Polymer Gels

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Peristaltic Motion of Polymer Gels**

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Many examples of matter-transporting actuators or devices based on electroactive polymers have recently been developed. However, the actuation is controlled by on–off switching of external inputs. In contrast, there are several autonomous phenomena that exhibit rhythms and spatial patterns under continuous (that is, nonswitched) conditions in biological systems. Herein we report a novel autonomous peristaltic motion of a synthetic polymer gel analogous to that in a living organism. Furthermore, the gel undergoes a cyclic reaction, rather than being externally switched, thereby mirroring the metabolic process. The peristaltic motion is induced by the Belousov–Zhabotinsky (BZ) reaction that takes place inside the gel, which acts as a reaction diffusion system. Furthermore, the motion has been harnessed to autonomously transport an object in aqueous solution. This novel material has great potential as a component in devices that transport matter.

Until now, polymers and gels have been widely studied from the points of view of both basic and applied research.[1,2] In particular, materials that swell or shrink in response to external changes such as temperature, pH value, electric field, and light are promising in various fields. Recently, many research groups have attempted to incorporate these intelligent materials into microdevices or soft actuators.[3] For example, a microfluidic device using microelectromechanical systems (MEMS) technology and poly(*N*-isopropylacrylamide) (polyNIPAAm), a thermosensitive polymer, has been demonstrated.[4] This device can adsorb and release proteins from solution by controlling resistive heating, which changes the degree of protein adsorption on the polyNIPAAm. Additionally, the development of transporting devices on a chip is becoming especially significant in the field of biotechnology. A position control device was designed using the NIPAAm gel encapsulated in a cylindrical glass tube.[5] The volume phase transition of the gel was induced at a specific position by local heating or cooling. The directional locomotion of the gel was generated by spatially controlled propagation of the volume phase transition along the length. A microrobotic arm made from a conducting polymer that can grip and carry objects for single-cell manipulation was created from a microfabricated circuit of conducting polymer actuators.[6] These actuators are based on the reversible volume change of the conducting polymers upon oxidation and reduction.

However, these systems require complex fabricated circuits or external control devices because the resulting mechanical motion is driven by on–off switching of external signals. On the other hand, there are several autonomic phenomena such as peristaltic motion, heartbeat, and brain waves, in biological systems that exhibit spontaneous motion without external stimuli. If intelligent materials were to display such independent motion or functions, novel biomimetic devices such as autonomous matter transporters or self-beating micropumps could function without external control. Thus, devices mirroring living organisms could be created without electronic wiring. There are currently only a few reports of the incorporation of such autonomous devices into artificial systems.

In this study, we have succeeded in the realization of peristaltic motion of a synthetic polymer gel at the macroscopic scale that is produced by dissipating the chemical energy of the BZ reaction.[7,8] This reaction is well known as a dissipative system that generates spatiotemporal dynamic patterns—chemical waves—under stationary conditions. The BZ reaction generates the periodic redox changes of the metal catalyst moiety: $[\mathrm{Ru(bpy)_2(4\text{-}vinyl\text{-}4'\text{-}methylbpy)}]^{2+} \leftrightarrow [\mathrm{Ru(bpy)_2(4\text{-}vinyl\text{-}4'\text{-}methylbpy)}]^{3+}$ ($[\mathrm{Ru}]^{2+} \leftrightarrow [\mathrm{Ru}]^{3+}$, bpy = 2,2′-bipyridine). We have synthesized an ionic gel that consists of cross-linked NIPAAm and ruthenium monomers. When the gel is immersed in an aqueous solution containing the substrates of the BZ reaction except for the catalyst, the BZ substrates penetrate into the polymer network and the BZ reaction occurs within the gel. The polymer gel has a lower critical solution temperature (LCST) because of inclusion of the thermoresponsive NIPAAm component. The LCST of the polymer gel is

