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Chemical Robots

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1. Introduction

A wide variety of soft actuators have been studied with the progress of the intelligent materials. Especially, stimuli-responsive polymers and gels which swell or shrink in response to the environmental changes such as temperature (Hirokawa & Tanaka, 1984), electric field (Tanaka et al., 1984), light (Suzuki & Tanaka, 1990)], etc have been applied to the actuation devices. In previous decades, researchers have demonstrated an energy conversion system transforming chemical energy into mechanical energy using collagen fibers (Tanaka et al., 1950). And also, since volume phase transition of gels was found, many kinds of applications such as, robotic hands (Hu et al., 1995), and matter transporting device (Yeghiazarian et al., 2005), have been studied in various fields. The phase transition of polymer gel is induced by hydrogen bonds, coulomb, hydrophobic and van der Waals interactions. Thus, by changing the external physicochemical conditions, these applications can be realized. For major example, poly(N-isopropylacrylamide) (PNIPAAm) is well-known to a thermo-sensitive polymer gel and exhibits a discontinuous volume change. In application, a microfluidic device using MEMS technology and PNIPAAm, could adsorb proteins from solution and release them due to the adsorption change of PNIPAAm by controlling resistive heating (Huber et al, 2003). Recently, there are numbers of studies on robotics with intelligent materials (Otake et al, 2002).

However, these systems need complex and fabricated circuits or external control devices because the function of the polymer gel is driven by on-off switchings of external physicochemical signals. On the other hand, in biological systems, there are several autonomic phenomena exhibiting spontaneous motion without any on-off switching of external stimuli such as peristaltic motion, heartbeat, brain waves, etc. If such system is to be achieved in an artificial system, a novel actuation device which does not depend on external control would be expected. Therefore, this novel system is a kind of molecular computing and which we call "Chemical Robotics." There is no need for the conventional mechanical assembly, wiring, and the electric source because the system is a self-organized system, which performs a chemical signal processing to control a chemomehcanical body like a biological system. However, there are few reports realizing such autonomous systems. As an attempt using cardiac muscle cells and synthetic polymers, researchers have demonstrated a self-walking bioactuator driven by the ATP solution (Feinberg et al, 2007). Although utilization of biopolymer or cell system is one possible way, our aim is to realize a completely artificial system.

In this book, we introduce self-oscillating gel actuators for chemical robotics. The polymer gel prepared here has a cyclic reaction network like metabolic process in itself. With a cyclic reaction, the gel exhibits a very small but significant volume change by the chemical energy (Yoshida et el, 1996). The periodic self-oscillating motion of the gel is produced by dissipating chemical energy of the oscillatory Belousov-Zhabotinsky (BZ) reaction (Zaikin et al., 1970). The BZ reaction is the most commonly known oscillating reaction. In an unstirred solution, the BZ reaction generates chemical waves and spatial pattern formations as a reaction-diffusion system. The overall process of this 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: $Ru(bpy)_3^{2+} \leftrightarrow Ru(bpy)_3^{3+}$. We have synthesized an ionic polymer gel which consists of the cross-linked PNIPAAm and ruthenium monomer of the metal catalyst of the BZ reaction. When the gel is immersed in the aqueous solution containing the substrate of the BZ reaction except for the catalyst, the substrate penetrates into the polymer network and the BZ reaction occurs in the gel. The polymer has the lower critical solution temperature (LCST) because of themosensitive constituent poly-NIPAAm. The LCST of the polymer in the oxidized Ru(III) state becomes higher than that in the reduced Ru(II) state due to the charge increase of the catalyst. At constant temperature, therefore, redox changes of the catalyst lead to hydrophilic changes of the polymer chains. Consequently, periodical redox changes induced by the BZ reaction produce periodical swelling-shrinking changes of the gel as shown in Figure 1. The displacement of the self-oscillating gel is several dozen micrometers and the period is from several dozen seconds to minutes (Yoshida et el, 1996) as shown in Figure 2. The displacement and period strongly depend on the initial concentrations of the BZ substrates and temperature.

In our previous work, we have designed the ciliary typed gel actuators (Maeda et al, 2004, 2006) by fabrication and molding of the self-oscillating gel as shown in Figure 3. Ciliary motion was generated by the chemical waves due to the reaction diffusion dynamics. Since the mechanical displacement of the actuator was very small and the interaction between the gel and the floor was strongly hydrophobic, the motility of the gel actuator was small.

To improve the motility of the gel, we have realized the large deformation of the gel with gradient structure. For this material design, we made a gradient structure in the gel using the hydrophobic interaction during the polymerization (Maeda 2007, 2008). Concretely, as the third component, hydrophilic 2-acrylamido-2-methylpropanesulfonic acid (AMPS) monomer was copolymerized into the polymer networks to make the gel lubricated and to cause concentration gradient in the gel as shown in Figure 4. During the polymerization, the monomer solution faces two different surfaces of plates: a hydrophilic glass surface and a hydrophobic Teflon surface. Since $Ru(bpy)_3^{2+}$ monomer is hydrophobic, it is easy to migrate to the Teflon surface side. As a result, a uniform distribution in the direction of the thickness is formed for the component, and the resulting gel has gradient distribution for the content of each component in the polymer network. At the surface side where the content of hydrophilic AMPS is higher, the swelling ratio of the gel becomes larger than that at the opposite side in the same gel where the content of hydrophobic $Ru(bpy)_3^{2+}$ is higher. Consequently, the gel in water bends to the direction of the surface which was faced to the Teflon plate during polymerization as shown in Figure 5. Finally we could observe the self-walking motion of the gel driven by the BZ reaction. Recently, we

In this book, we introduce our recent research of a self-motion of the gels and the gel actuators driven by the oscillating reaction.
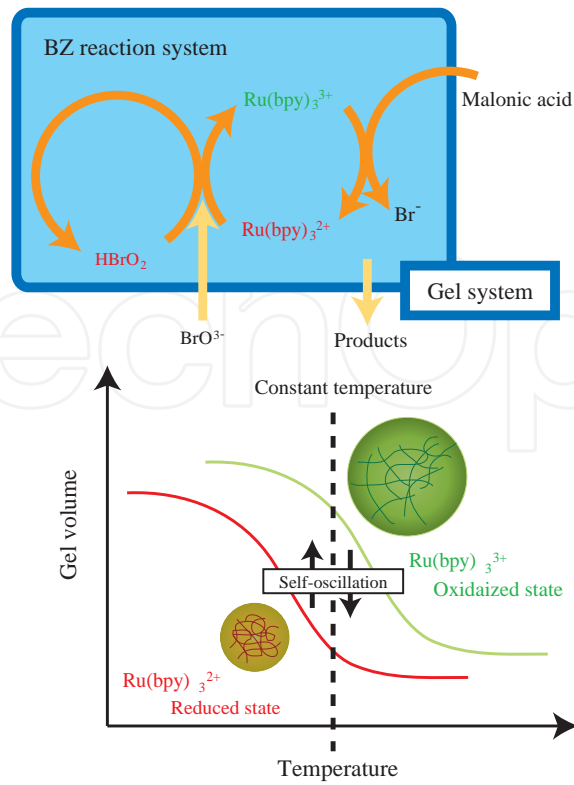
Fig. 1. Conventional oscillating gel.

