Self-oscillating polymer gels as biomimetic and smart softmaterials

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Abstract

In living systems, there are many autonomous and oscillatory phenomena to sustain life such as heart beating. We developed "self-oscillating" polymer gels that undergo spontaneous cyclic swelling–deswelling changes without any on–off switching of external stimuli, as with heart muscle. The self-oscillating gels were designed by utilizing the Belousov-Zhabotinsky (BZ) reaction, an oscillating reaction, as a chemical model of the TCA cycle. We have systematically studied these self-oscillating polymer gels since they were first reported in 1996. Potential applications of the self-oscillating polymers and gels include several kinds of functional material systems such as biomimetic actuators, mass transport systems and functional fluids. In this review, our recent progress on the self-oscillating polymer gels is summarized. Copyright © 2018 VBRI Press.

Keywords: Polymer gel, smart softmaterials, biomimetics, self-oscillation.

Introduction

Polymer gels are defined widely as crosslinked polymer networks that are swollen in solvents. In the field of polymer science, polymer gels have made rapid progress since the discovery of "volume phase transition" phenomena by Tanaka in 1978 [1,2]. Many kinds of stimuli-responsive polymer gels that exhibit reversible swelling-deswelling change in response to environmental changes (e.g, solvent composition, temperature, pH change, light, electric field, etc.) have been developed. Especially, from the late 1980's, new functional gels called "intelligent" or "smart" gels have been created, and their applications to bio- or biomimetic materials such as actuator (artificial muscle), drug delivery systems (DDS), tissue engineering, purification or separation systems, biosensor, shape memory materials, molecular recognition systems, etc. [3-10]. has been exploited. In these researches, a concept of "chemo-mechanical gels" to convert chemical energy of chemical/biochemical reaction to mechanical energy of gels has been proposed as a model of artificial muscles to realize soft actuators. Furthermore, with the progress of polymer synthesis technology and supramolecular science, gels with unique network structures have been designed to provide rapid response [11], toughness [12-15], and self-healing properties [7, 16-18], etc.

In these ways, many kinds of stimuli-responsive polymers and gels inspired by living systems have been studied. Other than stimuli-responsive function, one of characteristic and important behaviors in living systems is autonomous oscillation, that is, spontaneous changes with temporal periodicity (called "temporal structure") such as heartbeat, brain waves, pulsatile secretion of hormone, cell cycle, and biorhythm. However, there are few studies on polymer and gel systems undergoing self-oscillation under constant condition without any on-off switching of external stimuli. If such autonomous systems can be realized by using completely synthetic polymers, unprecedented biomimetic materials may be created.

From this viewpoint, we have studied polymer gels with autonomous function. We attempted to develop a novel gel that provides mechanical oscillation by itself without external control in a complete closed and non-oscillating outer solution. Consequently, we succeeded in developing such a self-oscillating polymer and gels by incorporating oscillating chemical reaction in polymer network, i.e., by constructing built-in circuit of energy conversion cycle producing mechanical oscillation within polymer network itself. In contrast to conventional stimuli-responsive gels, the "self-oscillating" polymer gels autonomously undergo periodic swelling/deswelling oscillation without on-off switching of external stimuli in a closed solution **(Fig. 1)**.

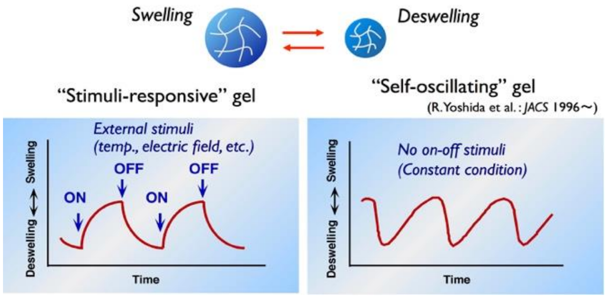

Fig. 1. Stimuli-responsive and self-oscillating gels.

