Development of novel self-oscillating gel actuator

for achievement of chemical robot

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ABSTRACT- In our previous studies, we succeeded in construction self-oscillating gel actuator such as a self-walking gel and a dynamic motion of a gel actuator. However, the speed of the swelling－deswelling self-oscillation is too slow in order to realize practical chemical robot. In this study, we succeeded in the wide-range control of the period for the swelling－deswelling self-oscillation of a novel polymer gel by selection of the initial concentration of the Belouzov-Zhabotinsky (BZ) substrates and the temperature. The novel polymer gel was composed of a non-thermoresponsive and biocompatible poly-vinylpyrrolidone (PVP) main chain covalently-bonded to the ruthenium catalyst for the BZ reaction. Moreover, we clarified the influence of the initial concentration of the BZ substrates and the temperature on the period and the self-oscillating behavior. By optimizing the initial concentration of the BZ substrates, we cause the swelling－deswelling self-oscillation in 0.5 Hz. The maximum frequency (0.5Hz) of the novel gel was 20 times higher than that of the conventional-type self-oscillating gel. Moreover, we showed that the displacement of the self-oscillation for the gel has a trade-off relationship against the frequency of the self-oscillation.

I. INTRODUCTION

Recently, many actuators based on intelligent materials have been developed. Especially stimuli-responsive polymers and gels that have a unique nature of volume change in response to external stimuli such as a temperature [1], pH [2], electric field [3], light [4], etc. are expected for applying to the many actuation devices because of the light weight, the flexibility and the low noise, etc. In the past, many chemomechanical systems converting chemical energy to mechanical energy have been demonstrated. Since volume phase transition of polymer gels was found by Tanaka [5], applications of polymer gels such as a drug delivery system[6], robotic hands [7] and matter transport device [8], have been proposed in various field. The phase transitions of polymer gels are induced by coulomb, hydrophobic, van der Waals interactions and hydrogen bonds. For major example, poly(N-isopropylacrylamide) (PNIPAAm), which is a thermo-sensitive polymer, undergoes a discontinuous volume change along with rising

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temperature. In application, a microfludic device using MEMS technology and PNIPAAm, could absorb proteins from solution and release them due to the adsorption change of PNIPAAm by controlling resistive heating [9]. And recently, there are numbers of studies on robotics with intelligent materials [10-11]. However, the applications made of the stimuli-responsive polymer gels require complex interconnections or external control devices because the triggers for driving the actuators are the external physicochemical signals. On the other hand, organic systems can generate the autonomous motion without external stimuli. If such system is to be achieved in an artificial system, a novel actuation device that does not depend on external control would be realized. In recent years, for understanding and mimicking the spontaneous mechanical works, self-oscillating gels and polymer chains was developed and researched from the view points of both experimental and theoretical research [12-18]. The driving force of the self-oscillating polymer systems is produced by the dissipating chemical energy of self-oscillating reaction, i.e., the Belouzov-Zhabotinsky (BZ) reaction or the pH oscillating reaction [19-21].