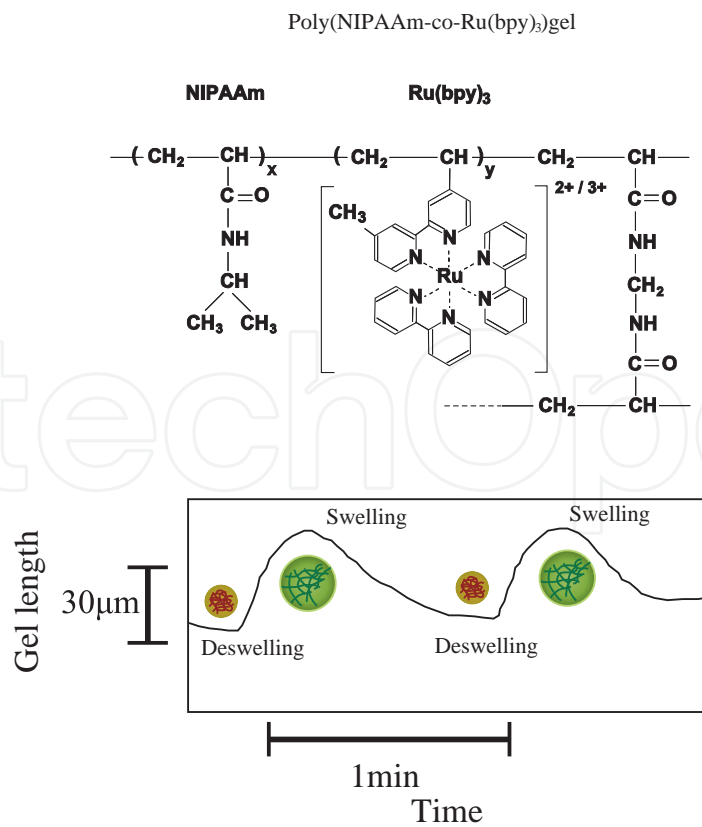Poly(NIPAAm-co-Ru(bpy)₃)gel

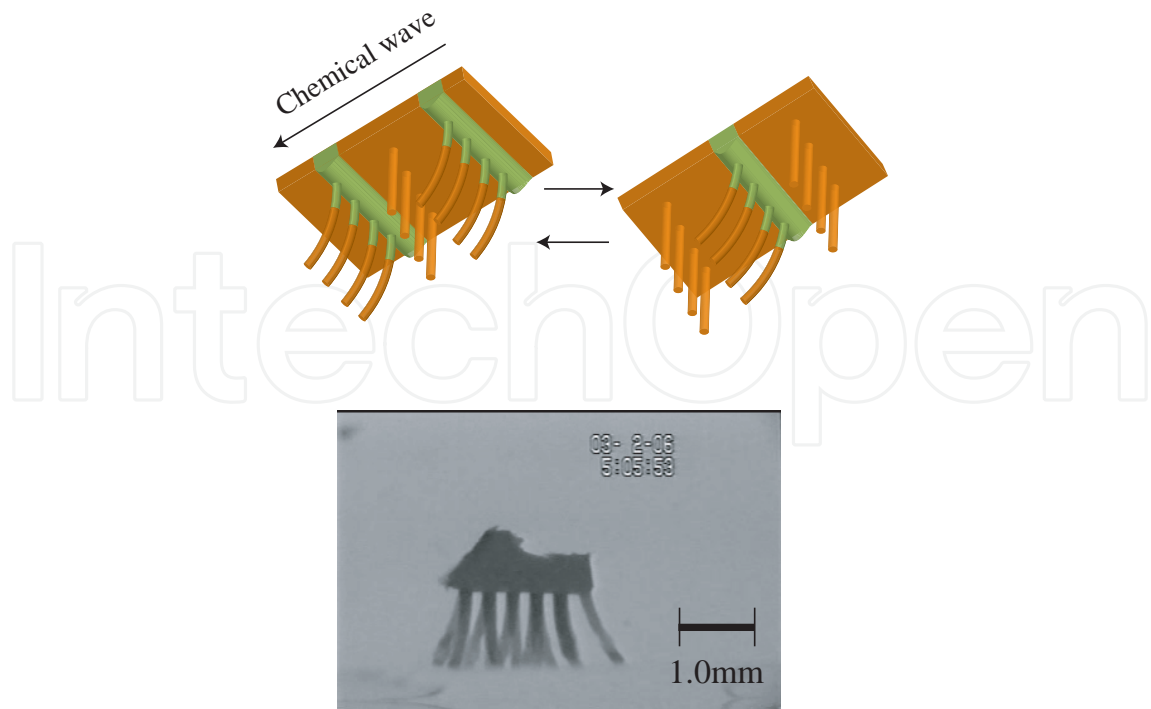Fig. 2. Chemical structure and oscillating behavior of self-oscillating gel.
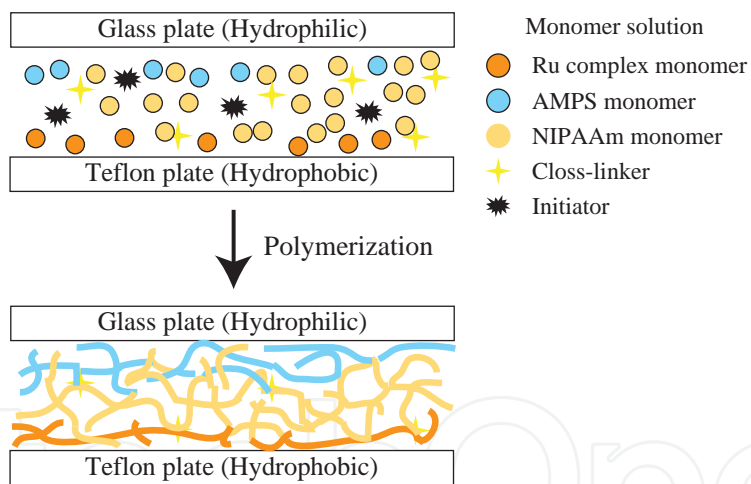
Fig. 3. Ciliary gel actuator.

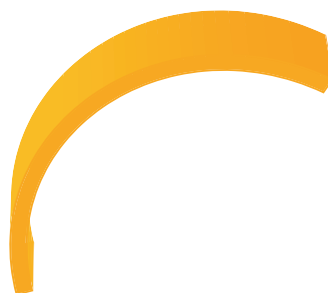Fig. 4. Preparation method of the poly (NIPAAm-co-Ru(bpy)$_3$-co-AMPS) gel with gradient structure.

Fig. 5. Illustration of the curved gel with gradient structure.

2. Design of chemical robots

2.1 Self-walking gel

For creating the large deformation of the gel, we introduced the gradient structure into the oscillating gel. To make the gradient structure in the gel, we used the hydrophobic interaction between the Ru(bpy)$_3^{2+}$ moiety and casting mold during the polymerization. As a result, the large periodical deformation of the gel coupled with the BZ reaction was achieved (Maeda et al, 2008). During the polymerization, the monomer solution faces two different surfaces of plates: a hydrophilic glass surface and a hydrophobic Teflon surface. Since Ru(bpy)$_3^{2+}$ monomer is hydrophobic, it is easy to migrate to the Teflon surface side. As a result, a uniform distribution in the direction of the thickness is formed for the component, and the resulting gel has gradient distribution for the content of each component in the polymer network. Thus, the hydrophilic AMPS component at the glass side was higher than that at the Teflon side. In contrast, the hydrophobic Ru(bpy)$_3^{2+}$ moiety at the Teflon side was higher than that at the glass side. Therefore, as for the gel at the AMPS rich side, the swelling ration was higher than that at the opposite side (at the Ru(bpy)$_3^{2+}$ rich side). Consequently the gel in water bends to the direction of the surface which was faced to Teflon plate during polymerization. The curvature in the oxidized state was larger than that in the reduced state all over the temperature range. This is because when the hydrophilicity of the polymer increases, the gel expands in the oxidized state. From the deviation of the curvature in the Ru(II) and the Ru(III) states, we expected that the gel caused the periodical bending-stretching motion induced by the BZ reaction at constant temperatures.
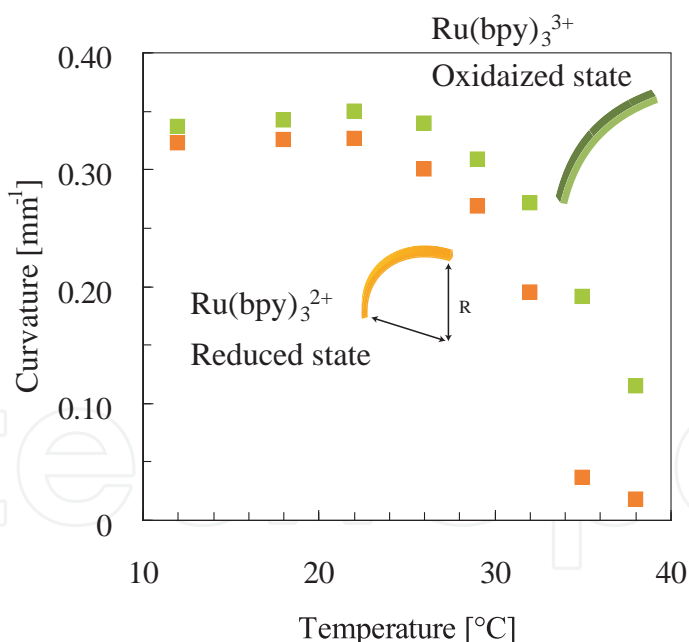

Fig. 6. Equilibrium swelling ratio expressed as curvature of the poly(NIPAAm-co-Ru(bpy)$_3$-co-AMPS) gel strip in cerium sulfate solutions as a function of temperature. Closed square: Ce$_2$(SO$_4$)$_3$ =0.005 M and HNO$_3$ = 0.894 M; Open square: Ce(SO$_4$)$_2$ = 0.005 M and HNO$_3$ = 0.894 M. The curvature is defined as 1/R. S. Maeda et al., Self-walking gel. *Adv. Mater.* 2007, 19, 3480-3484. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.