Design of self-oscillating polymer gel

For the design of such a gel, the Belousov-Zhabotinsky (BZ) reaction [19,20], which is well-known as an oscillating reaction which spontaneously exhibits temporal rhythm and spatial pattern, was focused. The overall process is the oxidation of an organic substrate, such as malonic acid (MA) or citric acid, by an oxidizing agent (typically bromate ion) in the presence of a catalyst under acidic condition. Metal ions or metal complexes with high redox potentials such as cerium ion, ferroin, or ruthenium tris(2,2'-bipyridine) ($Ru(bpy)_3^{2+}$) are widely used as catalysts. While the reaction proceeds, the catalyst undergoes spontaneous redox oscillation, showing periodical changes in color of the solution under stirring condition and concentric or spiral wave patterns under stationary condition. The wave of oxidized state propagating in the medium is called a "chemical wave". The BZ reaction is often analogically compared with the TCA cycle which is a key metabolic process taking place in the living body, and it is recognized as a chemical model for understanding several autonomous phenomena in biological systems.

We attempted to convert the chemical oscillation of the BZ reaction into a mechanical change in gels and generate an autonomous swelling-deswelling oscillation under non-oscillatory outer conditions. For this purpose, we prepared the gel composed of poly(*N*-isopropylacrylamide) (PNIPAAm) and $Ru(bpy)_3$ which is covalently bonded to the PNIPAAm network **(Fig. 2)**. When the poly(NIPAAm-*co*-$Ru(bpy)_3$) gel is immersed in the catalyst-free BZ solution containing the substrates (MA, $NaBrO_3$ and nitric acid), the reaction occurs in the gel by the catalytic function of the polymerized $Ru(bpy)_3$. The redox changes of the polymerized catalyst moiety ($Ru(bpy)_3^{2+} \rightleftarrows Ru(bpy)_3^{3+}$) change the volume phase transition temperature of the gel as well as the swelling ratio because the hydrophilicity of the polymer chains increases at the oxidized Ru(III) state and decreases at the reduced Ru(II) state. As a result, the gel exhibits an autonomous swelling-deswelling oscillation with the redox oscillation in the closed solution under constant condition. We reported the "self-oscillating" gel in 1996 for the first time [21].

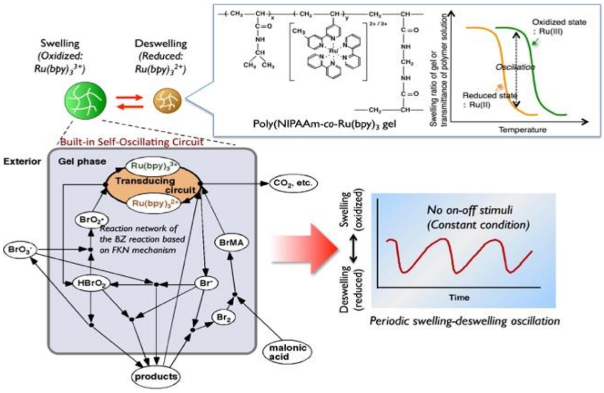

Fig. 2. Design concept of self-oscillating gel using the BZ reaction.

Development of self-oscillating polymer gels as functional softmaterials

Since then, we have developed many kinds of biomimetic or smart material systems **(Fig. 3)** [22-71]. These researches include (1) control of self-oscillating chemomechanical behaviors (e.g., concentration and temperature dependence of oscillation [27], on-off regulation of self-oscillation by external stimuli [29-32], control of self-oscillating behaviors by designing chemical structure of gel [33-37], remarkable swelling-deswelling changes by assembled self-oscillating microgels [38], comb-type self-oscillating gel [39]), (2) design of biomimetic soft-actuators (e.g., ciliary motion actuator using self-oscillating gel [40,41], self-walking gel [42], self-propelled motion [25], theoretical simulation of the self-oscillaiting gel [43,44], and (3) design of autonomous mass transport systems (e.g., self-driven gel conveyer: autonomous transportation on the self-oscillating gel surface by peristaltic motion [45,46], autonomous intestine-like motion of tubular self-oscillating gel [47,48]).

Further, there have been new developments toward autonomous polymer actuating systems with micro or nano-order scale such as polymer solution [49-57], polymer brush [58-61], polymer micelles [62-64], polymer vesicles [65-68], colloidsomes [69]. Especially, amoeba-like intermittent autonomous moving motion accompanying sol-gel oscillation under constant condition was achieved by strategically designed synthetic polymers [70,71]. There are possibilities to realize a biomimetic soft-machine which shows amoeboid motion.

