In-Phase Synchronization of Chemical and Mechanical Oscillations in Self-Oscillating Gels

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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, which is known as an oscillating reaction accompanying a rhythmical change in the redox potential. The swelling−deswelling cycle of a miniature cubic poly(NIPAAm-*co*-$Ru(bpy)_3$) gel was found to be synchronized with the chemical oscillation without a phase difference. 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. 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. In the synchronization process, a feedback mechanism from mechanical to chemical oscillation was also suggested. 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

Stimuli-responsive gels undergo either swelling or deswelling transition when varying external conditions surrounding the gels such as a change in solvent composition,[1,2] pH,[3] temperature,[4,5] electric field,[6] etc. For example, thermo-sensitive hydrogels consisting of *N*-isopropylacrylamide (NIPAAm) swell by cooling and deswell by heating.[4,5] 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.[7−12]

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.[13−17] The mechanical oscillation in our gel system was produced via the Belousov−Zhabotinsky (BZ) reaction.[18−21] Under appropriate conditions, the BZ reaction shows autonomous oscillations in its redox potential. The overall process is the oxidation of an organic substrate such as citric or malonic acid with the coexistence of an oxidizing agent (e.g., sodium bromate) and metal catalyst in an acidic condition. The metal ion or the metal complex such as cerium ion, ferroin, or ruthenium tris(2,2′-bipyridine) ($Ru(bpy)_3$) are widely used as a catalyst. In the course of the reaction, the catalyst ion periodically oscillates between the oxidized and reduced states as long as the substrate exists. The BZ reaction has a reaction network similar to that of a metabolic reaction (TCA cycle), and the significance has been recognized as a chemical model for understanding some aspects of biological phenomena.[22]

We have succeeded in synthesizing an ionic gel consisting of the cross-linked NIPAAm chain to which $Ru(bpy)_3$ was covalently bonded. The BZ reaction occurring within the gel phase generates periodic redox changes of the catalyst moiety: $Ru(bpy)_3{}^{2+} \rightleftarrows Ru(bpy)_3{}^{3+}$. This 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 undergoes a periodical swelling−deswelling change.

By using the self-oscillating gel, we expect several applications to new functional biomaterials that work under dynamic oscillating states similar to those of living systems, such as automobile actuators, new pacemakers, etc. For these mechanical applications, it would be necessary to generate remarkable and powerful swelling−deswelling oscillations in gel volume. These considerations have led to our present attempt to enhance swelling−deswelling amplitude of the gel through studies on the conditions of the BZ reaction. Generally, the oscillation period of the BZ reaction increases as the initial concentration of substrates decreases.[23] Therefore, it is expected that the amplitude of swelling−deswelling oscillation is altered by changing the initial concentration of substrates.

In the previous report,[17] we 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 (i.e., "chemical waves") spontaneously evolves and propagates along the length by the reaction−diffusion mechanism. (Here the "rectangular gel" is defined as a gel whose length in the direction of the major axis is much longer than the wavelength (several millimeters typically) of chemical wave.) It is demonstrated by the mathematical model simulations that the change in the overall gel length (Δl) is equivalent to that in the remainder of gel length divided by the