Figure 6 shows the periodical changes of gel motion in the aqueous solution containing the three reactants of the BZ reaction (malonic acid, sodium bromate and nitric acid) at the constant temperatures. The chemical wave evolves in the gel, and it propagates in the direction of the length at constant speed from one edge attaching the substrate to the other edge. With the propagation of the chemical wave, the distance between the two edges of the gel changes periodically because the spontaneous bending and stretching motion occurs (Figure 7). While the chemical wave exists in the gel (1→4), the gel stretches. After that, during the reduced state until the next wave appears (4→1), the gel bends. As shown in Figure 8, the displacement of the mechanical oscillation (Δl_{max}) changes with temperature because the difference in swelling ratio between reduced state and oxidized state depends on temperature. We can see that there is the optimum temperature (18°C) at which the amplitude becomes the maximum. To convert the bending and stretching changes to the vectorial work, we applied ratchet mechanism to our gel system. We prepared the ratchet floor with asymmetrical surface structure as shown in Figure 9. On the ratchet floor, the gel repeats bending and stretching autonomously, but sliding backwards is prevented by the teeth of the ratchet. As a result, the gel could move forward. Figure 10 shows successive profiles of the "self-walking" motion of the gel in the BZ reaction (Maeda et al, 2007). The period of chemical oscillation was about 112sec, and the walking velocity of the gel actuator was about 170μm/min.
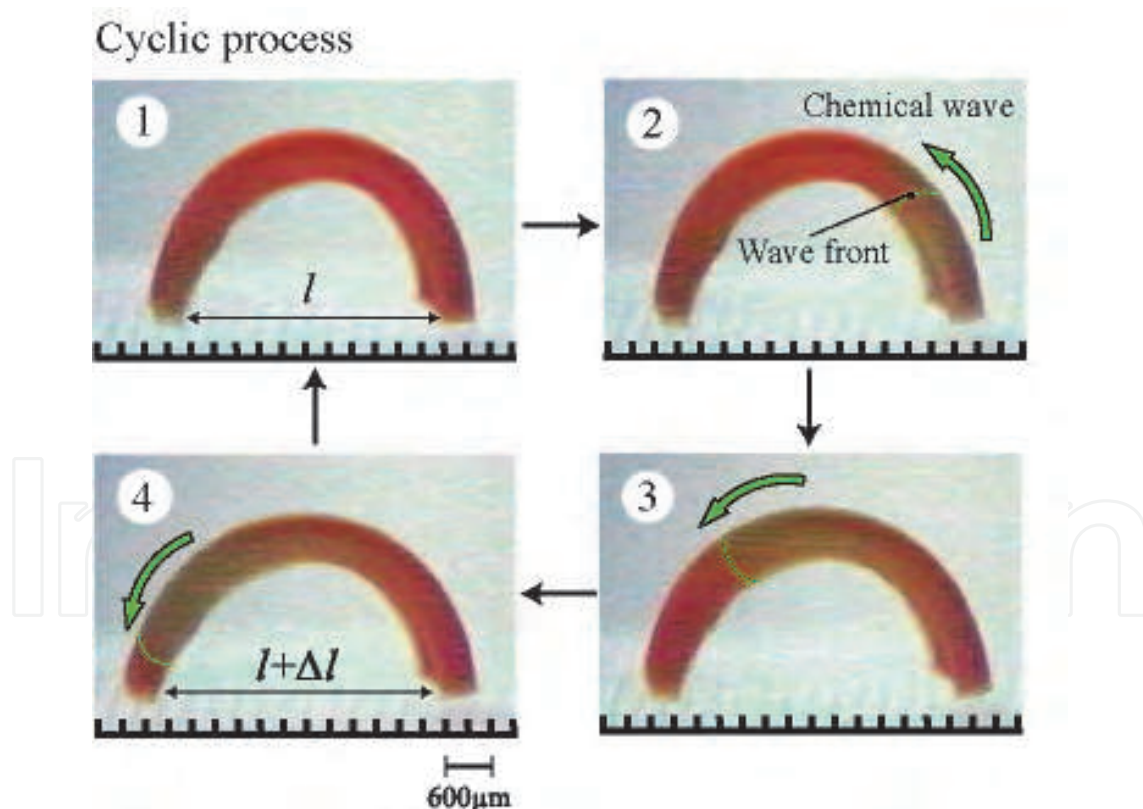

Fig. 7. Oscillating profiles of the bending-stretching motion for the gel. *l* is the direct distance between two edges of the curved gel strip at reduced state. Δl is the displacement of the direct distance when chemical wave propagates in the gel. S. Maeda et al., Self-walking gel. *Adv. Mater.* 2007, 19, 3480-3484. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.
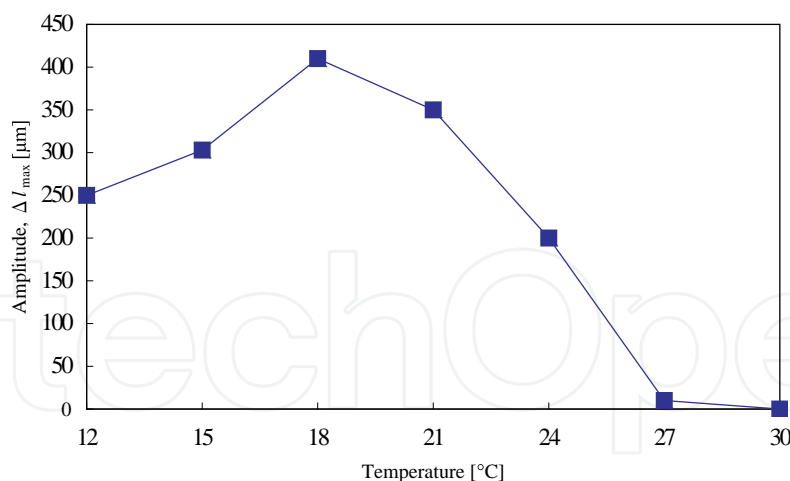
Fig. 8. Dependence of amplitude (the maximum of displacement, Δl_{max}) on temperature. S. Maeda et al., Self-walking gel. *Adv. Mater.* 2007, 19, 3480-3484. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.
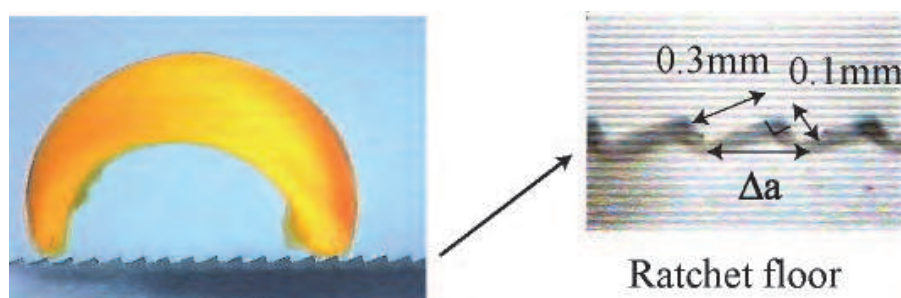

Fig. 9. Surface structure of the ratchet floor made of acrylic sheet. Δa stands for the interval of the ratchet teeth. S. Maeda et al., Self-walking gel. *Adv. Mater.* 2007, 19, 3480-3484. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.