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higher in the oxidized Ru^{III} state than in the reduced Ru^{II} state because of the charge increase of the catalyst moiety.[9] At constant temperature, therefore, redox changes of the catalyst moiety lead to hydrophilic changes of the polymer chains. Consequently, periodic redox changes induced by the BZ reaction produce periodic swelling–deswelling changes in the gel.[10–12] Recently, we have developed a self-walking gel actuator using such self-oscillating behavior.[13] However, it was difficult to directly observe the peristaltic motion synchronized with the chemical wave because the mechanical oscillations were too small in comparison with the gel size. Theoretical studies have predicted the occurrence of peristaltic motion within the gel.[14] Although the peristaltic motion of the gel has been indirectly evaluated from its color tones,[15] macroscopic peristaltic motion of the gel was not directly observed.

In general, the degree of response of hydrogels 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 differences between the swelling ratios of the reduced Ru^{II} state and oxidized Ru^{III} state in the poly(NIPAAm-co-[Ru]) gel at the equilibrium swelling state. In reality, the volume oscillation coupled with the redox oscillation of the ruthenium catalyst moiety in 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 under the equilibrium conditions such as those mentioned above. Therefore, the poly(NIPAAm-co-[Ru]) self-oscillating gel generated only a small mechanical oscillation. To produce a large mechanical oscillation compared to the gel size, a self-oscillating gel with a fast response to changes in the charge density of the metal catalyst in the BZ reaction was needed. We therefore prepared a microphase-separated self-oscillating gel. A NIPAAm gel with a microscale phase separation that underwent a quick response has previously been reported.[16] By preparing a NIPAAm gel above the LCST, the network structure becomes inhomogeneous. As a result, the NIPAAm gel forms a porous structure with polymer-rich domains and aggregations in the matrix of loosely bound network structures.[17] Consequently, polymer-rich domains inside the gel aggregate or disperse rapidly through the porous structure within the gel by an effluent pathway. The microphase separation in the gel depends strongly on the methods of gel preparation. To realize the microscale phase separation of the self-oscillating gel, the gel was synthesized in a water/methanol solution in the hydrophobic casting mold. Furthermore, we added hydrophilic 2-acrylamido-2-methylpropanesulfonic acid (AMPS) to the bound network structure in the gel to form clear polymer-rich domains because the ruthenium moieties in the gel agglutinated by hydrophobic interactions.

Firstly, we prepared a cubic poly(NIPAAm-co-[Ru]-co-AMPS) gel, the size of which was smaller than the wavelength of the chemical wave. Within the miniature gel, the redox change occurred homogeneously without evolution of chemical waves. The oscillating profiles of the redox changes as well as the swelling–deswelling changes were analyzed using the image-processing method. Figure 1 shows the self-oscillating behavior of the cubic gel in aqueous solution containing the three reactants of the BZ reaction (malonic acid, sodium bromate, and nitric acid) at constant temperature. The displacement of the mechanical oscillation was around 130 μm. The amplitude of the volume oscillation of the poly(NIPAAm-co-[Ru]-co-AMPS] gel is about ten times larger than that of the poly(NIPAAm-co-[Ru]) gel studied previously. It is therefore assumed that the large mechanical oscillations of the gel resulted from a rapid response to changes in the charge density of the metal catalyst in the BZ reaction. From this result, it is expected that the gel with a size larger than the wavelength of the chemical wave will undergo periodic peristaltic motion when the redox state of the [Ru] moiety in the gel changes periodically in the BZ reaction at constant temperature. Figure 2 a shows the periodic peristaltic motion of the gel driven by chemical waves of the BZ reaction. We succeeded in directly observing the periodic peristaltic motion of the gel: the local swelling regions in the gel propagated with the motion of the chemical waves. This was the first visual evidence of the peristaltic motion of the gel on the macroscopic scale. The observed shape changes of the gel were in good agreement with those predicted theoretically.[14] The volume change of the gel was followed by reaction diffusion dynamics.[8] The chemical wave speed of the BZ reaction within the gel was approximately 14.0 μm s^{-1}. Figure 2 b shows the spatiotemporal diagram constructed from sequential images. The width of the gel changed shape periodically by about 150 μm to approximately 20 % of its initial value. The period of the volume oscillation was about 86 s.