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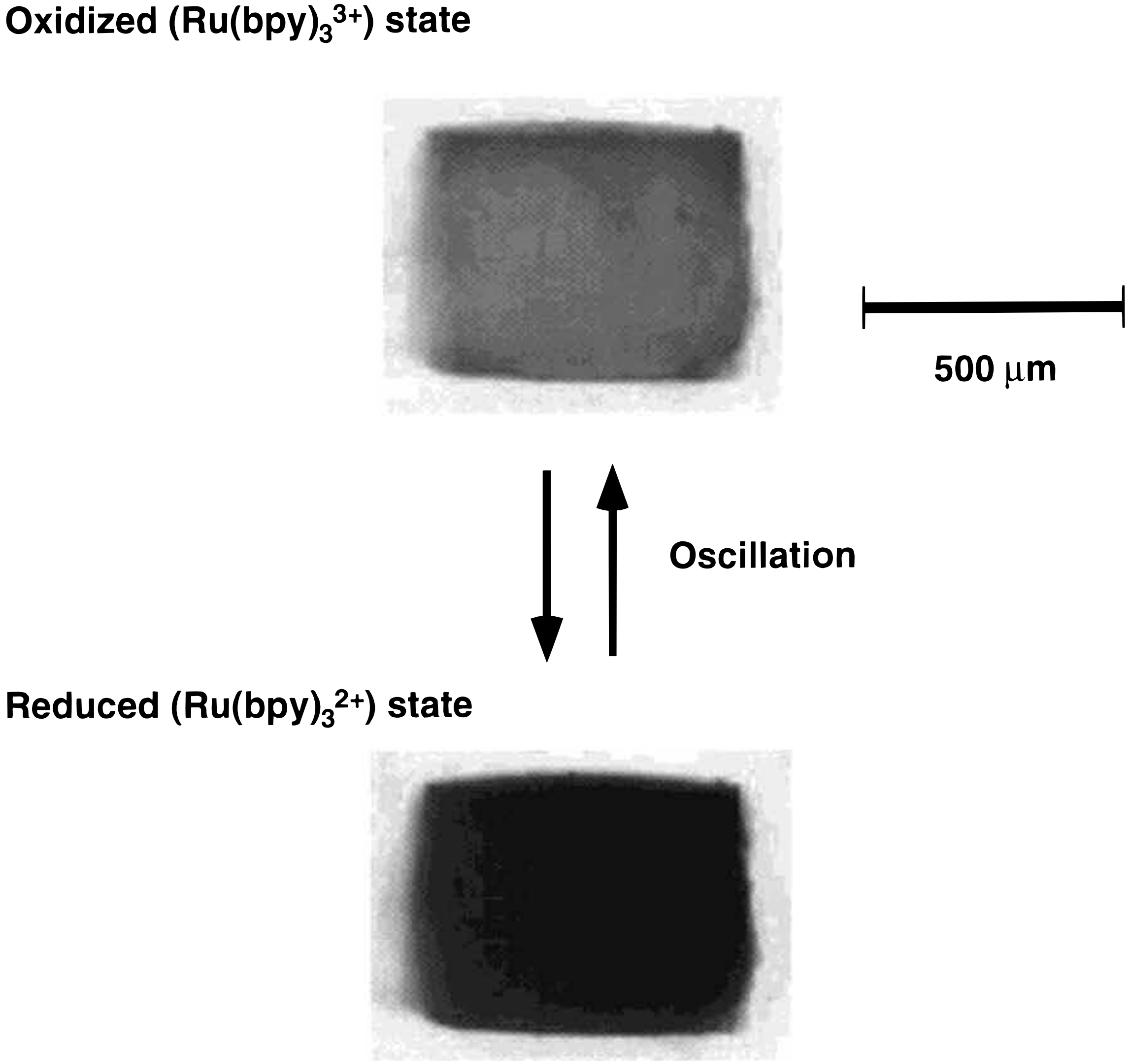

Figure 1. Images of the miniature cubic poly(NIPAAm-*co*-Ru(bpy)$_3$) gel undergoing redox changes. (Since the change of gel size is few percents, it is difficult to recognize the change of the size from this picture of the whole image. As for the actual size change, see Figure 2).

wavelength of the chemical wave (λ), i.e., Δl depends on mod(l/λ). This is because the swelling and the deswelling cancel each other per one period of oscillations under steady oscillating conditions. This means that the ratio of swelling−deswelling amplitude to the gel size decreases as the gel size increases.

Therefore, in this study, we deal with a miniaturized cubic poly(NIPAAm-*co*-Ru(bpy)$_3$) gel whose size is smaller enough than the wavelength of chemical wave. Within the miniature gel, the redox change homogeneously occurs without evolution of chemical waves. As for the miniature gel, the oscillating profiles of redox changes as well as the swelling−deswelling changes were analyzed by using an image-processing method. 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 Section

Materials. *N*-Isopropylacrylamide (NIPAAm; Eastman Kodak Co., Rochester, NY) was purified by recrystallization from its toluene solution with *n*-hexane. 2,2′-Azobisisobutyronitrile (AIBN; Wako Pure Chemical Industries, Co., Ltd., Osaka, Japan) was recrystallized from methanol. *N*,*N*′-Methylenebisacrylamide (MBAAm; Kanto Chemical Co., Tokyo, Japan) was used as received.

Preparation of Poly(NIPAAm-*co*-Ru(bpy)$_3$) Gels. Copolymer gels consisting of NIPAAm chains with covalently bound Ru(bpy)$_3$ residues were prepared according to our previous methods.[13] The Ru(bpy)$_3$ monomer was synthesized according to Ghosh and Spiro.[24] Both monomers of NIPAAm (0.156 g) and Ru(bpy)$_3$ (8.2 mg) were dissolved in 1 mL of O_2-free methanol, and then mixed with 2.8 mg of MBAAm and 6.6 mg of AIBN. This monomer solution was quickly injected into a space (0.5 mm) between two Mylar sheets which had been backed by a glass plate and separated by a Teflon spacer. The gelation was carried out at 60 °C for 18 h. To remove unreacted monomers, the gel membrane obtained was immersed in pure methanol for a day without stirring; this procedure was allowed to continue for a week with fresh methanol. Finally, the purified membrane was carefully hydrated through dipping it in a graded series of water−methanol mixtures, for 1 day each in 25, 50, 75, and 100% (v/v) of water.

