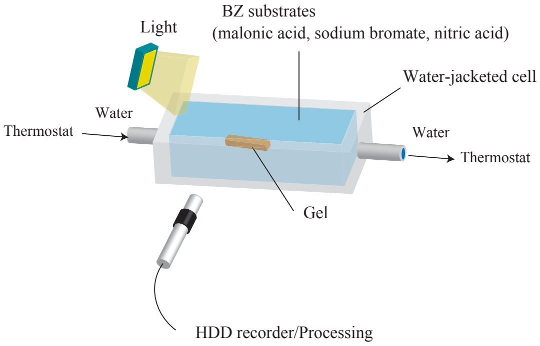

Fig. 3. Illustration of experimental setup.

III. RESULT AND DISCUSSION

Figure 4 shows plots of the relative swelling of the poly(NIPAAm-co-Ru(bpy)$_3$-co-AMPS) and poly(NIPAAm-*co*-Ru(bpy)$_3$) gels, versus time, *t*, elapsed after changing the solution outside the gels from the 0.894M HNO_3 solution to the 5mM $Ce(SO_4)_2$ and 0.894M HNO_3 solution for oxidizing Ru(bpy)$_3$.

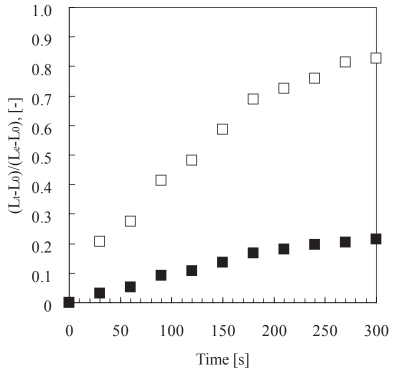

Fig. 4. Relative swelling of poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) and poly(NIPAAm-co-Ru(bpy)$_3$) gels, $(L_t-L_0)/(L_e-L_0)$, in the solution of 5 mM $Ce(SO_4)_2$, 0.894 M HNO_3 at 18 °C as functions of the time *t* elapsing after changing the solution. L_t, L_0 and L_e, are the lengths of the gel at t = t, initial state and equilibrium state.(□) poly(NIPAAm-*co*-Ru(bpy)$_3$-co-AMPS) gel;(■) poly(NIPAAm-*co*-Ru(bpy)$_3$) gel.

As shown in Figure 4, the swelling speed of the poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) gel was faster than that of the poly(NIPAAm-*co*-Ru(bpy)$_3$) gel at 18 °C. This result indicated that the swelling dynamics of the poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) gel is different from the poly(NIPAAm-co-Ru(bpy)$_3$) gel. The data supported that the time scale of the swelling kinetics and the chemical reaction matched. This result is significantly importance to cause large deformation of the gel by utilizing the BZ reaction.

Next, we prepared the cubic gel of which size was smaller enough than the wavelength of the chemical wave. Within the miniature gel, the redox change homogeneously occurred without evolution of chemical waves. As for the miniature gel, the oscillating profiles of the redox changes as well as the swelling-deswelling changes were analyzed by using the image-processing method. Figure 5 shows the self-oscillating behavior of the cubic gel in the aqueous solution containing the three reactants of the BZ reaction (malonic acid, sodium bromate and nitric acid) at the constant temperature. The displacement of the mechanical oscillation was around 130μm. In comparison with our previous researches, the amplitude of the volume oscillation for the poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) gel is about ten times as large as that for the poly(NIPAAm-*co*-Ru(bpy)$_3$) gel. This result clarified that the large mechanical oscillation of the gel required the rapid response to the change in the redox state of the metal catalyst induced by the BZ reaction. From this result, it is expected that the gel of which size is larger enough than the wavelength of the chemical wave undergoes periodical peristaltic motion when the redox state of the Ru(bpy)$_3$ moiety in the gel periodically change by the BZ reaction at the constant temperature.