In our previous studies, we synthesized the self-oscillating polymer gels [22-24] and polymer chains [25-29] that was composed of PNIPAAm main chain covalently-bonded to the [Ru(bipyridine)2(4-vinyl-4 '-methyl bipyridine)] (Ru (bpy)$_3$) for a catalyst of the BZ reaction. In the BZ reaction, the solubility of the Ru(bpy)$_3$ moiety in the polymer system periodically changes in the oxidized and the reduced state. The periodic solubility change of the Ru(bpy)$_3$ moiety in the polymer system caused the swelling － deswelling self-oscillation for the polymer gels (see Figure 1) and the aggregation-disaggregation self-oscillation for the polymer chains. Therefore, the self-oscillating polymer system are expected for new concept applications such as soft robots, artificial muscle and self-beating pump to discharge drugs in MEMS, etc. Actually, we have proposed and realized autonomous gel systems such as a self-walking gel and a dynamic motion of a gel actuator [23-24]. (see Figure 2) However, in order to apply the conventional-type self-oscillating gel to the many types of the actuators, the speed of the swelling－deswelling self-oscillation is too slow because the period of the self-oscillation for the poly(NIPAAm-co-Ru(bpy)$_3$ gel is about 1 minute. If we can decrease the period of the self-oscillation, the autonomous gel systems will have a much broader range of applications. One method to overcome this
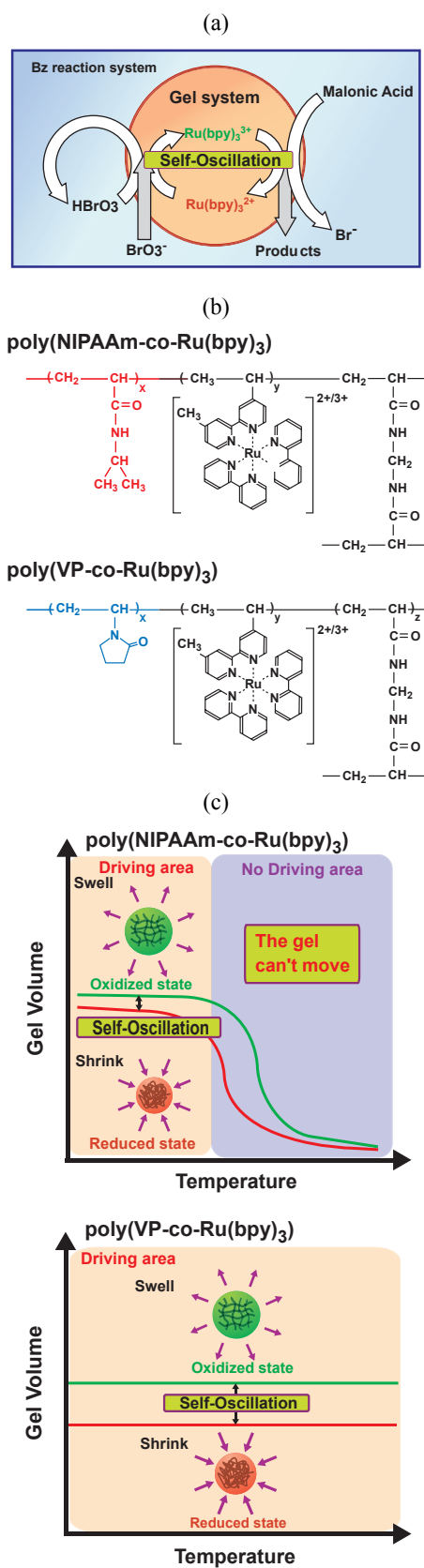
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(a)

(b)

poly(NIPAAm-co-Ru(bpy)₃)

poly(VP-co-Ru(bpy)₃)

(c)

poly(NIPAAm-co-Ru(bpy)₃)

poly(VP-co-Ru(bpy)₃)

Fig1. (a) The self-oscillating mechanism of polymer gel (b) Chemical structure of poly(NIPAAm-*co*-Ru(bpy)₃)gel and poly(VP-*co*-Ru(bpy)₃)gel (c) A conceptual diagram for conventional-type self-oscillating gel and novel self-oscillating gel.

problem is to raise the temperature in the driving environment so that the BZ reaction rate increases. However, the conventional-type self-oscillating gels shrinks at temperature of above LCST (Lower Critical Solution Temperature) because of the thermo-sensitive PNIPAAm main chain in the polymer gel (See Figure 1(c)). In order to realize the high-speed working, we attempted to synthesize a novel self-oscillating polymer gel that works without the temperature limitation. In this study, we selected a non-thermoresponsive and biocompatible poly-vinylpyrrolidone (PVP) as the polymer main chain of the novel self-oscillating gel (poly(VP-*co*-Ru(bpy)₃ gel) (see Figure 1)). As a result, we firstly succeeded in causing the swelling — deswelling self-oscillation at the high temperature condition. We studied the influence of the initial concentration of the three BZ substrates other than the metal catalyst and the temperature on the period of the self-oscillation. As a result, we clarified that the period of the self-oscillation for the novel gel can be controlled by the selection of the initial concentration of the three BZ substrates (malonic acid (MA), sodium bromated (NaBrO₃) and nitric acid) and the temperature. Moreover, by optimizing the initial concentration of the BZ substrates and the temperature, we first succeeded in causing the swelling — deswelling self-oscillation in 0.5Hz. This frequency (0.5Hz) of the novel gel was 20 times higher than that of the conventional-type self-oscillating gel (poly(NIPAAm-*co*-Ru(bpy)₃ gel).

