

論文の内容の要旨

Fabrication of self-oscillating hydrogel containing magnetic nanoparticles and
the regulation of dynamic behaviors

(磁性ナノ粒子を内包する自励振動ハイドロゲルの作製と動的挙動の制御)

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In the natural world, there are many oscillation systems that spontaneously cause spatiotemporal periodic changes, and they play a significant role in maintaining temporal and spatial order such as rhythm and pattern formation seen in life phenomena. Research on biomimetic/bioinspired materials that express new functions by mimicking, or inspiring from, such a spontaneous cyclic reaction will open up the way for the science of new functional soft materials in the future. In the past, researches have been carried out by using stimulus-responsive hydrogels to realize flexible movement like a living bodies through the on/off switch of external stimuli. In contrast, the self-oscillating hydrogels have been developed that shows an autonomous swelling/deswelling without the on/off switching of external stimuli by employing the Belousov-Zhabotinsky(BZ) reaction, which spontaneously undergoes periodic redox changes. Applications to biomimetic actuators and automatic material transport systems utilizing peristalsis associated with the propagation of chemical waves has been proposed. However, the regulation of dynamic behavior of the self-oscillating hydrogels has not yet been achieved in many ways. In particular, there are the reversible control of propagated chemical waves at desired time and on/off regulation of self-oscillation using a physical signal not affecting the BZ reaction.

The final goal of the doctoral dissertation is the regulation of dynamic behaviors, which appeared in the form of a chemical wave propagation and a volume oscillation depending on the size of self-oscillating hydrogels, by the external magnetic field. In order to achieve this

goal, the magnetic nanoparticles were introduced into self-oscillating hydrogels, and dynamic behaviors were regulated by magnetic activation modes, as shown in the **Figure 1**.

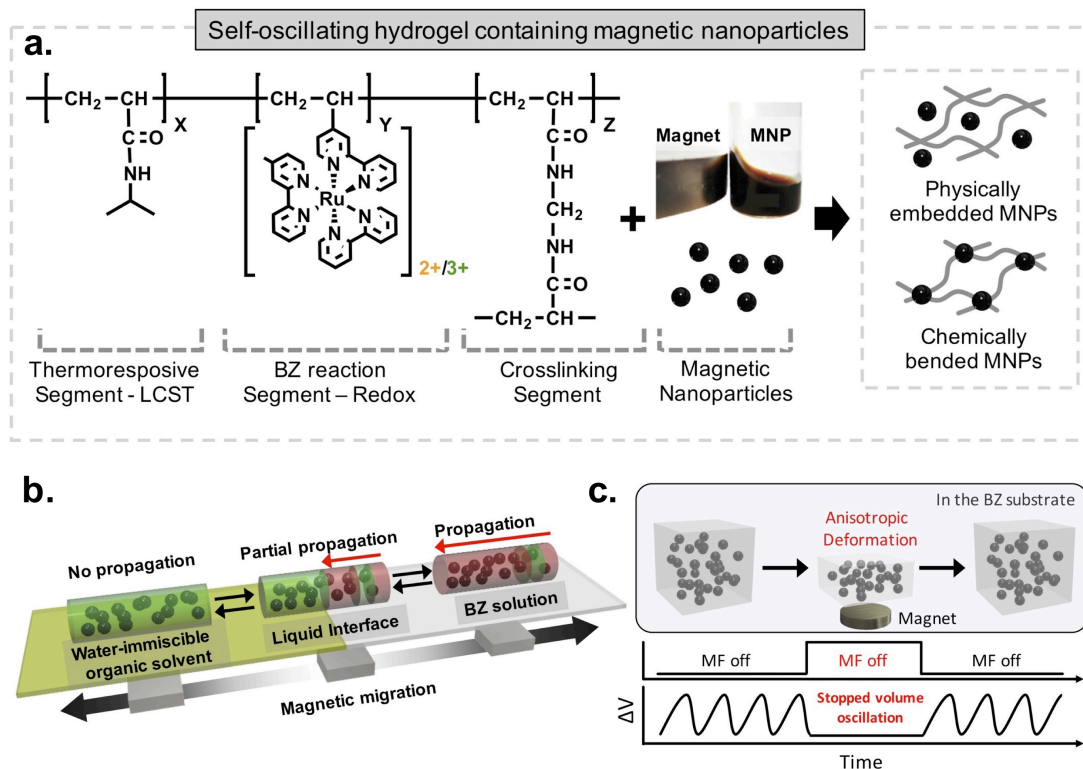


Figure 1. Overview of this dissertation. **(a)** Development of self-oscillating hydrogels containing magnetic nanoparticles (Chapter 2), **(b)** the directional control of chemical wave propagation by the magnetic migration (Chapter 3), and **(c)** the reversible on-off regulation of volume oscillation in the self-oscillating hydrogel by the magnetic deformation (Chapter 4), respectively.

In chapter 2., the synthetic strategy of self-oscillating hydrogels containing physically or chemically magnetic nanoparticles is investigated. First, a method for gelation to uniformly include magnetic nanoparticles is considered. The self-oscillating copolymer having an amino group is synthesized by using a RAFT polymerization method which is a type of precision polymerization method. Thereafter, a method for completing the gelation before the precipitation of the magnetic nanoparticles is established by synthesizing a copolymer having a functional group capable of chemically bonding to an amino group, mixing the two polymer solutions and quickly gelation the resultant mixture. Next, in order to prepare the self-oscillating

hydrogel chemically containing magnetic nanoparticles, the surface modification of magnetic nanoparticles was carried out by the silanization and the chemical conjugation, and the surface of magnetic nanoparticles modified to amine groups and vinyl groups, respectively. Then the functional groups were confirmed by zeta-potential, DLS and FT-IR measurements. In the case of magnetic nanoparticles having amino groups, the self-oscillating hydrogel chemically containing magnetic nanoparticles by mixing with the two copolymers described above. In the case of a magnetic nanoparticle having vinyl groups, it is prepared by the direct polymerization with a monomer.

In chapter 3., the directional control of chemical wave propagations is demonstrated by magnetic migrations of self-oscillating hydrogels physically containing magnetic nanoparticles with a change in the position of liquid interface consisted of aqueous BZ solution and water immiscible organic solvents (hexane and dichloromethane). The chemical waves started in the BZ solution and propagated to the interface between the two liquids. This propagation behavior revealed the possibility that the propagation direction of the chemical waves could be controlled by the position of the liquid interface. Therefore, by magnetic migration of the self-oscillating hydrogel in the liquid layer system, it could control not only the propagation direction but also the dynamic propagation behavior, such as a pause in the propagation and a switch in the propagation direction in an opposite way.

In chapter 4., the reversible on-off regulation of the volume oscillation in self-oscillating hydrogels by the magnetic deformation is investigated. The external magnetic field can lead to the network deformation of hydrogels containing magnetic nanoparticles, and the deformation degree can be controlled by their pore size. In order to achieve this concept, it was designed that the bulk-gel was composed of hydrogel beads chemically containing magnetic nanoparticles to form the porous structure and to prevent damage caused by applying a reversible magnetic field; therefore, hydrogel beads were prepared by the suspension polymerization. Finally, it is important to control the distance between the chemical bonding site of cross-linker to form the bulk-gel and it is expected that the bulk-gel composed of hydrogel beads can be deformed by the external magnetic field due to the porous structure through unlinked beads.

Finally, in Chapter 5, the researched in this dissertation are summarized, and future perspectives about self-oscillating hydrogels containing magnetic nanoparticles applicable to the energy conversion system using dynamic behaviors are described.