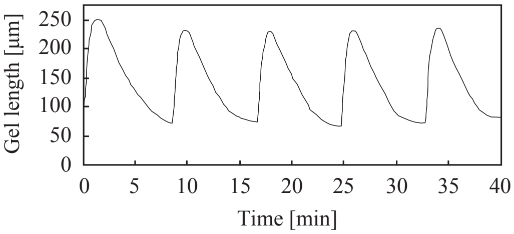

Fig. 5. Oscillating profile of cubic gel. Cubic gel (each side length is about 0.5mm) was immersed in 1ml of the mixture solution of the BZ substrates (62.5 mM malonic acid, 84mM sodium bromate, 0.894M nitric acid, 18°C).

Figure 6 shows the periodical peristaltic motion of the gel driven by the chemical waves of the BZ reaction. We firstly succeed in observing the periodical peristaltic motion of the gel directly. With the propagation of the chemical waves, the local swelling regions propagated in the gel. This is the first visual evidence of the peristaltic motion of the gel in the macroscopic scale. The shape change of the gel was in excellent agreement with the theory [22]. The aspects of the volume change of the gel followed the reaction diffusion dynamics [17]. The chemical wave speed of the BZ reaction was approximately 14.0-30.0μm/sec in the gel. Figure 7 shows the spatio-temporal diagram constructed from the sequential images. The width of the gel changed shape periodically with about 150μm. As shown in Figure 7, The change in the width of the gel increased c.a. 20% from the initial width of the gel. The period of the volume oscillation was about 86sec. Moreover, as shown in Figure 8, we succeeded in observation of the annihilation [17] of the swelling region due to its nonlinear phenomena in gel system.

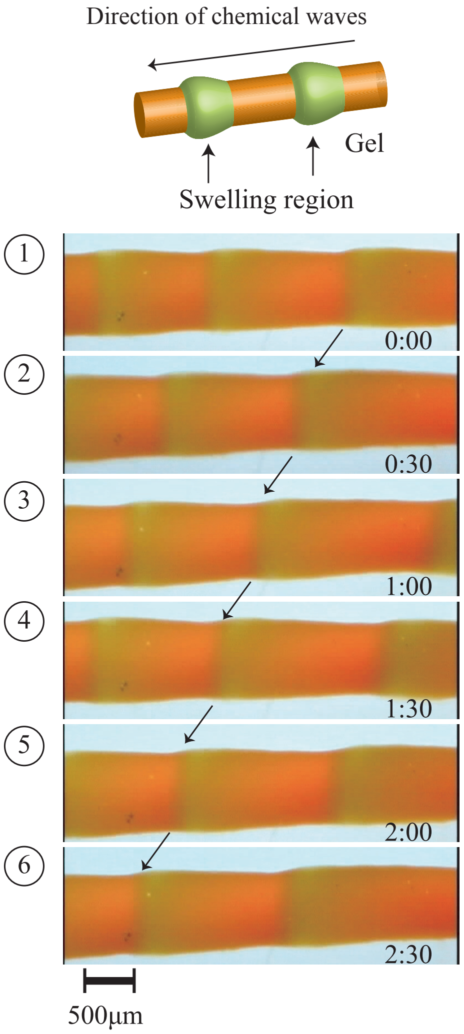

Fig. 6. Time course of peristaltic motion of poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) gel in 8ml of the mixture solution of the BZ substrates (62.5 mM malonic acid, 84mM sodium bromate, 0.894M nitric acid, 18°C). The green and orange color correspond to the oxidized and reduced state of Ru moiety in the gel, respectively.

Furthermore, we succeeded in conveying the object by utilizing the peristaltic motion of the gel. We set the cylindrical polyacrylamide gel as the object on the rectangular poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) gel in the aqueous solution containing the three reactants of the BZ reaction. Figure 9 shows the illustration of matter transport.

The peristaltic surface of the gel pushed and carried the object by rotating it in one direction at about 40μm/sec with the chemical wave propagation as shown in Figure 9. The gel conveyer carried the object with millimeter order autonomously. We clarified that the peristaltic motion of the gel can be controllable by changing the concentration of the BZ substrates because the spatiotemporal dynamic pattern changes with changing the outer solution.