Measurements of Chemical and Mechanical Oscillation Profiles for Gels. The gel membrane was cut into a miniature cube (each side length 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. In general, sulfuric acid is used as an acidic medium in the BZ reaction. However, since the swelling difference between the reduced (Ru(II)) and the oxidized (Ru(III)) states was more remarkable in the nitric acid than in the sulfuric acid with the same concentration, we used nitric acid in the experiment (see ref 13). The swelling−deswelling oscillations of the gel accompanying the redox oscillations were observed under a microscope (Olympus BX-50) equipped with a black−white CCD camera (SONY, model SSC-M370) and a video recorder (Panasonic, model AG-6760). We used monochromatic light passed through a blue filter (Kenko B-390) on the halogen light source. Color changes due to the periodical oxidation and reduction of the $Ru(bpy)_3$ moieties within the gel were measured by means of transmitted light. The time-dependent change in transmittance was then converted to gray-scale changes. The video images were transferred through a digital time base corrector (FOR.A, model FA-310) to a computer (NEC, model PC-9801RA) equipped with an image-acquisition board (MICRO-TECHNICA, MT98-MN). The redox reaction was thus recorded as 8-bit gray-scale changes. One-pixel line along the length of recorded gel image was stored at regular time intervals (3 s). The stored line images were sequentially lined up as a function of time on the computer. This image-processing procedure constructs a spatio-temporal diagram expressing both the redox changes in the gel and the displacement of the gel edge. From the diagram obtained, the swelling−deswelling profiles as a function of time were expressed as a track of the moving gel edge, and the time-dependent change in the oxidized fraction of $Ru(bpy)_3$ at a fixed position of the gel was expressed as 8-bit gray-scale changes by using the image processing software (NIH image 1.61).

Measurement of Oscillation Profiles in Bulk Solution. The oscillation of redox potential in the stirred aqueous BZ solution containing MA, $NaBrO_3$, HNO_3, and $Ru(bpy)_3Cl_2$ (0.33mM) were studied by the usual potentiometric method with a Pt electrode under air.

Results and Discussion

Self-Oscillation of Miniature Cubic Poly(NIPAAm-*co*-Ru(bpy)$_3$) Gel. The miniature cubic piece of poly(NIPAAm-*co*-Ru(bpy)$_3$) gel was immersed into an aqueous solution containing all the substrates (malonic acid, sodium bromate, and nitric acid) other than the catalyst. When the solution penetrates into the gel, the BZ reaction takes place within the gel phase with the aid of the $Ru(bpy)_3$ complex as the catalyst. As the reaction proceeds, the catalyst repeatedly changes between the oxidized (Ru(III)) and the reduced (Ru(II)) state.

In the miniature gel whose size is smaller enough than the wavelength of chemical wave (several millimeters under present conditions), the redox change of ruthenium catalyst can be regarded to occur homogeneously without pattern formation (Figure 1). The oxidation of the $Ru(bpy)_3$ moiety causes not only an increase in the swelling degree, but also a rise in the phase transition temperature of the poly(NIPAAm-*co*-Ru(bpy)$_3$) gel.[13−17] These characteristics may be interpreted by considering an increase in the cationic charges bound to the network due to the oxidation of Ru(II) to Ru(III) in the $Ru(bpy)_3$ moiety. This phenomena is identical with that generally observed in NIPAAm-based polyelectrolyte gels which their ionic charges were increased.[3] As a result, we may expect that our gel undergoes a cyclic swelling−deswelling alteration when the $Ru(bpy)_3$ moiety is periodically oxidized and reduced. Figure 2 shows the swelling−deswelling oscillations of the gel induced by the BZ reaction. The mechanical oscillations of the gel autonomously occurs with the same period as that of the redox oscillations. The swelling−deswelling change is isotropic, and the chemical and mechanical oscillations are synchronized without a phase difference (i.e., the gel exhibits swelling during the oxidized state and deswelling during the reduced state).

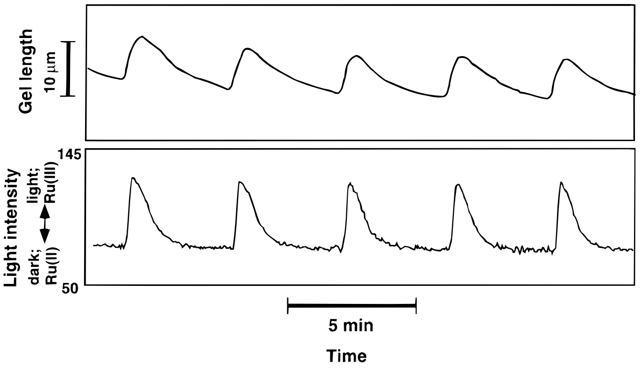

Figure 2. Periodical redox changes of poly(NIPAAm-*co*-Ru(bpy)$_3$) gel (lower) and the swelling−deswelling oscillation (upper) at 20 °C. Transmitted light intensity is expressed as an 8-bit gray-scale value. Outer solution: [MA] = 0.0625 M; [$NaBrO_3$] = 0.084 M; [HNO_3] = 0.6 M.