Preparation of self-oscillating polymer brushes (artificial cilia)

Functional surfaces that can control their wettability, permeability, and adhesiveness have attracted much attention because of their diverse potential applications. In particular, by incorporating stimuli-responsive polymers on material surfaces, the physical and chemical characteristics of the surfaces can change in response to external stimuli. Such stimuli-responsive surfaces can be used as smart surfaces with switchable properties, for example, in cell culture substrates, microfluidics, self-cleaning coatings, and filtration devices. To fabricate well-defined functional surfaces, surface modification techniques to graft synthetic polymers onto substrates have been intensively investigated. Among them, surface-initiated atom transfer radical polymerization (SI-ATRP) is a useful method to prepare well-defined, high-density polymer brush structures on substrates.

In contrast to functional surfaces modified by stimuli-responsive polymers, functional surfaces modified by self-oscillating polymers exhibit autonomous changes in their surface properties without requiring external stimuli, and novel applications such as autonomous mass transport systems on the micro- or nanoscale are expected. Self-oscillating polymer brushes have been prepared by grafting self-oscillating polymers onto a glass substrate using the SI-ATRP method **(Fig.3)** [58-61]. Chemical wave propagation was clearly observed on the surface.

Polymer solution systems toward autonomous softmachines

Transmittance and viscosity oscillation of polymer solution and microgel dispersion

In the case of the uncrosslinked linear polymer (poly(NIPAAm-*co*-Ru(bpy)$_3$), the polymer undergoes spontaneous cyclic soluble-insoluble changes and the transmittance of the polymer solution oscillates autonomously with redox changes of the copolymerized Ru(bpy)$_3$ **(Fig.3)** [49]. Further, we prepared submicron-sized poly(NIPAAm-*co*-Ru(bpy)$_3$) gel beads by surfactant-free aqueous precipitation polymerization and analyzed the oscillating behavior of the microgel dispersions [50-53]. The microgel dispersion also exhibited transmittance oscillation due to swelling and deswelling changes of the microgels. With increasing temperature, the oscillation period decreased and the amplitude increased a little. When the temperature increased near to the volume phase transition temperature of the reduced microgel, the microgels showed dispersing/flocculating oscillation as well as swelling-deswelling oscillation because the reduced and shrunken microgels lost colloidal stability, which resulted in a remarkable increase of amplitude in optical transmittance oscillation. Due to such behaviors, as mentioned before, the macroscopic self-oscillating gel prepared by crosslinking the assembled microgels exhibits a faster response and leads to larger amplitude of swelling-deswelling oscillation **(Fig. 3)** [38]. In both cases of the polymer solution and the microgel dispersion, viscosity oscillation was observed with optical transmittance oscillation [54-56].

Self-oscillating block copolymers

The self-assembly of block copolymers (BCPs) in bulk and solution has attracted significant attention for many decades. Self-assembled BCP structures are either thermodynamically stable or metastable. In contrast, temporal or spatiotemporal structures, which are one of the unique characteristics of living systems, are dissipative structures in a dynamic state far from equilibrium. By coupling the self-assembly of BCPs with dissipative structures formed by the BZ reaction, a novel class of “self-oscillating BCPs” has been fabricated, where the self-assembled structures of BCPs, driven by the BZ reaction, autonomously oscillate [62-64]. A diblock copolymer composed of poly(ethylene oxide) (PEO) as the hydrophilic segment and poly(NIPAAm-*co*-Ru(bpy)$_3$) as the self-oscillating segment was synthesized by reversible addition-fragmentation transfer (RAFT) polymerization. When