2.2 Peristaltic motion of polymer gel

Next, we tried to create the peristaltic motion coupled with the chemical wave directly. In previous work, however, it was difficult to observe the peristaltic motion coupled 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 (Yashin et al, 2006). Most recently, we first succeeded in observing the peristaltic motion of the gel (Maeda et al, 2008) directly by utilizing a novel gel with a porous structure. We focus on the kinetics of the polymer gel. The network motion of the gel was given by Tanaka, Hocker and Benedek (Tanaka et al, 1973), which is described as the cooperative diffusion. 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
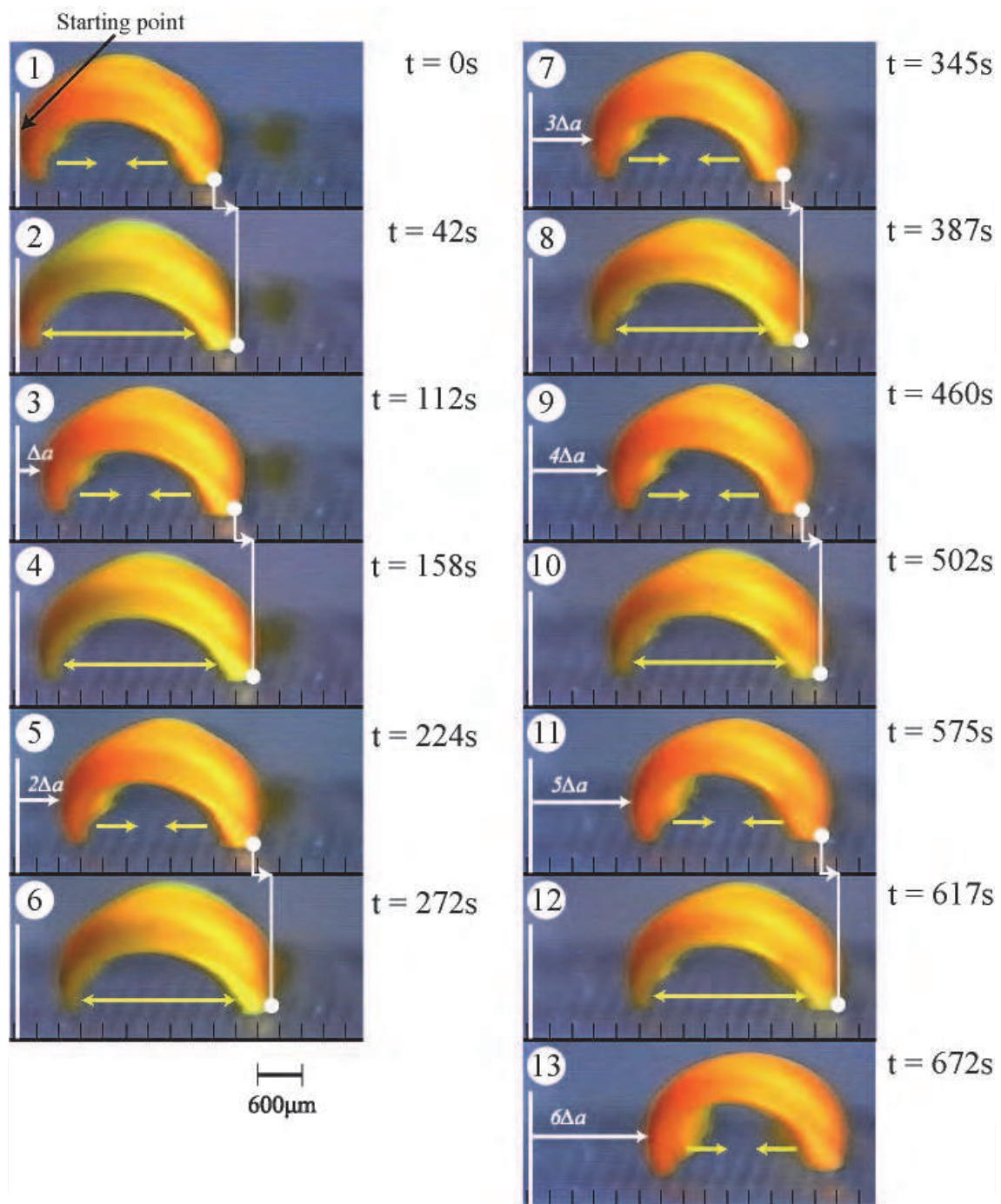
Fig. 10. Time course of self-walking motion of the gel actuator (odd number: bending process at the reduced state, even number: stretching process with propagation of chemical wave). During stretching process, the front edge can slide forward on the floor, but the rear edge is prevented from sliding backwards. Oppositely, during bending process, the front edge is prevented from backwards while the rear edge can slide forward. This action is repeated spontaneously, and as a result, the gel walks forward. In one period of the oscillation, the gel can take a step forward by Δa. Outer solution: 62.5 mM malonic acid, 84mM sodium bromate, 0.894M nitric acid, 18°C. S. Maeda et al., Self-walking gel. *Adv. Mater.* 2007, 19, 3480-3484. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.

mentioned. Therefore, the poly(NIPAAm-*co*-Ru(bpy)$_3$) self-oscillating gel generated the small mechanical oscillation. In order to produce the large mechanical oscillation in comparison with the gel size, the self-oscillating gel has to response firstly to the rate of the BZ reaction. For realizing this purpose, we prepared the microphase-separated self-oscillating gel. That is because that, in the previous work, it was reported that the NIPAAm gel with micro scale phase separation underwent quick response (Kabra et al, 1991). 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 that consists of two regions: one is polymer rich domains, and the other is 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 11. 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 selecting the synthesis temperature. 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. Generally, in the mixed solvent of water and methanol, the LCST of aqueous PNIPAAm solutions shifts to lower temperature (Hirotsu 1986, Tanaka 2009). So, it is assumed that the micro phase separated structure was introduced inside the gel.

As shown in Figure 12, the swelling speed of the microphase-separated self-oscillating 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 microphase-separated self-oscillating 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 13 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. The displacement of the volume oscillation for the microphase-separated self-oscillating gel is about ten times as large as that for the poly(NIPAAm-*co*-Ru(bpy)$_3$) gel. This result indicated 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.

Figure 14 shows the periodical peristaltic motion of the gel driven by the chemical waves of the BZ reaction. We first 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 aspects of the volume change of the gel followed the reaction diffusion dynamics. The chemical wave speed of the BZ reaction was approximately 14.0-30.0µm/sec in the gel.
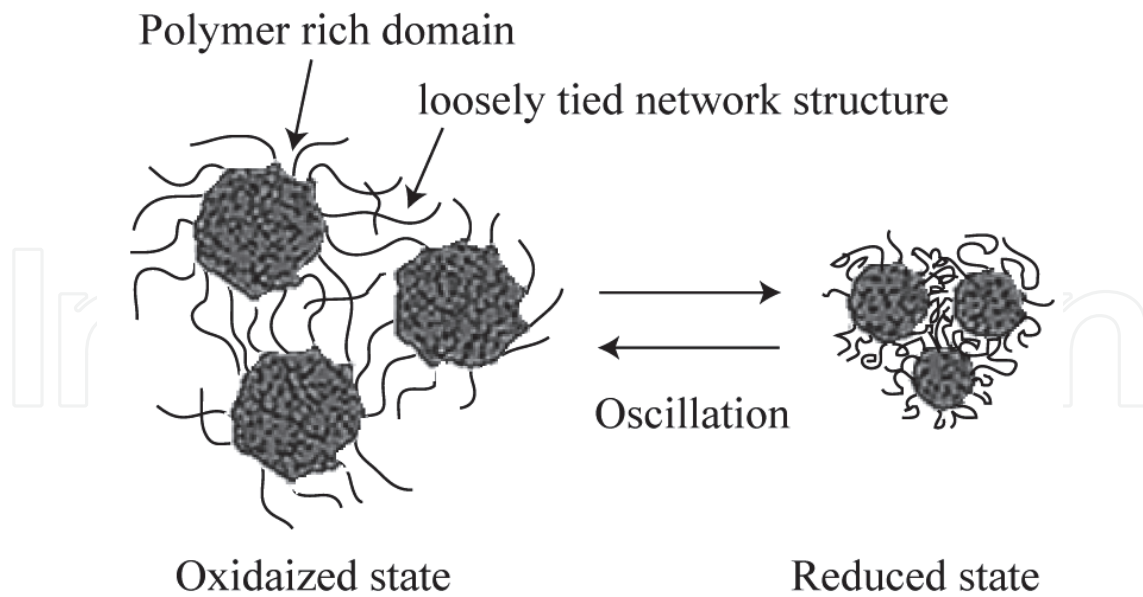
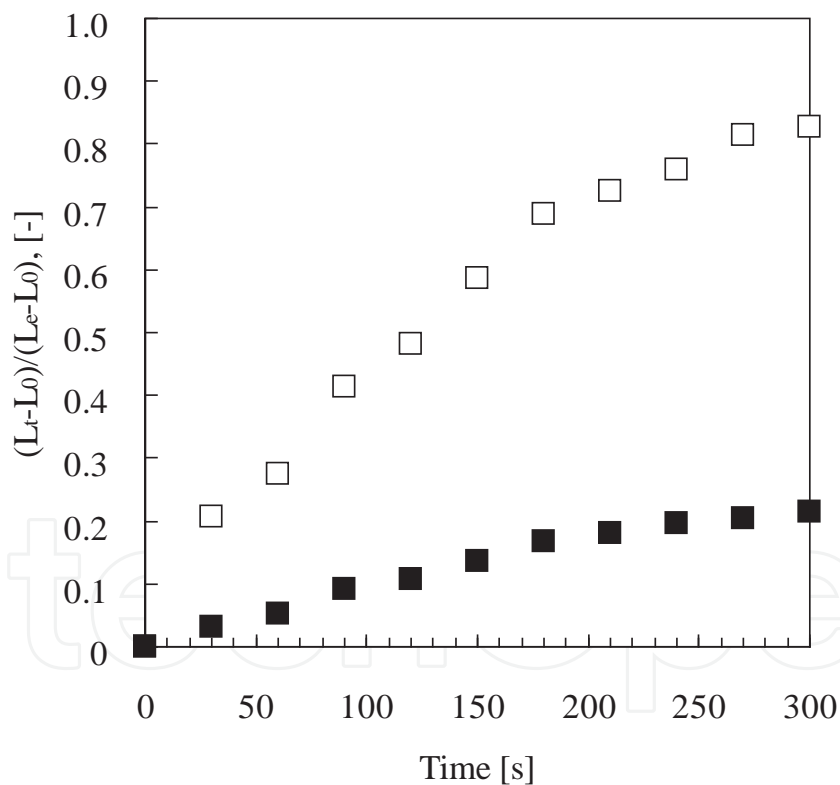Fig. 11. Illustration of the porous gel.