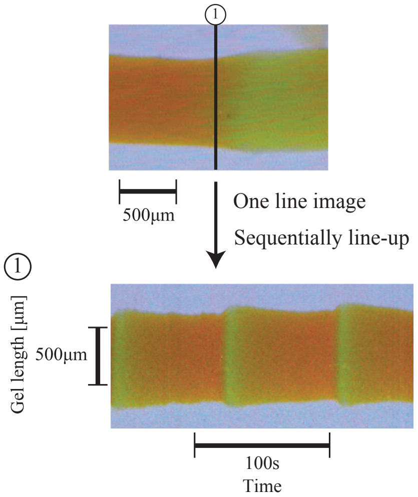

Fig. 7. Spatio-temporal pattern of gel oscillation.

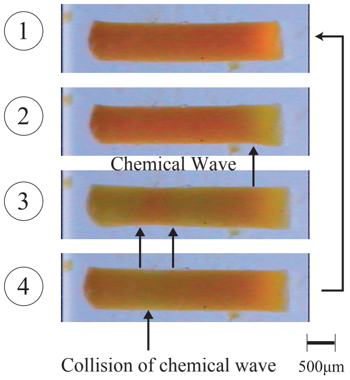

Fig. 8. Annihilation of swelling region in gel. Cylindrical gel was immersed in 1ml of the mixture solution of the BZ substrates (62.5 mM malonic acid, 84mM sodium bromate, 0.894M nitric acid, 18°C).

Finally, we evaluate the effect of the porous structure into the gel by utilizing the chemical wave. The chemical wave is driven by the diffusion of $HBrO_2$ into the reduced state ahead of the front. Therefore, the $HBrO_2$ reduces the local Br^- concentration via the Br^- consumption process (called "process A" in the Field-Koros-Noyes (FKN) mechanism [17]. Once $[Br^-]$ decreases below the critical value, the following autocatalytic process (called "process B") leads to the local oxidation and production of $HBrO_2$:

$$BrO_3^- + HBrO_2 + 2Mred + 3H^+ \rightarrow 2HBrO_2 + 2Mox + H_2O$$

The wave velocity of the BZ reaction is theoretically given by

$$v = \left(k_5 D[H^+][BrO_3^-]\right)^{1/2} \qquad (4)$$

where k_5(=42M^{-2}sec^{-1}) is the rate constant of the autocatalytic reaction of $HBrO_2$ and D is the diffusion coefficient of activator ($HBrO_2$). Simply, D is $0.15\times10^{-6}\sim0.55\times10^{-6}$. In comparison with the conventional self-oscillating gel, the diffusion coefficient is slightly small value (D of the conventional self-oscillating gel is about 1.0×10^{-6}). However, the polymer concentration of the novel self-oscillating gel is more than 5 times. That is, these experimental data supposed the porous structure of the gel.

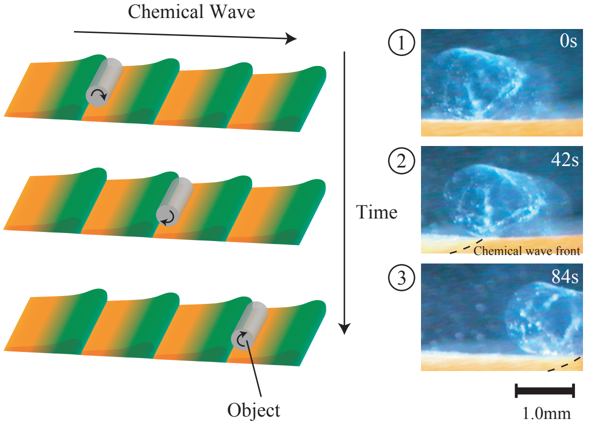

Fig. 9. Schematic illustration of the matter transport using peristaltic motion of the gel.

IV. PERSPECTIVE

Now, the actuation of the gel is operated under non-physiological environment where the three substrates of the BZ reaction coexist. If the actuation can drive under biological conditions, realization of novel intelligent bio-machines or devices without relying on the electricity would be expected. Therefore, we have been challenging the modification of the molecular structure of the gel in order to cause self-oscillation under physiological condition, that is, only in the presence of bio-related organic acids such as citric acid [27]-[30]. Moreover, recently, by optimizing the polymer design, we succeeded in modifying the driving speed of the gel in 0.5 Hz [31]. The maximum frequency (0.5Hz) of the novel gel was 20 times as large as that for the conventional-type self-oscillating gel. The autonomous peristaltic motion of the gel would create a new design method for matter transport, micro or nano devices, etc.

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