Change in Oscillating Behavior of the Gel with the Variation of Substrate Concentrations. It is common knowledge that the period of the BZ oscillations in solution systems varies depending on the initial concentration of the substrates.[23] The oscillation period increases with the decrease in concentration of substrates. The period should be an indicator for the overall reaction, through the measurement of which we tried to look at differences between the bulk and gel systems. In the research of the mechanism of the BZ reaction, a study of the period (T) as a function of initial concentrations of reactants has been made to provide a relatively simple test of the validity of a proposed mechanism and build a less detailed model for oscillations. As for the substrate concentration dependence of T with power law, experimental proof was given for MA−BrO_3^-−H_2SO_4−ferroin system by Smoes.[23] In our experiments, too, a good relationship has been obtained with the power law (Figure 3). 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 in s) and initial molar concentration of substrates[25] (the regions leading to stable oscillation: 0.05 M < [MA] < 2 M; 0.05 M < [$NaBrO_3$] < 1 M; 0.2 M < [HNO_3] < 1 M):

$$T_s = 2.97[\mathrm{MA}]^{-0.414}[\mathrm{NaBrO_3}]^{-0.796}[\mathrm{HNO_3}]^{-0.743} \quad (1)$$

The oscillation mechanism has been explained by the cyclic model composed of three sub-processes (FKN mechanism).[19−21] According to this mechanism, the overall reaction may be divided into the following three main processes: consumption of bromide ion (process A), autocatalytic reaction of bromous acid with oxidation of the catalyst (process B), and organic reaction with reduction of the catalyst (process C).

$$\text{process A: } \mathrm{BrO_3^-} + 2\mathrm{Br^-} + 3\mathrm{H^+} \rightarrow 3\mathrm{HOBr}$$

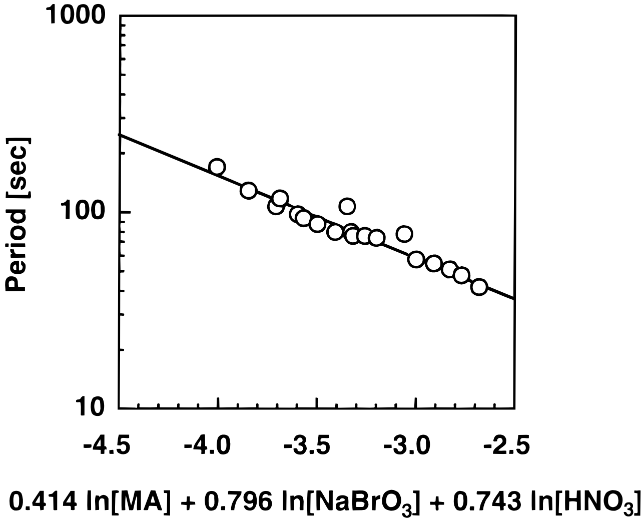

Figure 3. Period as a function of the initial concentrations of malonic acid, sodium bromate, and nitric acid for the bulk solution system.

$$\text{process B: } BrO_3^- + HBrO_2 + 2M_{red} + 3H^+ \rightarrow 2HBrO_2 + 2M_{ox} + H_2O$$

$$\text{process C: } 2M_{ox} + MA + BrMA \rightarrow fBr^- + 2M_{red} + \text{other products}$$

In eq 1, T_s is more sensitive to $[BrO_3^-]$ than [MA]. This is because process A, corresponding to the consumption of bromide ions, becomes a dominant factor in increasing the period. In the previous study,[25] we investigated the concentration dependence of the period for the reaction−diffusion system by inducing the BZ reaction in a rectangular poly(NIPAAm-*co*-Ru(bpy)$_3$) gel under conditions that chemical waves evolve and the total gel volume changes little. For this gel system, the following relation was obtained (the regions leading to stable oscillation: 0.02 M < [MA] < 0.5 M; 0.02 M < $[NaBrO_3]$ < 0.5 M; 0.3 M < $[HNO_3]$ < 0.8 M):

$$T_g = 2.66[MA]^{-0.659}[NaBrO_3]^{-1.445}[HNO_3]^{0.311} \quad \text{(without mechanical oscillations)} \quad (2)$$

The difference between eqs 1 and 2 could be understood by considering the immobilization effect, i.e., difficulties in the diffusion or mass-transfer of the substrate (from the bulk to the gel) as well as the product (from the gel to the bulk) due to the immobilization of the ruthenium catalyst.[25] For example, HNO_3 has an opposite effect on the period of oscillations in the solution and the gel system. H^+ ions are consumed during both the formation of $HBrO_2$ (process A) and the oxidation of the Ru(II) (process B), but produced in the reduction of Ru(III) with MA (process C). Thus, little influence of $[HNO_3]$ due to the transfer of H^+ ions from the bulk to the gel phase would be observed.