Fig. 12. Relative swelling of microphase-separated self-oscillating gel 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. (□) microphase-separated self-oscillating gel; (■) poly(NIPAAm-*co*-Ru(bpy)$_3$) gel. S. Maeda et al., Peristaltic motion of polymer gels. *Angew. Chem. Int. Ed.,* 2008, 47, 6690-6693. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.
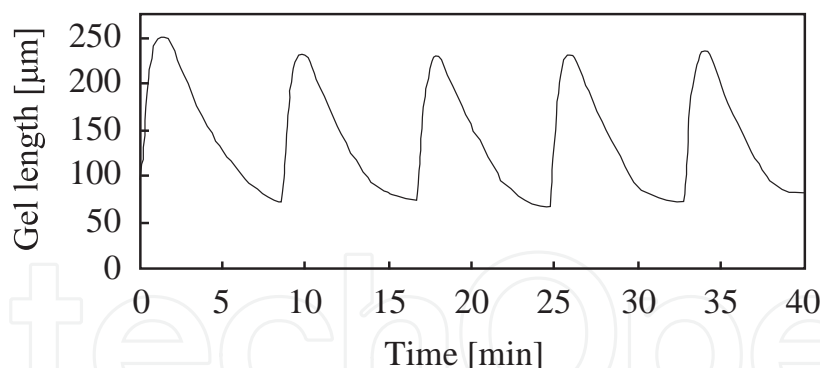
Fig. 13. Relative swelling of microphase-separated self-oscillating gel and poly(NIPAAm-co-Ru(bpy)$_3$) gels, $(L_t-L_0)/(L_e-L_0)$, in the solution of 5 mM Ce(SO$_4$)$_2$, 0.894 M HNO$_3$ at 18 °C as functions of the time t elapsing after changing the solution. L_t, L_0 and L_e, are the lengths of the gel at t = t, initial state and equilibrium state. (□) microphase-separated self-oscillating gel; (■) poly(NIPAAm-*co*-Ru(bpy)$_3$) gel. S. Maeda et al., Peristaltic motion of polymer gels. *Angew. Chem. Int. Ed.,* 2008, 47, 6690-6693. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.

2.3 Matter transport

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 microphase-separated self-oscillating gel in the aqueous solution containing the three reactants of the BZ reaction. Figure 7 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. The gel conveyer carried the object with millimeter order autonomously. It is assumed 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.