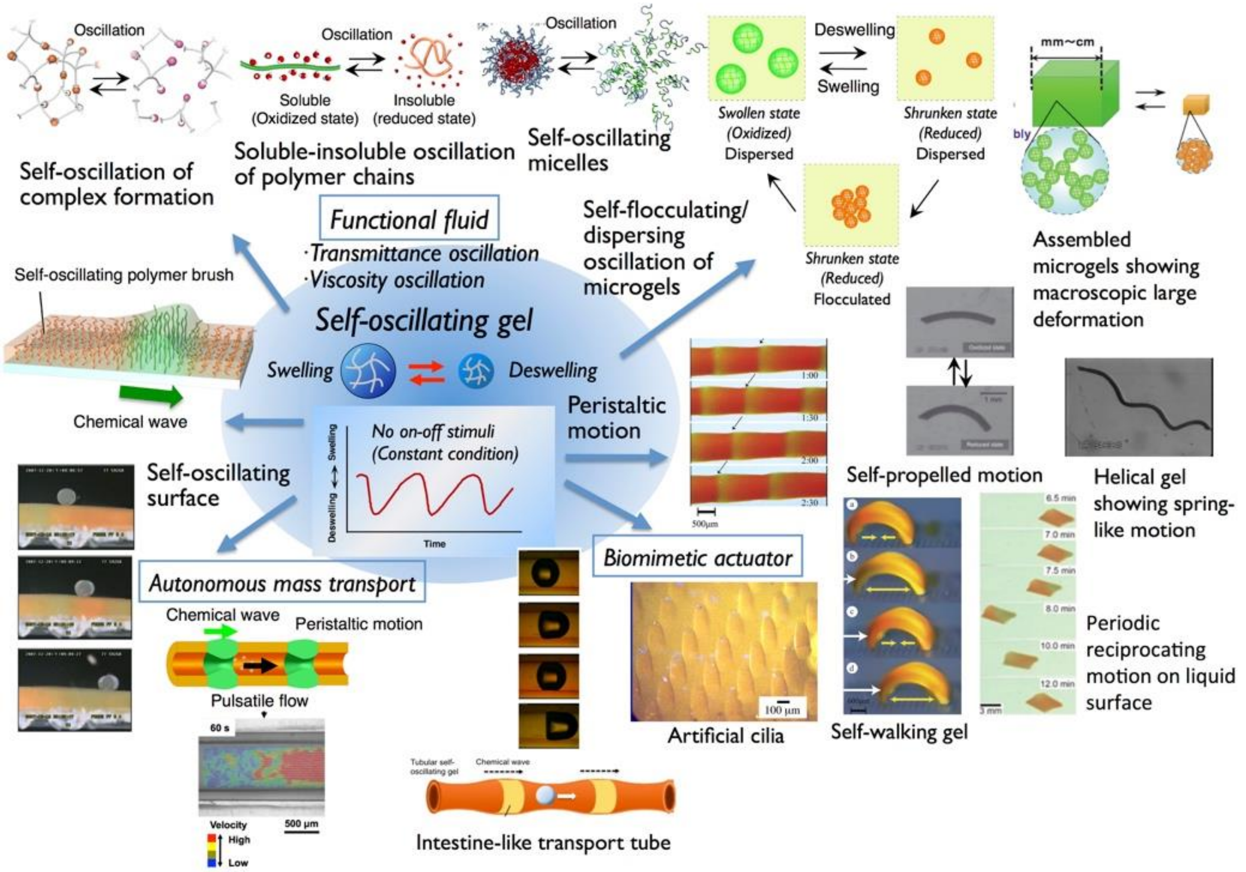

Fig. 3. Development of the self-oscillating gel using the BZ reaction.

the temperature was increased, the PEO-*b*-poly(NIPAAm-*co*-Ru(bpy)$_3$) block copolymer underwent a phase transition from unimers to micelles, driven by the change in the hydrophilicity of the self-oscillating segment. Importantly, in this system, the phase transition temperature is dependent on the redox states of the Ru(bpy)$_3$ centers. Therefore, there is a bistable temperature region, where micelles are stable in the reduced state, whereas unimers are stable in the oxidized state. Consequently, during the BZ reaction, autonomous structural oscillations between unimers and micelles (i.e., 'self-oscillating micelles') can be observed at the bistable temperature, and these oscillations follow the periodic changes in the redox state of Ru(bpy)$_3$ **(Fig. 4)**. From this starting point, many self-oscillating BCPs with dynamic autonomous behavior have been developed. In the following sections, we overview the recent development of self-oscillating BCP systems.