II. EXPERIMENTAL SECTION

A. Synthesis of the poly(Vinylpyrrolidone -co-Ru(bpy)₃) gel.

The gel was prepared as follows. 0.110g of Ru(bpy)₃ as a metal catalyst for the BZ reaction was dissolved in 0.877g of vinylpyrrolidone (VP). 0.012g of N,N'-methylenebisacrylamide (MBAAm) as a cross-linker, and 0.020g of 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator were dissolved in the methanol solution (3ml) (Figure 3). The two solutions were mixed together well, and then the mixed solution purged with dry nitrogen gas. The monomer solution was injected between Teflon plates separated by silicone rubber as a spacer(thickness:0.5nm), and then polymerized at 60°C for 18hours. After gelation, the gel strip 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. Measurements of the equilibrium swelling ratio of gels

The equilibrium swelling ratio of the gels was measured under the reduced and oxidized state, by using the oxidizing and reducing agents. Gels were put into two solutions of Ce(III) and Ce(IV) under the same acidity, $[Ce_2(SO_4)_3]$=0.001M and $[HNO_3]$=0.3M; $[Ce_3(SO_4)_2]$=0.001M and $[HNO_3]$=0.3M, respectively. The equilibrium swelling ratio of the gels was observed and recorded by using a microscope (Fortissimo Corp.WAT-250D), a LED light (LEDR-74/40 W), and a

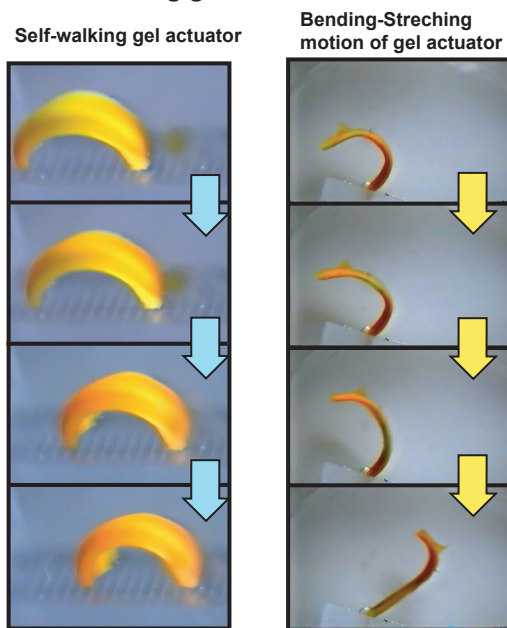video recorder (Victor corp. SR-DVM700). The
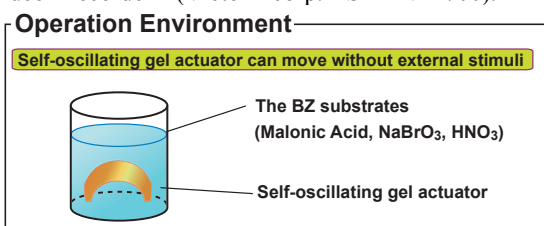
Fig. 2. Chemical robots made by self-oscillating polymer gel.

analysis was conducted by using the image processing software (Image J 1.38x). Measurements of the equilibrium swelling ratio were performed in a water-jacketed cell made of acrylic plates.

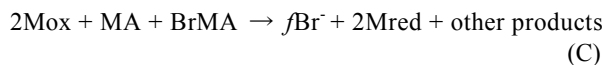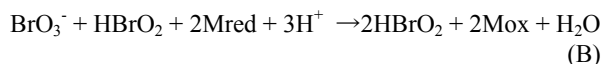*C. Measurements of the oscillating behavior of gels.*

The gel membrane was cut into rectangles(side length, about 2×20 mm) and immersed into 8mL of an aqueous solution containing malonic acid (MA), sodium bromate (NaBrO$_3$), and nitric acid (HNO$_3$). Shape changes of the gel strip were observed and recorded using a microscope (OLYMPUS.IX71), and a video recorder (corp. SR-DVM700). The analysis was conducted by using the image processing software (Image J 1.38x). A one-pixel line along the length of recorded gel image was stored at the gel quickly turned time interval (0.05 s). The stored pixel line images were sequentially lined up as a function of time by the computer. This image processing procedure constructs a spatio-temporal diagram. From the obtained diagram, the time-dependent change in the gel edge was traced for observing the behavior of the volume change.