2.4 Control of autonomous swelling-deswelling behavior for a polymer gel

The conventional oscillating gel shrinks at temperatures above the LCST (lower critical solution temperature) because oscillating gel has the thermo sensitive PNIPAAm chain. To realize high-speed driving, we attempted to synthesize a novel self-oscillating polymer gel that drives without the temperature limitation. In this study, we selected a non- thermo sensitive and biocompatible poly(vinylpyrrolidone) (PVP) as the polymer main chain of the novel self-oscillating gel (poly(VP-*co*-Ru(bpy)$_3$ gel)) (Nakamaru, 2009). As a result, we first succeeded in causing the volume 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. for the novel gel can be controllable by the selection of the initial concentration of the three BZ substrates (malonic acid, sodium bromate, 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 volume oscillation with frequencies 0.5 Hz. This frequency (0.5 Hz) of the novel gel was 20 times as large as that of the conventional-type self-oscillating gel (poly(NIPAAm*co*-Ru(bpy)$_3$ gel). We expect that the novel oscillating polymer system lead to a wide development of application.
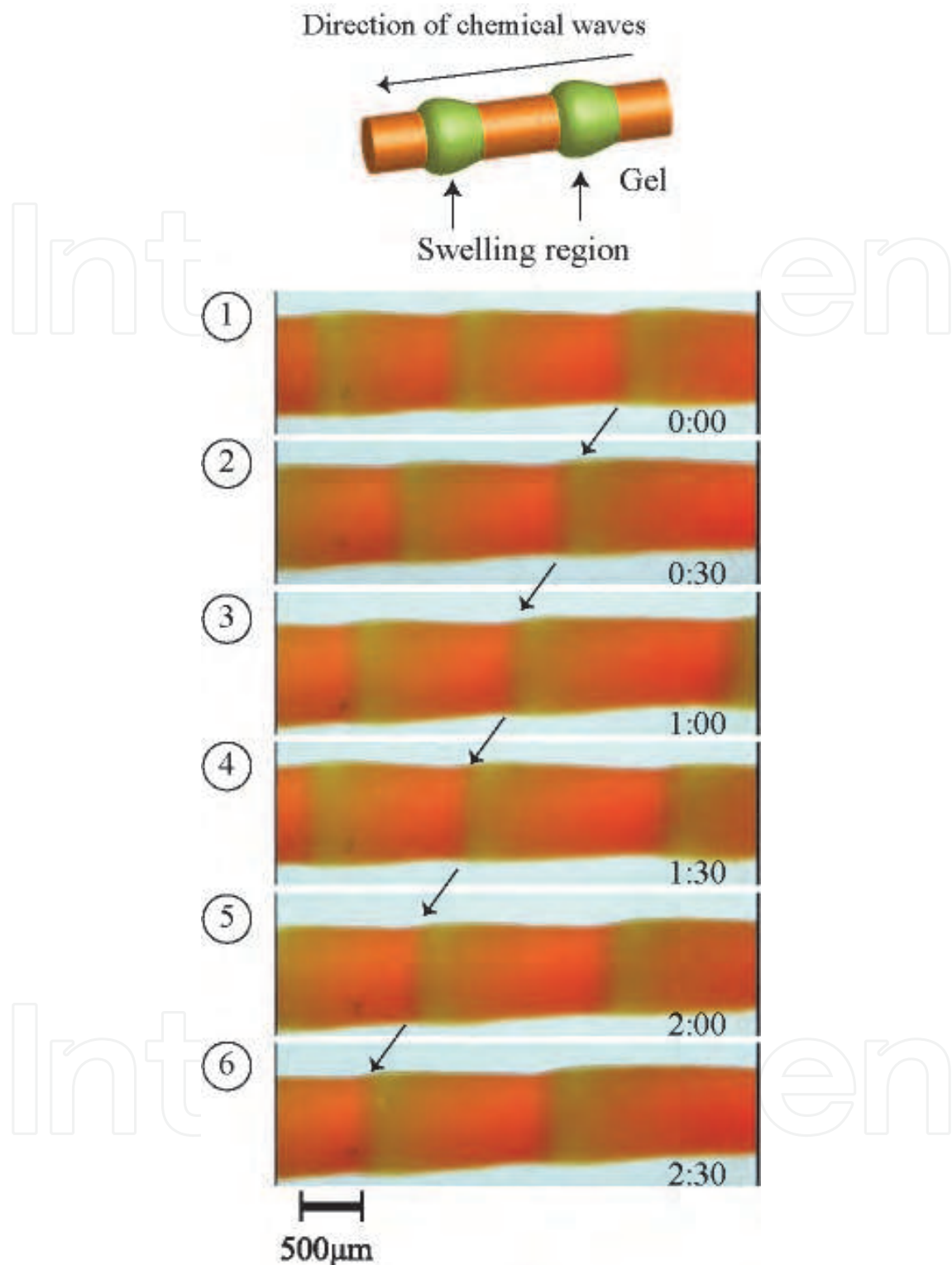
Fig. 14. Time course of peristaltic motion of microphase-separated self-oscillating gel in 8ml of the mixture solution of the BZ substrates (62.5 mM malonic acid, 84mM sodium bromate, 0.894M nitric acid, 18°C). The green and orange colors correspond to the oxidized and reduced state of Ru moiety in the gel, respectively. S. Maeda et al., Peristaltic motion of polymer gels. *Angew. Chem. Int. Ed.,* 2008, 47, 6690-6693. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.
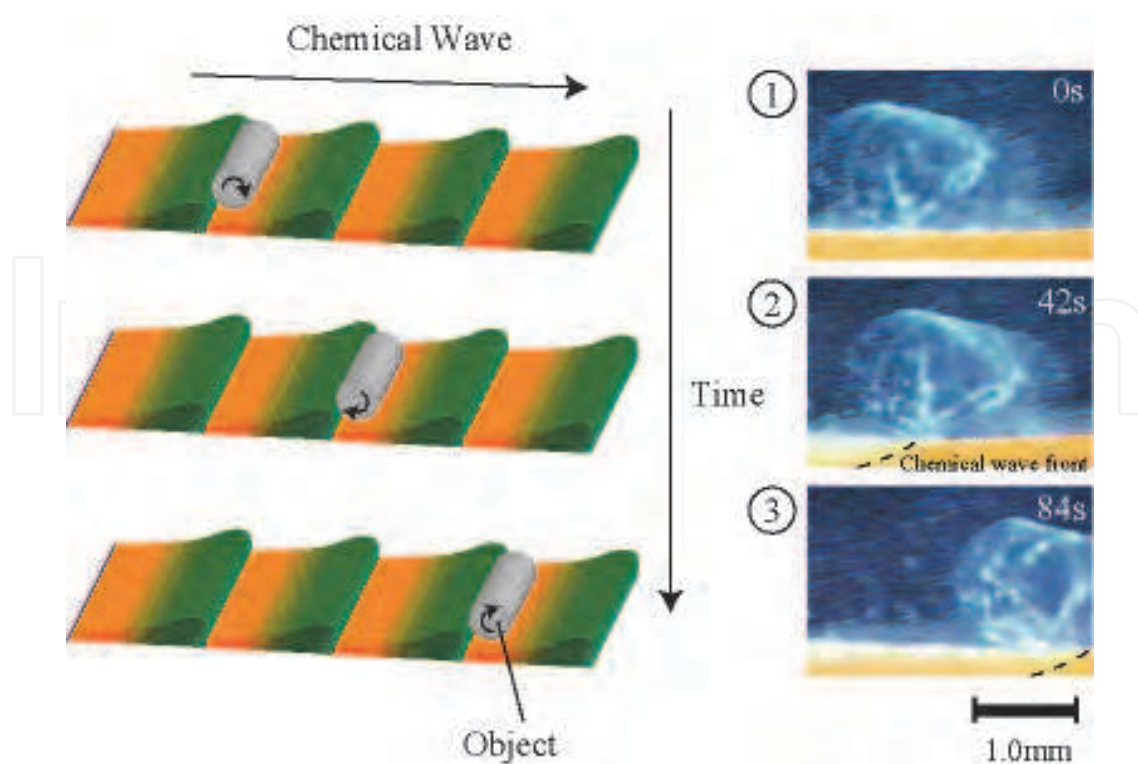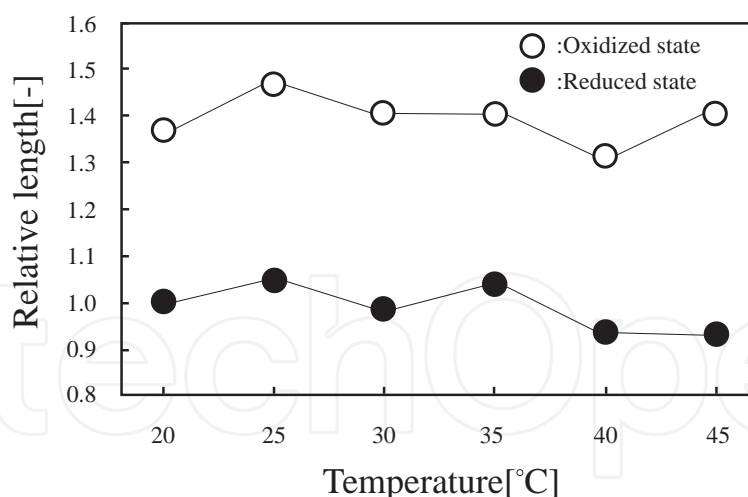
Fig. 15. Schematic illustration of the matter transport using peristaltic motion of the gel. S. Maeda et al., Peristaltic motion of polymer gels. *Angew. Chem. Int. Ed.*, 2008, 47, 6690-6693. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.


Fig. 16. Equilibrium swelling ratio of poly(VP-*co*-Ru(bpy)$_3$) gel in cerium sulfate solutions as a function of temperature. (●) [Ce$_2$(SO$_4$)$_3$] = 0.001M and [HNO$_3$] = 0.3M; (○) [Ce(SO$_4$)$_2$] = 0.001M and [HNO$_3$] = 0.3M. The relative length is defined as the ratio of characteristic diameter at the initial state at 20°C. Reprinted from ref. (Nakamaru et al, 2009) with permission; © The American Chemical Society(Polymers Fig.8)
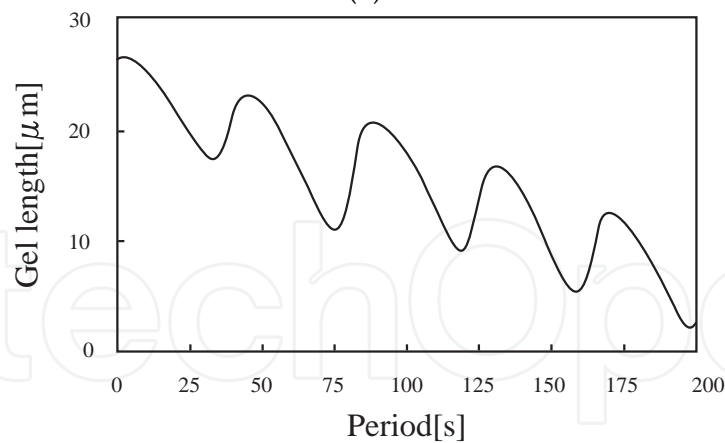
Figure 16 shows the equilibrium swelling behaviors of the poly(VP-*co*-Ru(bpy)$_3$) gels in the Ce(III) and Ce(IV) solutions under the same acidic condition. In the Ce(III) solution, the gel kept a tinge of orange, which indicated that the copolymerized Ru(bpy)$_3$ moiety in the gel
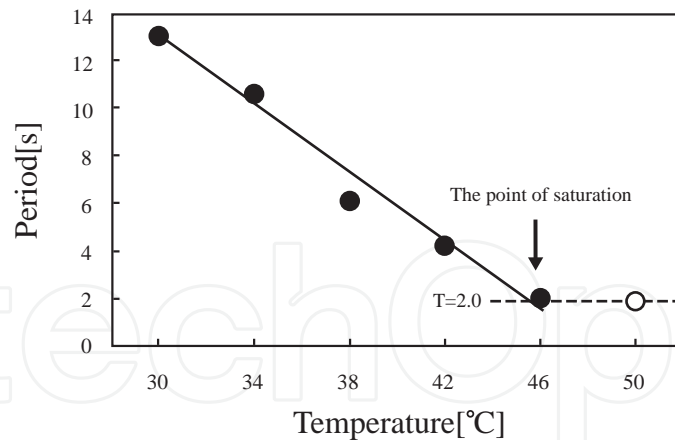
(a)
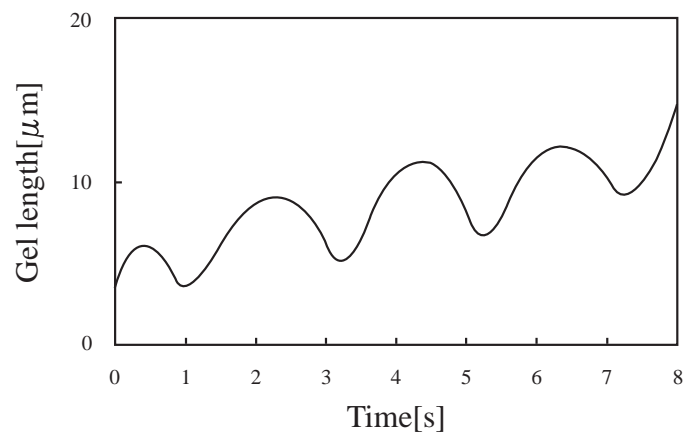
(b)