Self-oscillating vesicles

The self-assembled structures in dilute aqueous solutions of amphiphilic diblock copolymers change from spherical micelles to cylindrical micelles and then to vesicles as the volume fraction of the hydrophobic segment increases. Therefore, PEO-*b*-poly(NIPAAm-*co*-Ru(bpy)$_3$) diblock copolymers with a longer chain of the poly(NIPAAm-*co*-Ru(bpy)$_3$) block were synthesized to fabricate vesicles [65-67]. The autonomous association/dissociation of vesicles with micrometer dimensions was observed directly by optical microscopy. In common with vesicles in living cells, vesicle fusion was also confirmed during the association process. Considering the dynamic nature of biological vesicles, such as nuclear envelopes, synaptic vesicles, and cell membranes, the self-oscillating vesicles are a novel type of biomimetic vesicle with dynamic behavior.

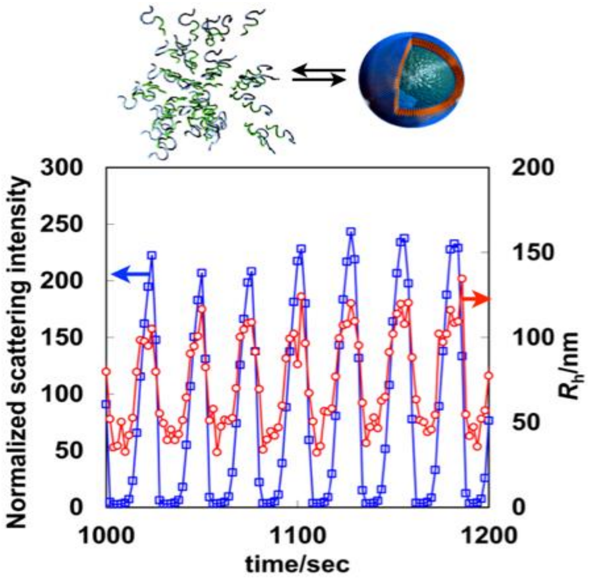

Fig. 4. Time variation of the normalized scattering intensities (blue) and R_h values (red) during the BZ reaction.

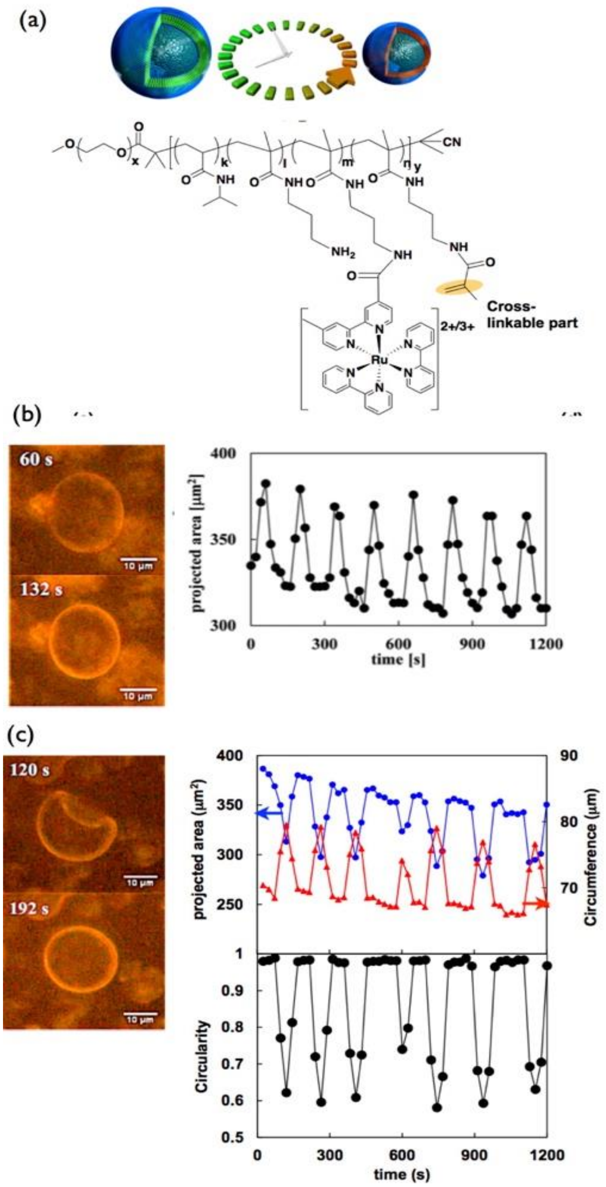

Fig. 5. (a) Schematic illustration of the self-oscillations of cross-linked vesicles and chemical structure of the cross-linkable self-oscillating diblock copolymer. (b) Optical images of swollen and deswollen states of the vesicle and time-variation of the projected area during the volume oscillation. (c) Optical images of buckled and unbuckled states of the vesicle and time-variation of the projected area (upper, blue), circumference (upper, red) and circularity (lower) during the shape oscillation.