If the $[HNO_3]$ in the surrounding solution increases, the concentration of NO_3^- within the gel phase would also increase. The increasing $[NO_3^-]$ would be compensated by decreasing concentration of other anions within the gel phase such as BrO_3^- and Br^-. That is, the increase in $[HNO_3]$ in the bulk solution leads to not only the increase in $[H^+]$ in the gel but also the decrease in $[BrO_3^-]$ and $[Br^-]$ there. As a result, the dependence of the period on $[HNO_3]$ in the gel system may become opposite to that in the solution system. From the comparison between eqs 1 and 2, it was found that higher concentration of BrO_3^- was necessary to produce the same oscillation period in the gel than in the bulk solution.[25] The result may be interpreted not only by difficulty in diffusion of BrO_3^- from the bulk to the gel, but also by the effect of increasing NO_3^- in the gel as mentioned above.

In the case of the miniature cubic gel which undergoes mechanical swelling−deswelling oscillations, the relation becomes as follows (the regions leading to stable oscillation: 0.01 M < [MA] < 0.5 M; 0.08 M < $[NaBrO_3]$ < 0.5 M; 0.3 M < $[HNO_3]$ < 1.7 M):

$$T_g = 60.3[MA]^{-0.155}[NaBrO_3]^{-0.436}[HNO_3]^{0.469} \quad \text{(with mechanical oscillations)} \quad (3)$$

This concentration dependence is different from eq 2, although the same poly(NIPAAm-*co*-Ru(bpy)$_3$) gel was used. Yamaguchi et al.[26] reported that chemical oscillations are not induced when the thickness of gel is below the critical value. This is because the rate of decrease in concentration of chemical intermediates (such as $HBrO_2$, etc.) due to diffusion from the gel into the surrounding aqueous phase exceeds their production rate, resulting in conditions where oscillation cannot take place (i.e., dilution effect). In the case of the miniature gel, the dilution of intermediates must be more remarkable than in the rectangular gel because the size and aspect ratio of the gel is much smaller. The dilution effect, especially that for the activator ($HBrO_2$), leads to an increase in the period of chemical oscillations. As a result, the period becomes longer for the miniature gel than for the rectangular gel. This consideration well explains the difference between eqs 2 and 3. That is, (i) the proportionality constant in eq 3 (60.3) is much larger than that in eq 2 (2.66), and (ii) the absolute values of the powers for MA and $NaBrO_3$ in eq 3 (0.155 and 0.436, respectively) are smaller than those in eq 2 (0.659 and 1.445, respectively), which means that the period for the miniature gel is longer at the region of high concentration of substrates where the diffusion effect of substrates can be neglected ([MA] > 0.5 M, $[NaBrO_3]$ > 0.5 M). Other than the dilution effect, concentration change of substrates or products within the gel phase accompanying the swelling−deswelling oscillations may have some effects on the chemical oscillations. This feedback effect will be discussed later.

Since the change in substrate concentration varies the period of chemical oscillations, it is expected that the period and amplitude of swelling−deswelling oscillations of the gel are altered. From eq 3, it was found that T_g is most sensitive to $[HNO_3]$. Therefore, we attempted to increase the amplitude of swelling−deswelling oscillations by changing the concentration of HNO_3. Figures 4 and 5 show 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 0.6 M (see Figure 2) to 0.675 and 0.894 M, respectively. It was found that the period and amplitude of swelling−deswelling oscillations were increased with the increase in HNO_3 concentration.

In the bulk solution system, redox potential typically shows a sharp change from the reduced to the oxidized state followed by a more gradual return. According to the FKN mechanism,[19−21] the sharp switch from the reduced to the oxidized state is associated with the autocatalytic reaction in process B. In the gel, we can observe such a typical waveform of oxidation pulse (Figure 2) similar to that in bulk solution system. However, the waveform showed a tendency to deform to rectangular shape with a plateau period when the amplitude of swelling−

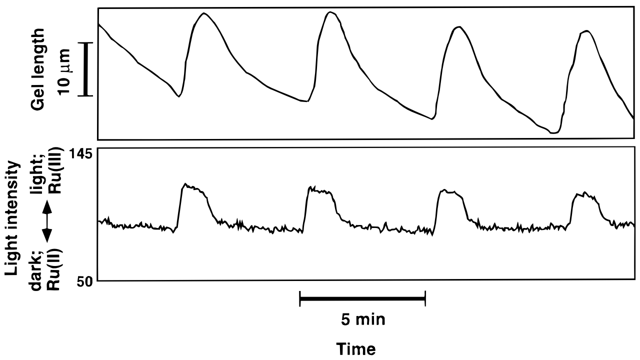

Figure 4. Periodical redox changes of poly(NIPAAm-*co*-Ru(bpy)$_3$) gel (lower) and the swelling−deswelling oscillation (upper) at 20 °C. Outer solution: [MA] = 0.0625 M; [NaBrO$_3$] = 0.084 M; [HNO$_3$] = 0.675 M.