III. RESULTS AND DISCUSSION

Figure 3 shows the equilibrium swelling behaviors of the poly(VP-*co*-Ru(bpy)$_3$) gels in the Ce(III) and Ce(IV) solutions under the same acidic condition. In the Ce(III) solution, the gel kept a tinge of orange, which indicated that the copolymerized Ru(bpy)$_3$ moiety in the gel was in the reduced state. On the other hand, in the Ce(IV) solution, the gel color quickly turned from orange to green, which showed the Ru(bpy)$_3$ moiety in the gel had changed the reduced state to the oxidized state. In the oxidized state, the equilibrium volume of the gel was larger than that in the reduced state in all temperature conditions. This is because the solubility of the Ru(bpy)$_3$ moiety has significantly different properties in the oxidized and reduced states. The reduced Ru(bpy)$_3$ moiety in the gel has an extreme hydrophobic property. This property is attributed to the conformation of the bipyridine ligands surrounding the Ru ion, which induces the deswelling behavior. That is, the bipyridine ligands surrounding the Ru ion exert a greater influence on the solubility of the polymer chain in the reduced state compared with the ionization effect of the Ru ion [25-29]. On the contrary, the oxidized Ru(bpy)$_3$ part in the gel has a great hydrophilic property. This is because the change in the orientation of the bipyridine ligands surrounding the Ru ion disturbed the interaction among the Ru(bpy)$_3$ moieties in the polymer gel. The driving force of the swelling－deswelling self-oscillation is originated in the different solubilities of the Ru(bpy)$_3$ moiety in the reduced and oxidized states as shown in Figure 3. In the reduced state and oxidized state, there is no observation of the volume phase transition because of the PVP main chain of the gel without LCST.

Figure 4 shows the logarithmic plots of the period against the initial concentration of one BZ substrate under fixed concentration of the other two BZ substrates at a constant temperature ($T = 20$ °C). As shown in Figure 4, all the logarithmic plots have a good linear relationship. Therefore, the period [T (s)] of the swelling－deswelling self-oscillation can be expressed as a[substrate]^b, where a and b are the experimental constants and the brackets indicate the initial concentration. Moreover, as shown in Figure 4, the period of the self-oscillation has the saturation point at the following initial concentration: [MA] = 0.07 M (Figure 4a), [NaBrO3] = 0.5 M (Figure 4b), and [HNO3] = 0.7 M (Figure 4c). The period at the saturated point in Figure 4a is significantly higher than that in Figure 4b,c. This tendency can be explained by considering the mole fraction of the reduced Ru(bpy)$_3$ moiety in the gel. This is because the reduced Ru(bpy)$_3$ moiety in the gel has a significantly high hydrophobic property. Therefore, the number of the hydrophobic reduced Ru(bpy)$_3$ moiety in the gel exerts an influence on the self-oscillating behavior. The Field－Koros－Noyes (FKN) mechanism explains the overall process of the BZ reaction [21-22]. According to the FKN mechanism, the overall reaction is divided into the following three main processes: consumption of Br$^-$ ions (process A), autocatalytic formation of HBrO$_2$ (process B), and formation of Br$^-$ ions (process C).

$$BrO_3^- + 2Br^- + 3H^+ \rightarrow 3HOBr \tag{A}$$

$$BrO_3^- + HBrO_2 + 2Mred + 3H^+ \rightarrow 2HBrO_2 + 2Mox + H_2O \tag{B}$$

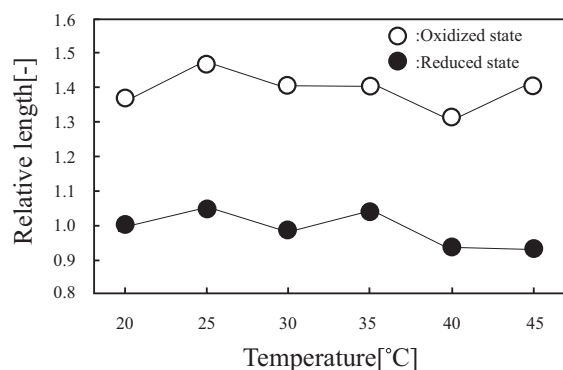$$2Mox + MA + BrMA \rightarrow fBr^- + 2Mred + other\ products \tag{C}$$

Fig. 3. Equilibrium swelling ratio of poly(VP-*co*-Ru(bpy)₃) gel in cerium sulfate Solutions as a function of temperature. (●) [Ce₂(SO₄)₃] = 0.001M and [HNO₃] = 0.3M; (○) [Ce(SO₄)₂] = 0.001M and [HNO₃] = 0.3M. The relative length is defined as the ratio of characteristic diameter at the initial state at 20°C.