(c)

Fig. 17. (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, NaBrO$_3$ = 0.48M and HNO$_3$ = 0.48M). (c) Self-oscillating profile of cubic poly(VP-*co*-Ru(bpy)$_3$) gel at 20°C (MA = 0.08M, NaBrO$_3$ = 0.48M and HNO$_3$ = 0.48M). Cubic gel (each side length is about 2mm and 20mm) was immersed in 8ml of the mixture solution of the BZ substrates. Reprinted from ref. (Nakamaru et al, 2009) with permission; © The American Chemical Society

was in the reduced state. On the other hand, in the Ce(IV) solution, the gel quickly turned from orange to green, which showed the Ru(bpy)$_3$ moiety in the gel changed the oxidized state form the reduced state. In the oxidized state, the equilibrium volume of the gel was larger than that in the reduced state in all temperature condition. This is because the solubility of the Ru(bpy)$_3$ moiety has significantly difference properties in the oxidized and the reduced state. In the reduced and the oxidized state, there is no observation of the volume phase transition because of the PVP main chain of the gel without LCST.

Furthermore, as shown in Figure 17 the period of the swelling-deswelling self-oscillation decreased with increasing the temperature because the temperature affects the BZ reaction rate in accordance with the Arrenius equation[34]. 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 (Yoshida et al, 1996). The self-oscillating behaviors of the poly(Vp-*co*-Ru(bpy)$_3$) gel at 20°C and 50°C were shown in the Figure 17(b) and 17(c), repectively. The displace of the volume change self-oscillation at 20°C and 50°C were about 10µm and 4µm, respectively. These results clarified that the displacement of the swelling-deswelling self-oscillation for the gel has the trade-off relationship against the period of the self-oscillation, that is, the length of the volume change decreased with increasing the period. Therefore, we are investigating the corrective strategy for the trade-off relationship between the period and the displacement of the gel in order to realize autonomous soft actuators that cause the large deformation at the high speed.

2.5 A Pendulum-like motion of nanofiber gel actuator synchronized with pH oscillating reaction

In this study, we forcused on the pH oscillating reaction. Very recently, we succeeded in manufacturing a novel nanofiber hydrogel actuator driven by the pH oscillating reaction, based on a bromate/sulfite/ferrocyanide. The novel nanofiber gel actuator was composed of electrospun nanofibers synthesized by copolymerizing acrylic acid and hydrophobic butyl methacrylate as a solubility control site. By changing the electrospinning flow rate, the nanofiber gel actuator introduced an anisotropic internal structure into the gel. Therefore, the unsymmetrical motion of the nanofiber actuator was generated.

We have tried to apply the electrospinning method to the fabrication of the gel actuator in this stuidy. This is because electrospinning has a lot of merit such as low cost, relatively high production rate, and having applicability to many types of polymers. Figure 18 shows the schematic illustration of the electrospinning set-up. As a high voltage is applied to a metallic capillary of the syringe, charges that have built up on the surface of droplet on the top of the capillary, will overcome the surface tension and induce the formation of a liquid jet. The charged jet then undergoes stretching into continuous nanofibers and accelerates toward a grounded collector. On the way to the collector, the solvent evaporates. As a result, a non-woven mat composed of nanofibers is deposited on the collector.

By utilizing the electrospinning method, we can construct the novel design of nanofiber gel actuators because it does not require a mold to synthesize the gel. In our previous study, by introducing an anisotropic structure into the nanofiber gel, we succeeded in the fabrication of a novel nanofiber hydrogel actuator that generates bending and stretching motions synchronized with the external manual pH changes (Nakagawa et al, 2010). However, the external pH was controlled manually. If the autonomous-type polymer gel actuator is realized, new transducers and molecular devices will be realized. In order to construct an

autonomous polymer gel system, we utilized Landolt pH-oscillator based on a bromated/ sulfite/ferrocyanide reaction. By coupling with this pH-oscillator, we realized a nanofiber gel actuator that shows the bending and stretching motions over a constant period and displacement.

Figure 19 shows the method of introducing the anisotropic structure into the nanofiber gel. First, the 1.0 mL of the polymer solution in the syringe was sprayed at a flow rate of 2.0 mL/hour (sprayed for 30 minutes), and then the flow rate was changed to 1.0 mL/hour (sprayed for 60 minutes). The electrospun fibers were collected on the grounded glass substrate as a collector. The distance between the collector and the syringe tip was 15 cm. The temperature and humidity were 25 °C and 70%, respectively. After the electrospinning, the obtained sheet, with a thickness of about 200 μm, was dried overnight at 50 °C. In order to drive the nanofibrous gel actuator synchronized with autonomous pH oscillation, we focused on the Landolt pH-oscillator, based on a bromated/ sulfite/ ferrocyanide reaction discovered by Edblom et al. (Edblom et al, 1986). This reaction causes the autonomous cyclic pH changes with a wide range at room temperature.

Figure 20 shows a motion of the nanofiber gel actuator (Nakagwa, 2010). The bending and stretching motions of the gel actuator synchronized with the pH oscillating reaction. As shown in Figure 20, we defined R as the length between two edges of the gel. Figure 21 shows the trajectory of the nanofiber gel strip. As shown in Figure 21, the gel strip caused the pendulum-like motion. As the external pH is below the pKa, the nanofiber gel stretches because of the deswelling originating from the hydrogen bonding (1→3). However, when the pH is above the pKa, the gel bends because of the swelling originating from the repulsive force among the anionic polymer chains (4→6).
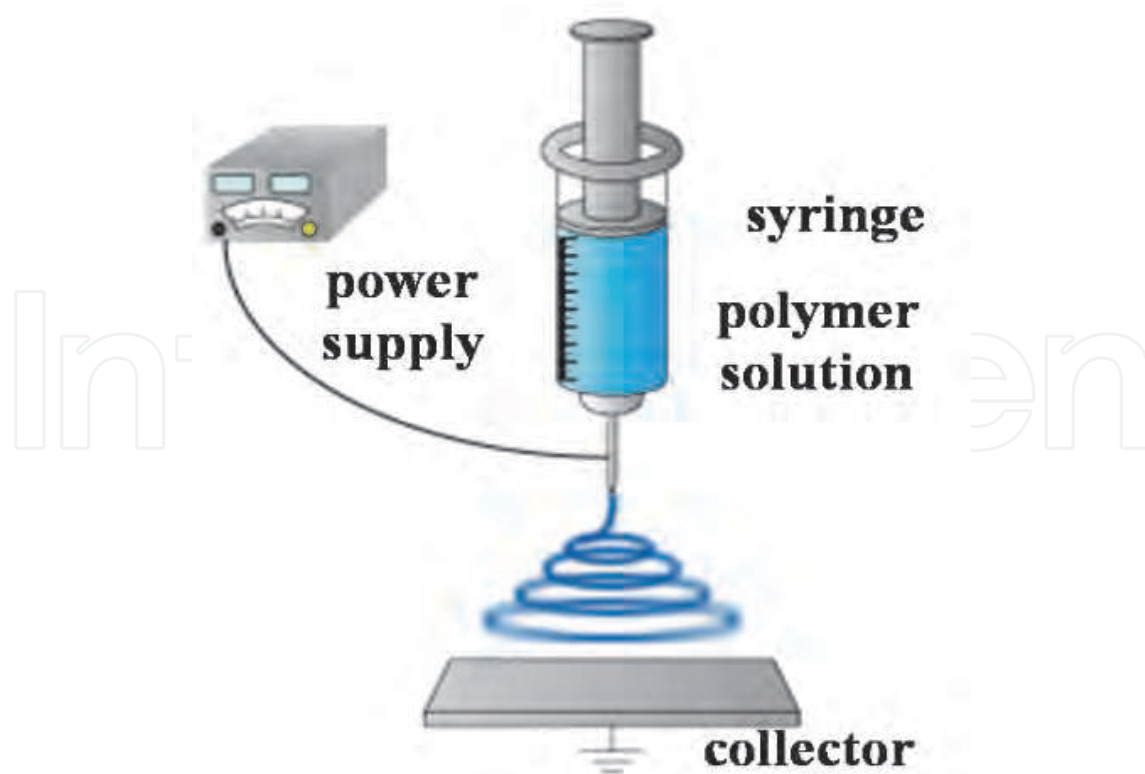