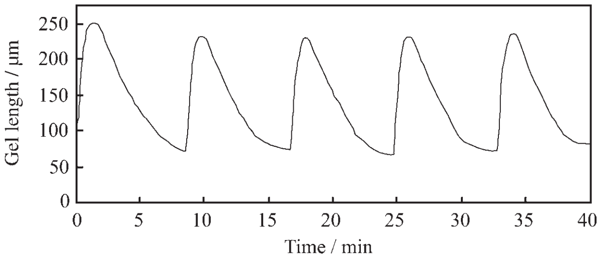

Figure 1. Oscillation profiles of cubic poly(NIPAAm-co-[Ru]-co-AMPS) gel. The cubic gel (length of each side ca. 0.5 mm) was immersed in a solution (1 mL) of the BZ substrates (malonic acid (62.5 mM), sodium bromate (84 mM), and nitric acid (0.894 M) at 18 °C).

We have also succeeded in conveying a cylindrical polyacrylamide gel by utilizing the peristaltic motion of the rectangular poly(NIPAAm-co-[Ru]-co-AMPS) gel in an aqueous solution containing the three components of the BZ reaction. Figure 3 a shows a schematic illustration of the principle of matter transport. The peristaltic surface of the gel autonomously pushed and carried the object, which has dimensions of the millimeter order, by rotating it in one direction. This resulted the object moving at about 40 μm s^{-1} as the chemical wave propagated (Figure 3 b). Since the spatiotemporal dynamic pattern changes with the concentration of substrates in solution, the peristaltic motion of the gel can be controlled by changing the concentration of the BZ, substrates as it is these that control the spatiotemporal dynamic pattern.