In processes B and C, the Ru(bpy)₃ moiety in the gel works as the catalyst: the reduced Ru(bpy)₃ moiety is oxidized (process B), and the oxidized one is reduced (process C). Therefore, as the initial concentration of the MA increased, the mole fraction of the reduced Ru(bpy)₃ moiety in the gel increased in accordance with the FKN mechanism. With increasing in the mole fraction of the reduced Ru(bpy)₃ in the gel, the shrinking force originating in the hydrophobic reduced Ru(bpy)₃ greatly increased as well. Generally, as for a polymer gel, deswelling speed is faster than the swelling one. Once the gel collapses, it takes a lot of time for the aggregated polymer domain in the gel to recover the elongated state. This is because the polymer aggregation state is thermodynamically more stable in the polymer gel. Therefore, as the shrinking force increased, the swelling speed of the poly(VP-*co*-Ru(bpy)₃)gel significantly decreased. As a result, in the higher MA condition, the period at the saturated point was long (T = 182.5) compared with the other condition (T = 33.7 (Figure 4b) and T = 45.0 (Figure 4c). On the other hand, in the case of Figure 4b, the period at the saturated point was greatly shorter than that in Figure 4a. In the condition of Figure 4b, the swelling force originating in the hydrophilic oxidized Ru(bpy)₃ moiety increased due to the increase in the mole fraction of the oxidized Ru(bpy)₃ moiety in the gel in accordance with the FKN mechanism. Therefore, the gel can cause the swelling－deswelling self-oscillation at high speed due to the strong recovering force originated from the higher mole fraction of the hydrophilic oxidized Ru(bpy)₃ moiety in the gel. Moreover, under the conditions of Figure 4c, the period for the poly(VP-*co*-Ru(bpy)₃) gel had a different aspect from that of the conventional-type poly(NIPAAm-*co*- Ru(bpy)₃) gel [39]. The period of the self-oscillation decreased with the increase of the initial concentration of the BZ substrates because of the increase in the collision frequency among the BZ substrates. Therefore, we considered that the relationship between the period and the [HNO₃] for the poly(VP-*co*- Ru(bpy)₃) gel is of a more natural tendency. In addition, in the condition of Figure 4c, the control range of the period by changing the initial concentration of the HNO₃ for the gel was much wider than that for the poly(NIPAAm-*co*-Ru(bpy)₃ gel.
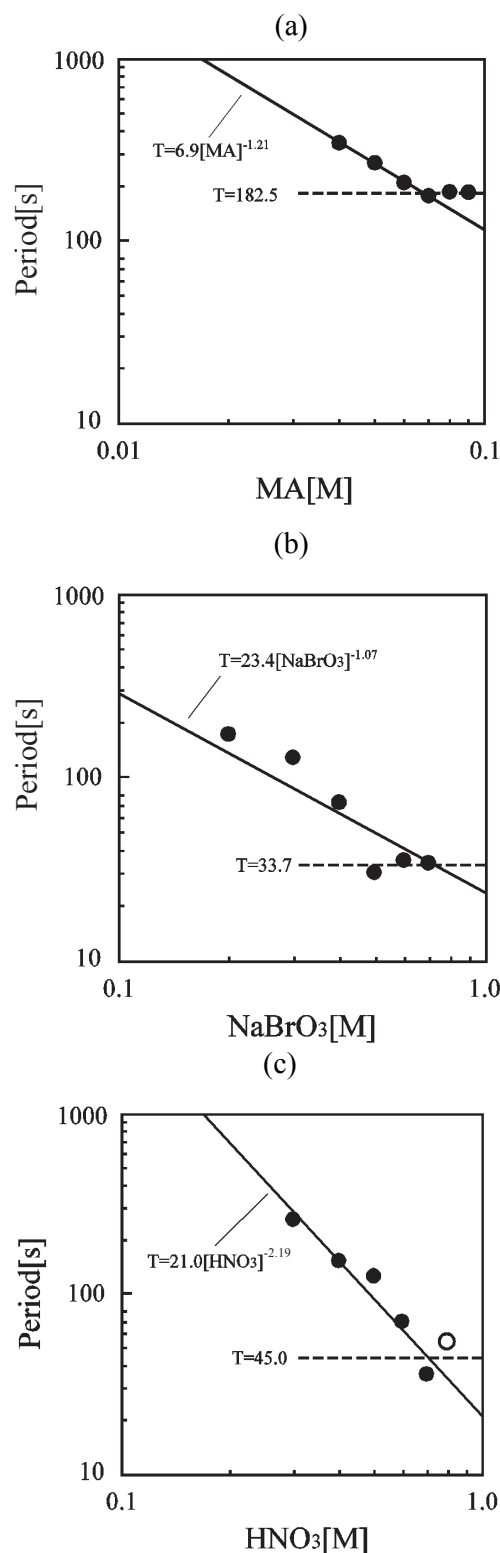