Cross-linked polymersomes showing self-beating motion

The unique oscillatory motion of vesicle membranes similar to living cell membranes based on BCP self-assembly have also been demonstrated by covalently cross-linking the membranes of BCP vesicles (i.e., polymersomes). We prepared cross-linkable self-oscillating diblock copolymers containing double bonds in the self-oscillating segment **(Fig. 5(a))** [68]. The diblock copolymer formed vesicles at high temperatures. The cross-linked diblock copolymer vesicles were obtained by UV irradiation of the aqueous solution of the diblock copolymer with photo-initiators at a temperature above the unimer-to-vesicle phase transition temperature. The autonomous volume oscillations of cross-linked vesicles are shown in **Fig. 5(b)**. In addition to the volume oscillations, unique oscillations in the shapes of some cross-linked vesicles were observed. The images on the left of **Fig. 5(c)** show the two states observed during the shape oscillation, i.e., the buckled and the unbuckled states. The mechanism of the shape oscillations with buckling and unbuckling deformations can be explained as follows: When $Ru(bpy)_3$ in the vesicles is oxidized, membrane hydration occurs, causing tangential stress and increasing the surface area of the vesicles. If the tangential stress is larger than the buckling threshold, a buckling deformation occurs, increasing the surface area and reducing the stress. In contrast, when $Ru(bpy)_3$ is reduced, tangential stress is applied in the opposite direction, reducing the surface area. Consequently, recovery from the buckled state to the unbuckled state takes place. As a result, periodic shape changes, including buckling and unbuckling deformations, are driven by the cyclic changes in the redox state of $Ru(bpy)_3$ over the course of the BZ reaction. Self-oscillating cross-linked vesicles showing dynamic structural changes provide an artificial cell model and might be useful to understand the dynamic nature of biological membranes.

Self-oscillating colloidosomes

Recently, an increasing number of researchers have investigated the fabrication of hollow microstructures based on templating emulsions stabilized by colloidal particles, so called "colloidosomes". Based on this strategy using the self-assembly of colloidal particles onto water/oil emulsions, which act as hollow particle templates, we have fabricated "self-oscillating colloidosomes" that exhibit unprecedented and complex shape oscillations [69]. During the BZ reaction, the shapes of the colloidosomes undergo buckling deformations, similar to the cross-linked BCP vesicles described before. However, compared to the shape oscillations of the cross-linked BCP vesicles, the oscillatory profiles of colloidosomes had more complex waveforms, attributed to the existence of three stages of oscillations, i.e., i) unbuckled and swollen, ii) unbuckled and deswelled, and iii) buckled **(Fig. 6(a))**. This three-stage behavior can be explained by the fast relaxation kinetics of colloidosomes due to their porous structure. As a result, relaxation from the buckled state to the unbuckled swollen state occurred in the oxidized state, resulting in complex oscillatory waveforms. Furthermore, other complex oscillatory changes such as multiple buckling deformations and movement of buckling points were observed for large colloidosomes **(Fig. 6(b))**. Interestingly, complex oscillatory shape deformations of cell membranes have been observed in cells with large diameters, for example, fibroblast cells.