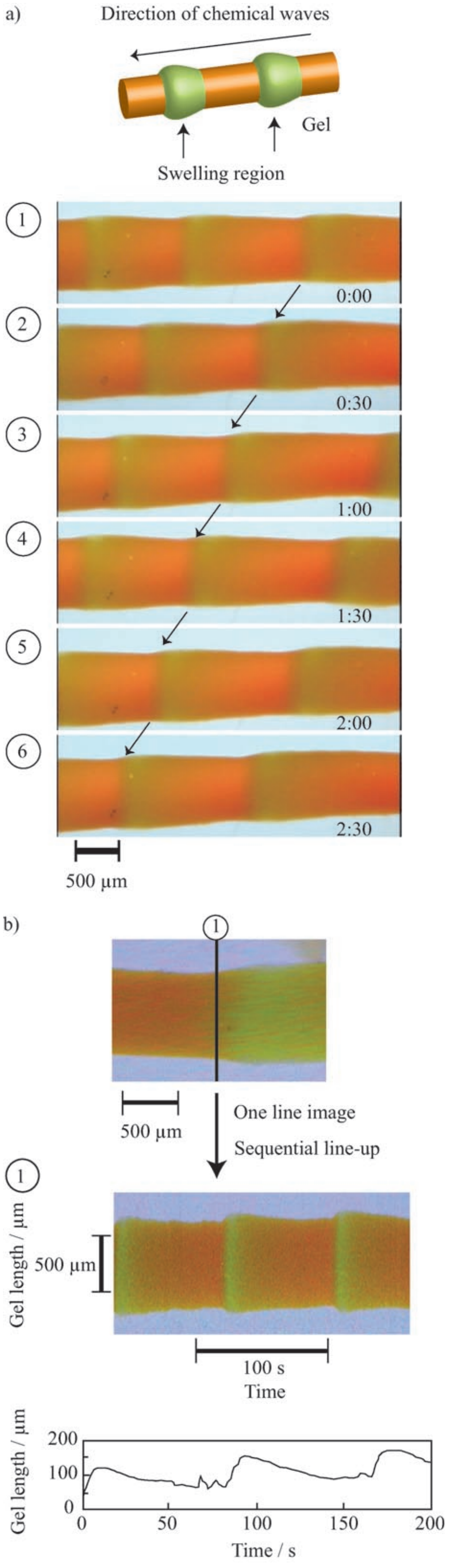

Figure 2. a) Time course of peristaltic motion of poly(NIPAAm-co-[Ru]-co-AMPS) gel in a solution (8 mL) of the BZ substrates (malonic acid (62.5 mM), sodium bromate (84 mM), and nitric acid (0.894 M), 18 °C). The green and orange colors correspond to the oxidized and reduced states of the Ru moiety in the gel, respectively. b) Spatiotemporal pattern of the gel oscillation.

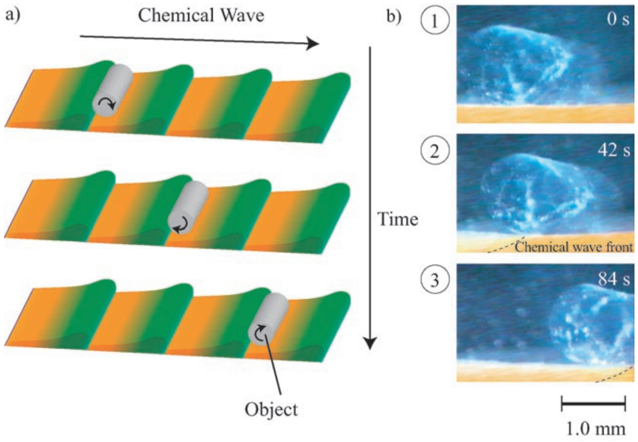

Figure 3. a) Schematic illustration of matter transport using the peristaltic motion of the gel. b) Images of matter transport by rotation in one direction by the peristaltic motion of the gel. Cylindrical polyacrylamide gel (diameter = 1.2 mm, length = 2.0 mm) was set on poly(NIPAAm-co-[Ru]-co-AMPS) gel (width = 3.0 mm, length = 6.0 mm, thickness = 2.0 mm) in a solution of the BZ substrates (malonic acid (62.5 mM), sodium bromate (84 mM), and nitric acid (0.894 M), 18 °C).

The actuation of the gel is operated under a nonphysiological environment where the three substrates of the BZ reaction coexist. The BZ reaction has been shown to occur in the presence of only organic acids.[18–20] Therefore, if actuation of the active polymer system can be achieved when operated under physiological conditions, that is, in the presence of only bio-related organic acids such as citric acid, novel intelligent bio-machines or devices that function without external electrical power could be envisaged. These details are currently under investigation. The autonomous peristaltic motion of the gel would create a new design method for matter transport as well as micro-, or nanodevices.

Experimental Section

Poly(NIPAAm-co-[Ru]-co-AMPS) gels were prepared as follows: NIPAAm (0.156 g), $[Ru]^{2+}$ (16.2 mg), *N,N'*-methylenebisacrylamide (MBAAm, 2.8 mg), and 2,2'-azobis(isobutyronitrile) (AIBN, 6.6 mg, initiator) were dissolved in O_2-free methanol (0.5 mL). AMPS (5.5 mg) was dissolved in O_2-free pure water (0.5 mL). The two solutions were then mixed together and the monomer solution was injected into a casting mold. In this study, we designed a cylindrical hole (diameter: 0.8 mm) in the hydrophobic wax plate (The Kindt-Collins Company) as a casting mold by using PC software (Mini-CAD7) and then formed a hole in the wax plate using a CAM machine (MIMAKI, NC-5). The monomer solution was then polymerized at 60 °C for 18 h. After polymerization, the gel was soaked in pure methanol for 1 week to remove any remaining monomers. The gel was carefully hydrated by immersion for 1 day in a graded series (75, 50, 25, and 0 %) of methanol/water mixtures. The polyacrylamide gel was prepared following a conventional method[21] (see the Supporting Information).

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