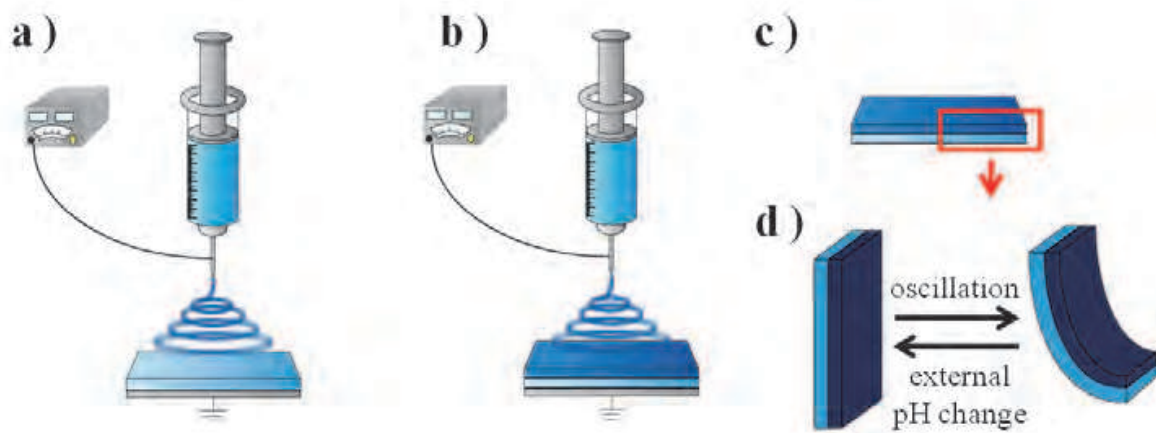Fig. 18. Schematic illustration of electrospinning set-up.

Fig. 19. (a) Electrospinning at a flow rate of 2.0 mL/hour (sprayed for 30 minutes).
(b) Electrospinning at a flow rate of 1.0ml/hour (sprayed for 60 minutes). (c) Drying in 50 °C over night. (d) Cutting into 15 mm × 3 mm × 200 μm.
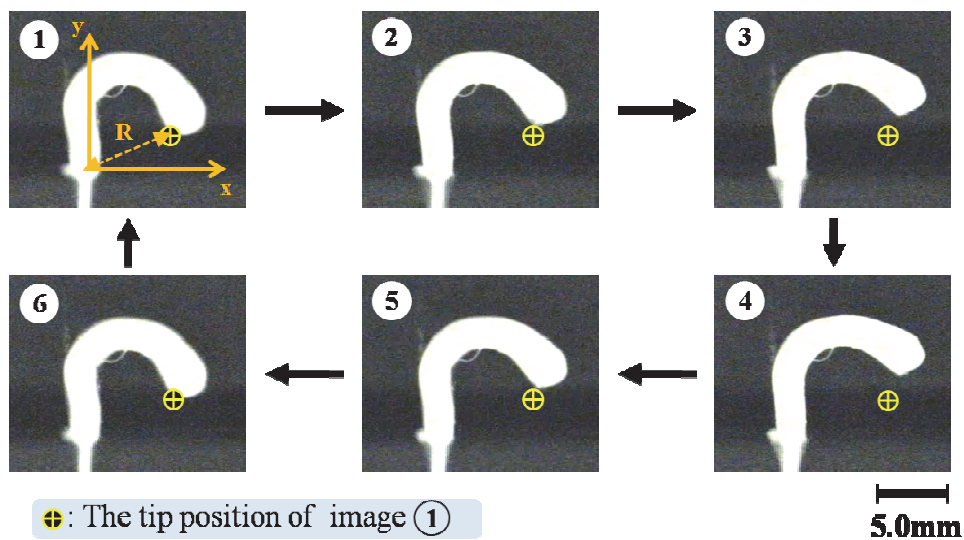

⊕ : The tip position of image ①

5.0mm

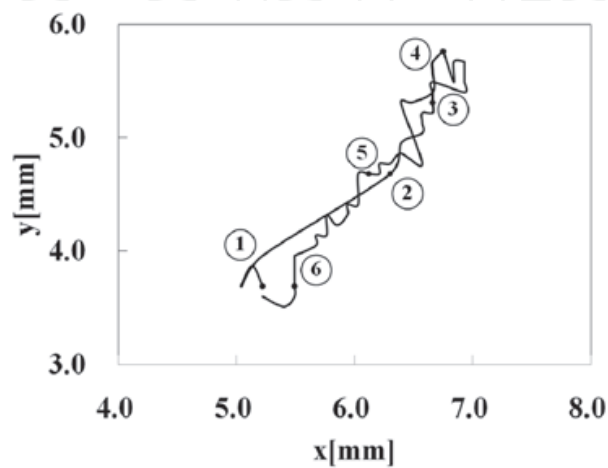Fig. 20. Periodical pendulum motion of poly(AAc-*co*-nBMA) nanofiber gel.

Fig. 21. Trajectory of the tip of the gel relative to its attachment position during pH oscillation.

3. Conclusion

In this book, we introduced novel autonomous polymer gel actuators driven by the oscillating chemical energy. We expect autonomous gel actuators are the preliminary step for "Chemical Robotics". The chemical robot is different from the mechanical robot in terms of assembly, material, driving force, etc. At the present stage, an operating condition for the self-motion is limited. Our next work is to develop the various gel motions caused by the reaction diffusion system.

4. Acknowledgment

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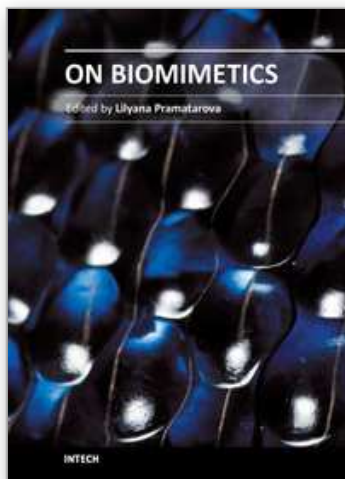
On Biomimetics

Edited by Dr. Lilyana Pramatarova

Bio-mimicry is fundamental idea â€˜How to mimic the Natureâ€™ by various methodologies as well as new ideas or suggestions on the creation of novel materials and functions. This book comprises seven sections on various perspectives of bio-mimicry in our life; Section 1 gives an overview of modeling of biomimetic materials; Section 2 presents a processing and design of biomaterials; Section 3 presents various aspects of design and application of biomimetic polymers and composites are discussed; Section 4 presents a general characterization of biomaterials; Section 5 proposes new examples for biomimetic systems; Section 6 summarizes chapters, concerning cells behavior through mimicry; Section 7 presents various applications of biomimetic materials are presented. Aimed at physicists, chemists and biologists interested in biomineralization, biochemistry, kinetics, solution chemistry. This book is also relevant to engineers and doctors interested in research and construction of biomimetic systems.

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