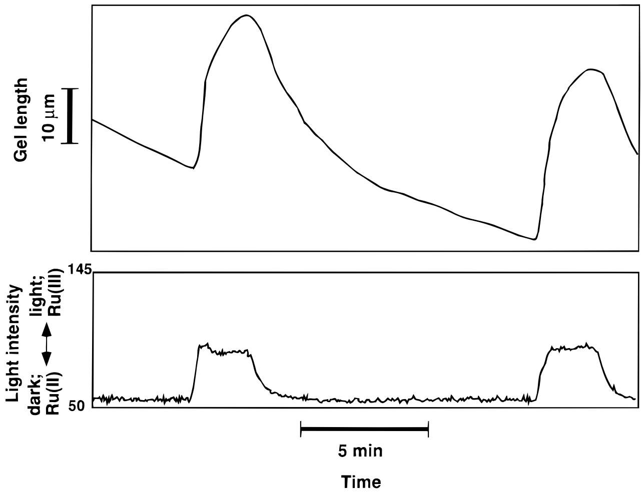

Figure 5. Periodical redox changes of poly(NIPAAm-*co*-Ru(bpy)$_3$) gel (lower) and the swelling−deswelling oscillation (upper) at 20 °C. Outer solution: [MA] = 0.0625 M; [NaBrO$_3$] = 0.084 M; [HNO$_3$] = 0.894 M.

deswelling oscillation increased (Figures 4 and 5). The wave deformation suggests that the reaction rate of reduction in process C is lowered. In the previous study,[25] we observed that the rate of reduction of the Ru(III) in process C becomes slow when the initial concentration of MA was low. The result could be understood by considering the difficulties in the diffusion or mass-transfer of MA from the bulk to the gel due to immobilization of the ruthenium catalyst. In the present study, however, [MA] is high enough to neglect such a diffusion effect. Therefore, the deformation of waveform may be caused by the dilution of MA within the gel phase due to the larger swelling (i.e., water uptake) of the gel during the oxidation process prior to process C. 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.

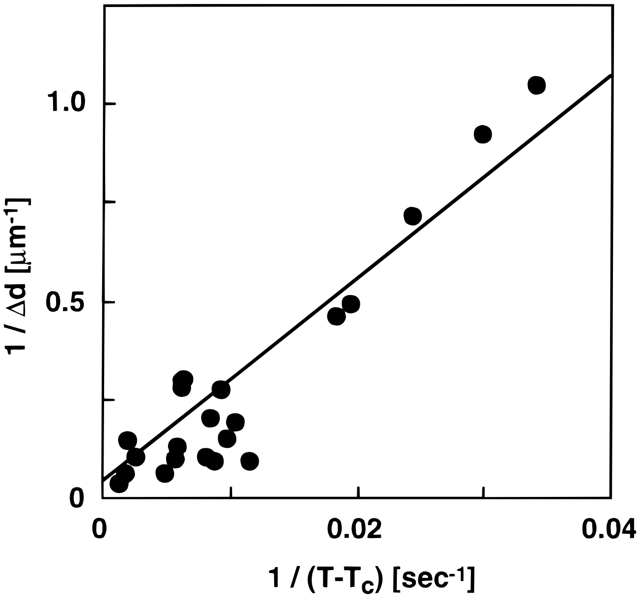

Figure 6. Dependence of the swelling−deswelling amplitude (Δ*d*) on the period of chemical oscillation (*T*). T_c is the critical period (= 94 s).

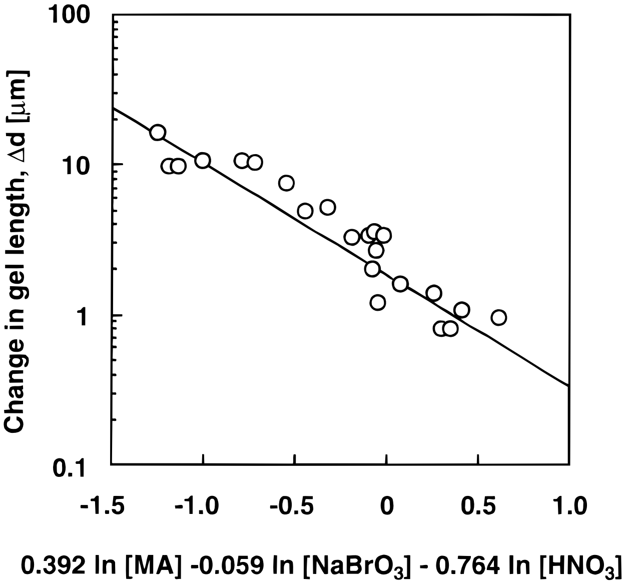

Figure 7. Dependence of the swelling−deswelling amplitude (Δ*d*) on the initial concentration of substrates.