Fig. 4. Logarithmic plots of period (T in s) vs initial molar concentration of one BZ substrate at a constant temperature (T=20 °C) under fixed concentrations of the other two BZ substrates; (a) [NaBrO₃] = 0.084M and [HNO₃] = 0.3M, (b) [MA] = 0.0625M and [HNO₃] = 0.3M, (c) [MA] = 0.0625M and [NaBrO₃] = 0.084M. (●) plots and (○) plots show the linear relation and the saturated line vs initial concentration of one BZ substrate, respectively.
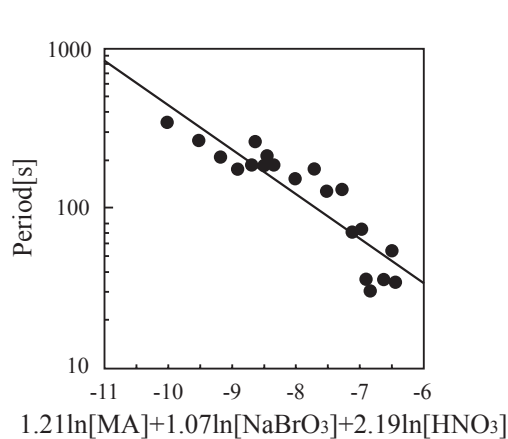
Figure 5. Period as a function of initial concentrations of malonic acid, sodium bromate and nitric acid for the poly(VP-*co*-Ru(bpy)₃)gel.

According to the linear relationship of the period [T(s)] in Figure 4, we obtained the following empirical relationship for the poly(VP-*co*-Ru(bpy)₃) gel as shown in Figure 5.

T = 0.048[MA]$^{-1.21}$ [NaBrO3]$^{-1.07}$ [HNO3]$^{-2.19}$

Furthermore, as shown in Figure 6, the period of the swelling－deswelling self-oscillation decreased with the increasing the temperature because the temperature affects the BZ reaction rate in accordance with the Arrhenius equation. The period of the swelling － deswelling self-oscillation to the temperature for the poly(VP-*co*-Ru(bpy)₃) gel has the linear relationship. The period (2 second) reached the saturation at 46 ˚C in the BZ condition ([MA] = 0.08M, [NaBrO₃] = 0.48M and [HNO₃] = 0.48M). This is because the swelling－deswelling speed of the gel is slower than the changing rate of the redox states of the Ru(bpy)₃ in the gel. That is, the self-oscillating behavior for the gel cannot follow the changing the redox state of the Ru(bpy)₃ moiety. maximum frequency (0.5Hz) of the poly(VP-*co*-Ru(bpy)₃) The gel was 20 times higher than that of poly(NIPAAm-*co*-Ru(bpy)₃ gel [39]. The self-oscillating behaviors of the poly(VP-*co*-Ru(bpy)₃) gel at 20°C and 50°C were shown in the Figure 6(b) and 6(c), respectively. The displace of the volume change self-oscillation at 20°C and 50°C were about 10 μ m and 4 μ m, respectively. These results clarified that the displacement of the swelling－deswelling self-oscillation for the gel has a trade-off relationship against the period of the self-oscillation, that is, the length of the volume change declined with the decreasing the period. Therefore, we are investigating the corrective strategy for the trade-off relationship in order to realize autonomous soft actuators that cause the large deformation at the high speed. The results will be reported in IROS.