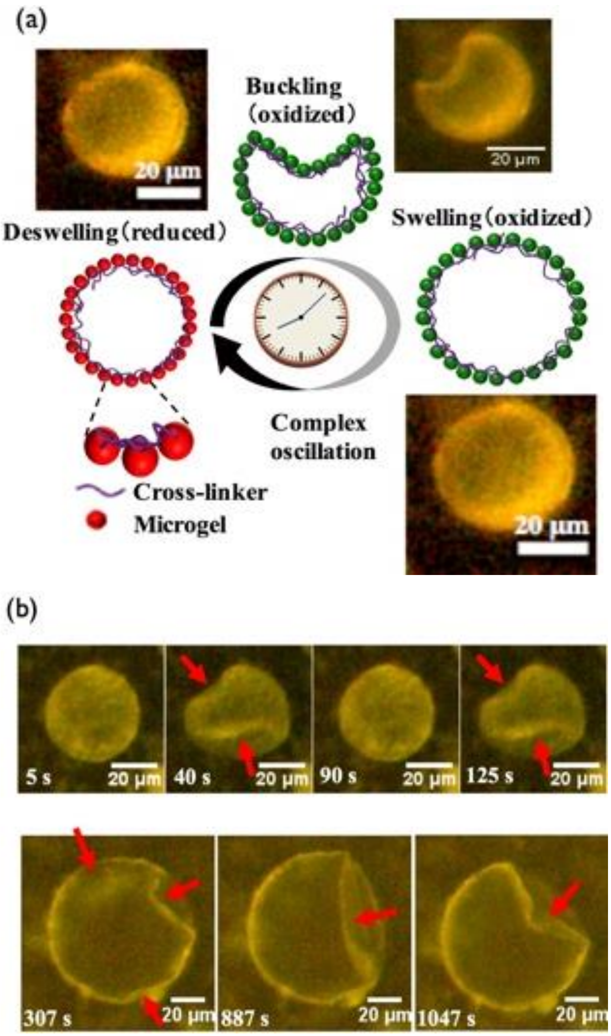

Fig. 6. (a) Schematic illustration of the shape oscillation of the colloidosome. (b) The complex oscillatory behavior is accompanied by multiple buckling deformations and the movement of buckling points.

Viscosity oscillations of self-oscillating multiblock copolymers

Although even the simplest AB-type diblock copolymers offer a variety of self-assembled morphologies, multiblock copolymers with more than two segments offer an even greater array of self-assembled structures. By precisely designing the self-oscillating multiblock copolymers, microscopic structural oscillations can be converted to macroscopic viscosity oscillations [70]. Therefore, ABA-type triblock copolymers, composed of a self-oscillating A-segment and a hydrophilic B-segment, were synthesized. It is well known that ABA triblock copolymers with a thermoresponsive A-segment and a solvophilic B-segment can undergo sol-to-gel transitions through the formation of micellar networks in a concentrated solution. Therefore, it is expected that microscopic oscillations in the formation and deformation of micellar networks can be converted to macroscopic oscillations in the bulk viscoelastic properties by using the ABA-type self-oscillating triblock copolymers. As expected, we succeeded in realizing autonomous viscosity oscillation by microscopic self-oscillation between formation and break-up of the network structure by preparing ABA triblock copolymer.

Amoeba-like self-oscillating polymeric fluids with autonomous sol-gel transition

However, the viscosity amplitude was limited (~2 mPa s). In order to achieve the significant increase in the amplitude of oscillation, we designed a ABC tri-BCP that is responsible for drastic structural changes. As a result, this copolymer shows a sol-gel transition with association and dissociation of percolated network structures similar to that in a living amoeba under constant condition without any external stimuli [71]. The target multiblock copolymer was synthesized by RAFT polymerization incorporating a thermoresponsive A segment, a hydrophilic B segment, and a self-oscillating C segment **(Fig. 7(a))**. The thermoresponsive A segment is composed of *N*-isopropylacrylamide (NIPAAm) and *n*-butylacrylate (BA). It showed a lower critical solution temperature (LCST)-type phase transition (T_A). In contrast, the self-oscillating C segment was designed to have a LCST-type aggregation temperature (T_C) higher than T_A to achieve a stepwise aggregation which suppress the formation of a loop chain. As a result, the efficient formation of a network structure could be achieved. Here, the redox state of Ru(bpy)$_3$ introduced in the C segment affected T_C. T_C in the oxidized state ($T_{C,\ Ox}$) increased more than it did in the reduced state ($T_{C,\ Red}$). Therefore, a bistable temperature (T_b) emerges between $T_{C,\ Red}$ and $T_{C,\ Ox}$. At T_b, an autonomous micellar connection/dispersion oscillation coupled with a redox change of Ru(bpy)$_3$ driven by the BZ reaction could occur without applying any external stimuli. Consequently, in a concentrated polymer solution, autonomous viscosity oscillation and sol-gel oscillation could be realized through percolation of the micellar network structure **(Fig. 7(b))**.