Dependence of Swelling−Deswelling Amplitude on the Period, Redox Amplitude, and Initial Substrate Concentration. Figure 6 summarizes the correlation 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, Δ*d*) and the period of chemical oscillations (*T*) for several initial conditions with different substrate concentrations. There must be finite maximum value for Δ*d* because gel is a cross-linked polymer network. And also, if the redox oscillation occurs with very high frequency, mechanical change cannot follow the chemical oscillation. Therefore, the relationship between Δ*d* and *T* would be fitted by the following equation most well:

$$1/\Delta d = c/(T - T_c) + 1/\Delta d_{max} \tag{4}$$

where *c* is a constant, and Δd_{max} is the maximum value of Δ*d*. T_c is a critical period below which period mechanical oscillations are not observed, i.e., T_c means the minimum period of redox perturbation for the mechanical changes of gel to follow. The relationship means that Δ*d* 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 periodical redox changes is rate-determining for the mechanical oscillations.

Changing substrate concentration varies not only the period but also the amplitude of chemical oscillations[23] (i.e., the difference in mole fraction of Ru(III) between the most oxidized and reduced states in the redox oscillation). The variation of redox amplitude may also affect the swelling−deswelling amplitude of the gel. According to the Lambert−Beer law, the logarithm of the transmitted light intensity (I), which is expressed as an 8-bit gray-scale value by image-processing, is proportional to the concentrations of reduced catalyst (in our measurement system, the law becomes $-\ln(I/I_0) \propto [\mathrm{M_{red}}]$). It was apparent from the same image-processing method as ours that the shape of the concentration variations differed only slightly from that of the measured wave profiles of transmitted light.[27,28] Therefore, we can consider that the difference in light intensity between the most oxidized and reduced states in the redox oscillations (ΔI) corresponds to the degree of change in mole fraction of Ru(III). As a result of plotting Δd as a function of ΔI, the observed Δd and ΔI are related almost linearly. This means that the swelling−deswelling changes of the gel are amplified as the mole fraction of Ru(III) changes greatly in the chemical oscillation.

Figure 7 shows the dependence of Δd on the initial concentration of substrates. Empirically, the relation between Δd and the substrate concentrations can be expressed as follows:

$$\Delta d = 2.38[\mathrm{MA}]^{-0.392}[\mathrm{NaBrO_3}]^{0.059}[\mathrm{HNO_3}]^{0.764} \qquad (5)$$

The concentration dependence of Δd for each substrate is not equal to that of T (see eq 3). This is because Δd is affected not only by oscillation period but also by redox amplitude. From eq 5, it was found that Δd is negative dependence for [MA], almost independent of [BrO_3^-], and most sensitive to [HNO_3]. These results may be interpreted in connection with the eq 3 and the bifurcation behavior of chemical oscillation with changing substrate concentration. Characteristics of chemical reaction were investigated from the change in redox potential (E_{ORP}) for the bulk solution system. An increase in E_{ORP} means increasing concentration of oxidized catalyst, which corresponds to increasing intensity of transmitted light for the gel system. Figure 8 shows E_{ORP} for the bulk solution system as a function of one substrate concentration when the other substrate concentrations were fixed. At lower concentration, oscillation does not take place (steady state, SS). When the concentration exceeds a certain value, a stable and periodic oscillation takes place (oscillating state, OSC). At higher concentration, however, the oscillation stops and the solution becomes the steady state again. The amplitude of redox oscillation at OSC increases with an increase in catalyst concentration (data not shown here). From eq 3 and Figure 8a, the increase in [MA] decreases both the period and the amplitude of chemical oscillations. This results in negative dependence of Δd on [MA]. The increase in [BrO_3^-] decreases the period but unchanges or slightly increases the redox amplitude (see eq 3 and Figure 8b). These opposite effects compensate the dependence of [BrO_3^-], and results in independence of Δd on [BrO_3^-]. The increase in [HNO_3] increases both the period and amplitude of the chemical oscillations (see eq 3 and Figure 8c). These synergetic effects enhance the dependence on [HNO_3], and result in positive and strong dependence of Δd on [HNO_3].

From these results, it was 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. Figure 9 shows the swelling−deswelling oscillations of the gel in which larger content of Ru(bpy)$_3$ was introduced (10 wt % in feed). The change in gel size with ca. 20% to the initial gel size was obtained. This swelling−deswelling ratio is comparable to that of typical