IV. CONCLUSION

We clarified the influence of the initial concentration of the BZ substrates and the temperature on the period of the swelling － deswelling self-oscillation for the novel poly(VP-*co*-Ru(bpy)₃) gel. The logarithmic plots of the period against the initial concentration of one BZ substrate under fixed the other two BZ substrates showed the good
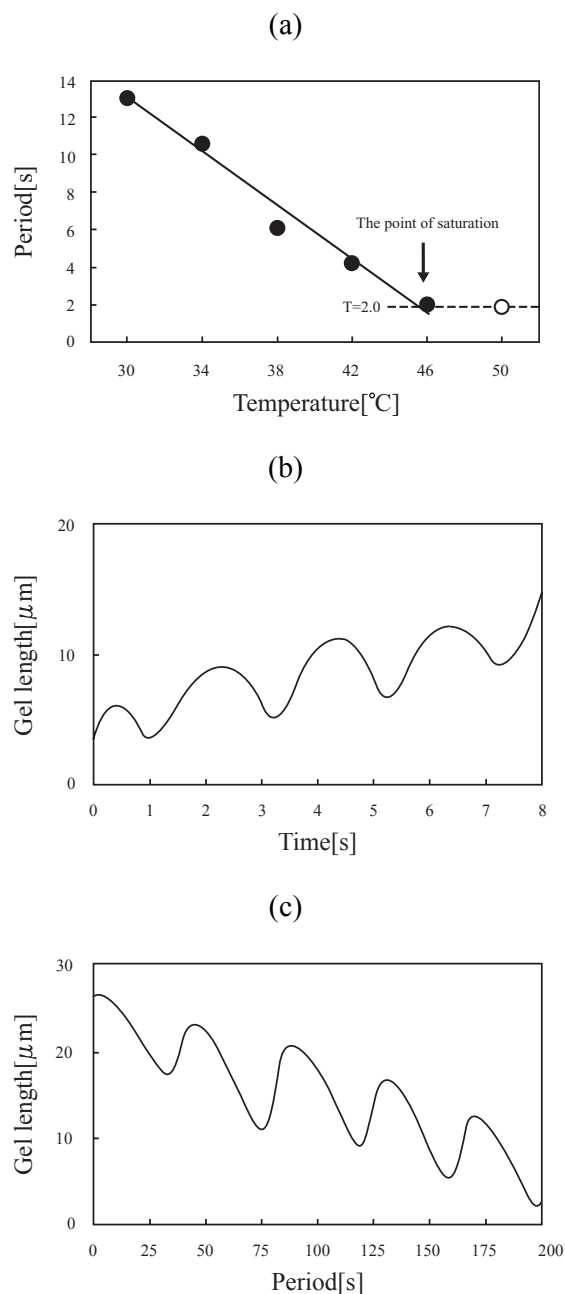
(a)

(b)

(c)

Figure 6. (a) Dependence of the self-oscillation period on the temperature. (●) plots and (○) plots show the linear relation and the saturated line vs temperature, respectively. (b) Self-oscillating profile of cubic poly(VP-*co*-Ru(bpy)₃) gel at 50˚C (MA = 0.08M, NaBrO₃ = 0.48M and HNO₃ = 0.48M). (c) Self-oscillating profile of cubic poly(VP-*co*-Ru(bpy)₃) gel at 20˚C (MA = 0.08M, NaBrO₃ = 0.48M and HNO₃ = 0.48M). Cubic gel (each side length is about 2mm and 20mm) was immersed in 8ml of the mixture solution of the BZ substrates.

linear relationships. Moreover, the period of the self-oscillation decreased with the increasing the temperature in accordance with the Arrhenius equation. The maximum frequency (0.5Hz) of the poly(VP-*co*-Ru(bpy)₃) gel was 20 times as large as that of poly(NIPAAm-*co*-Ru(bpy)₃ gel. Therefore, the period of the swelling－deswelling self-oscillation for the gel can be controlled in wide range by optimizing the initial

concentration of the three BZ substrates and the temperature. In addition, we showed that the displacement of the self-oscillation for the gel has the trade-off relationship against the period of the self-oscillation.

V. ACKNOWLEDGMENT.

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