When the polymer concentration was 5.0 wt%, the viscosity amplitude reached a maximum of 1,960 mPa s. This value is comparable to the amplitude occurring in living amoeba, and about 10^3 times larger than that observed in previous reports. Further, *G*' and *G*'' were measured as a function of time to investigate the profile of the viscoelastic oscillation **(Fig. 7(c))**. As a result, autonomous sol-gel oscillations were observed **(Fig. 7(d))**. It is notable that a self-oscillating sol-gel transition was observed repeatedly and reversibly under constant condition without any external stimuli. **Fig. 7(e)** and **(f)** show the behavior of the small droplet of the polymer solution filled inside a tilted glass capillary. We could clearly observe an intermittent forward motion of the droplet inside the capillary. This intermittent motion is due to spontaneous and periodic sol-gel transitions of the polymer solution. Thus, we successfully demonstrated an intermittent forward motion of the polymer solution.

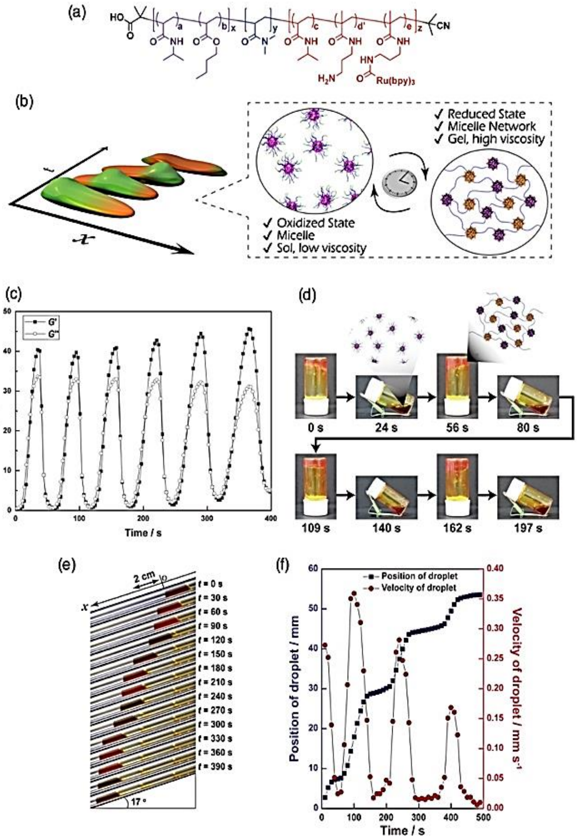

Fig. 7. (a) Chemical structure of the ABC triblock copolymer. (b) Conceptual illustration of the autonomous and periodic sol-gel transition based on structural changes driven by redox changes of the ABC triblock copolymer. (c) Oscillating profiles of *G*' and *G*'' of ABC triblock copolymer solution (5.0 wt%) at 30 °C, with $\gamma = 2.0$ % and $f = 1.0$ Hz. (d) Direct observation of an autonomous sol-gel oscillation of the ABC triblock copolymer solution (5.0 wt%) at 30 °C. (e) Intermittent forward motion of a droplet of the ABC triblock copolymer solution inside a glass capillary by autonomous and periodic sol-gel transition at 26 °C. (f) The position and the velocity of the droplet inside the glass capillary.

Concluding remarks

As mentioned above, we have developed novel "self-oscillating" polymer gels that exhibit oscillation like heart muscle under constant external conditions. Since the first report INS 1996, we have systematically studied those polymer gels as well as their applications to smart materials. Herein, our recent progress on the self-oscillating materials was summarized. As an innovative study to propose novel potential of polymer gels and achieve an autonomous behavior by coupling chemical and mechanical oscillators in polymer systems, the study has attracted much attention in the research field of polymer science, materials science, physical chemistry, theoretical simulation, biophysics, *etc*. The future applications for biomaterials would be also envisioned. We will continue advance our research toward more innovations.

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