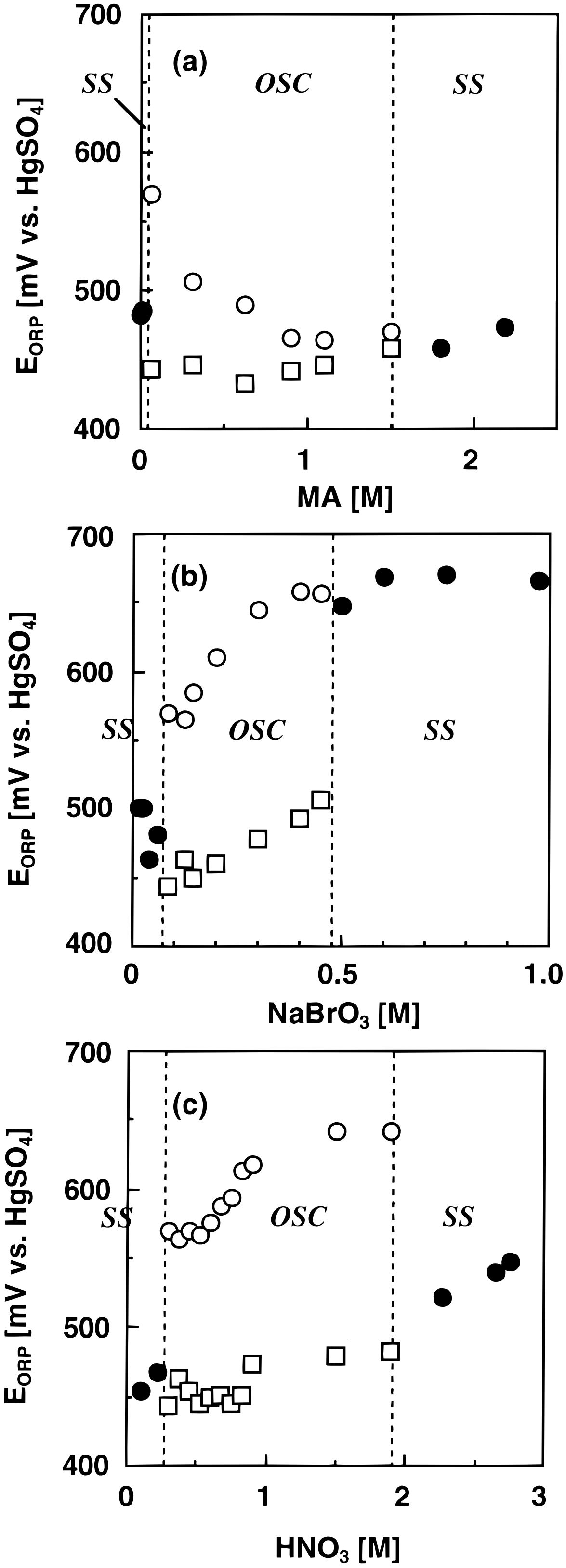

Figure 8. Bifurcation structure of the BZ oscillation in the bulk solution systems with the change in the initial concentration of (a) MA, (b) $NaBrO_3$, and (c) HNO_3. Open circle and open square mean the maximum and minimum values of redox potential in the BZ solution at the oscillating state (OSC). Closed circle means the redox potential at the nonoscillating (steady) state (SS). The concentrations of the other substrates were fixed at (a) [$NaBrO_3$] = 0.084 M, [HNO_3] = 0.3 M, (b) [MA] = 0.0625 M, [HNO_3] = 0.3 M, (c) [MA] = 0.0625 M, [$NaBrO_3$] = 0.084 M.

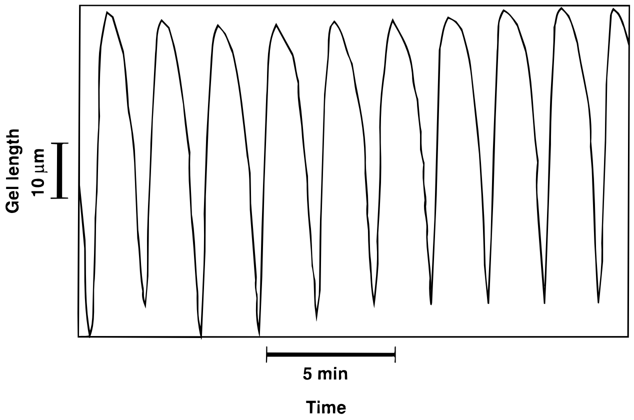

Figure 9. The swelling−deswelling oscillation for the poly(NIPAAm-*co*-Ru(bpy)$_3$) gel (Ru(bpy)$_3$ = 10 wt % in feed) at 20 °C. Outer solution: [MA] = 0.0625 M; [NaBrO$_3$] = 0.084 M; [HNO$_3$] = 0.894 M.

stimuli-responsive gels which have been studied for the application to actuators, etc. By the design of appropriate gel structure and reaction condition, new biomimetic materials may be possible.

Conclusions

For the miniature cubic poly(NIPAAm-*co*-Ru(bpy)$_3$) gel, the oscillating profiles of the swelling−deswelling changes as well as the redox changes were studied by using an image-processing method. The results obtained are summarized as follows. (i) The period of redox oscillation (T) depends on the initial concentration of substrates. In the gel system accompanied with mechanical oscillations, the concentration dependence of T was different from that 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. (ii) The swelling−deswelling amplitude of the gel (Δd) increased with an increase in the period and amplitude of the redox oscillations. (iii) There is a marked difference in the concentration dependence of Δd for each of the three substrates. This is due to not only the difference in the concentration dependence of period, but also the bifurcation behavior of redox oscillation with changing substrate concentration. In particular, a rise in HNO$_3$ concentration increases both the period and amplitude of the chemical oscillations, which results in positive and strong dependence of Δd on [HNO$_3$]. (iv) 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. Δd with ca. 20% to the initial size was obtained as the maximum value.

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