Self-Oscillating Gel

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Conventional stimuli-responsive hydrogels provide one unique action, either swelling or deswelling in response to external stimuli such as a change in solvent composition,[1,2] pH,[1−3] temperature,[4−6] etc. Here we report a novel polymeric gel which autonomously swells and deswells periodically in a closed homogeneous solution without any external stimuli, similar to autonomic phenomena in life such as heartbeat. The mechanical oscillation is achieved by inducing the Belousov−Zhabotinsky (BZ) reaction[7] within the gel. We prepare a copolymer gel of *N*-isopropylacrylamide (IPAAm) in which ruthenium(II) tris(2,2′-bipyridine) ($Ru(bpy)_3^{2+}$), a catalyst for the BZ reaction, is covalently bonded to the polymer chain. The poly(IPAAm-*co*-$Ru(bpy)_3$) gel swells and deswells at the oxidized and reduced states of $Ru(bpy)_3$, respectively. The BZ reaction in the gel generates periodic redox changes of $Ru(bpy)_3$, and the chemical oscillation induces mechanical oscillation of the polymer network.

Many polymeric gels undergo abrupt volume change in response to external stimuli, and they have been utilized to design intelligent materials which imitate stimuli-responding functions in living systems, such as actuators[8,9] and pulsatile drug release devices,[10−12] etc. In contrast to the unique gel action of either swelling or deswelling toward a stable equilibrium state, many physiological systems maintain rhythmical oscillations in a nonequilibrium state, as represented by the autonomic heartbeat, brain waves, periodic hormone secretion, etc. If such self-oscillation without any external stimuli is achieved for gels, a new concept will be created for functional materials that work under dynamic oscillating states similar to life systems, such as self-walking actuators, new pacemakers and timers, drug delivery systems synchronized with human circadian rhythms, etc. For example, a strategy for an oscillatory drug release system utilizing a gel membrane coupled with an enzyme reaction is studied numerically by Siegel et al.[13] In a previous report,[14] we achieved periodic swelling−deswelling changes of gels soaked in an autonomous pH-oscillating solution in a continuously-stirred tank reactor. However, gels that provide volume oscillation without external control in a closed solution have not been developed yet. In gel systems, the only oscillatory phenomenon known both theoretically and experimentally is sol/gel transition.[15−17]

The BZ reaction is well-known for exhibiting temporal and spatial oscillating phenomena with periodic redox changes of the catalysts in a closed solution, and its significance has been recognized in understanding some aspects of life phenomena in transmission of information, pattern recognition and self-organization, etc.[18−21] We attempt to convert the chemical oscillation of the BZ reaction to the mechanical changes of gels and generate an autonomic swelling−deswelling oscillation under nonoscillatory outer conditions. Whereas hydrogels have been used as the BZ reaction medium in order to suppress hydrodynamic convection and immobilize the catalyst,[21] we utilize a gel in which the BZ reaction causes periodic redox changes within the polymer network. In conventional stimuli-responsive gels, gels in which enzymes are immobilized by physical entrapping in the networks have been prepared to convert chemical change to mechanical work.[22] These gels undergo volume phase transition by addition of a substrate. In these systems, gels act as immobilization support and they demonstrate either swelling or deswelling only when environmental chemical change occurs. In our novel gel, however, the polymer networks themselves undergo reaction and spontaneously create their periodic motion without any environmental change.

We synthesized ruthenium (4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine)bis(hexafluorophosphate) ($Ru(vmbpy)(bpy)_2(PF_6)_2$) as a polymerizable BZ catalyst from 4,4′-dimethyl-2,2′-bipyridine according to the procedure reported by Spiro et al.[23] IPAAm monomer (0.156 g), $Ru(vmbpy)(bpy)_2(PF_6)_2$ (8.21 mg), *N*,*N*′-methylenebis(acrylamide) (2.79 mg) as a cross-linker, and *N*,*N*′-azobis(isobutyronitrile) (6.56 mg) as an initiator were dissolved in 1 mL of methanol which had been previously purged with nitrogen gas. The solution was then injected between two Mylar sheets separated by a Teflon gasket (0.5 mm thickness) and backed by glass plates. The solution was polymerized at 60 °C for 18 h. The gel membrane was immersed in methanol to remove unreacted compounds for 1 week, with the methanol being changed every day. The membrane was then soaked in 75/25, 50/50, 25/75, and 0/100 vol %/vol % methanol/distilled water mixtures for 1 day each. The prepared poly(IPAAm-*co*-$Ru(bpy)_3$) gel is tinged with orange and transparent in pure water, suggesting that $Ru(bpy)_3$ is homogeneously copolymerized in the reduced state.

The synthesized gel has the chemical structure that the $Ru(bpy)_3$ as a redox moiety is copolymerized into the poly(IPAAm) gel network. The homopolymer gel of poly(IPAAm) is well-known for exhibiting remarkable swelling and deswelling changes in response to temperature, demonstrating the phase transition at around 32 °C in pure water.[4−6] In the case that vinylferrocene is introduced into the thermosensitive polymer gels as a redox moiety, the phase transition temperature increases

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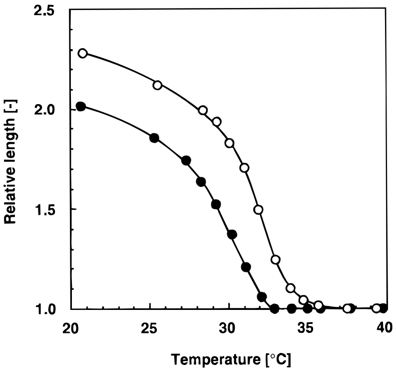

Figure 1. Equilibrium swelling ratio of poly(IPAAm-*co*-Ru(bpy)$_3$) gel in cerium sulfate solutions as a function of temperature. (●) $Ce_2(SO_4)_3$ = 0.001 M and HNO_3 = 0.3 M; (○) $Ce(SO_4)_2$ = 0.001 M and HNO_3 = 0.3 M. The relative length is defined as the ratio of characteristic diameter to that at the shrunken state over the phase transition temperature.

or decreases with the change in the oxidized or reduced state, respectively.[24-26] This temperature shift is due to the change in the hydrophilic−hydrophobic properties of polymer chains with oxidation and reduction. Figure 1 shows the swelling behavior of poly(IPAAm-*co*-Ru(bpy)$_3$) gel in two solutions of Ce(III) and Ce(IV), respectively, under the same acidity. In the Ce(III) solution, the gel keeps a tinge of orange, which suggests that the copolymerized Ru(bpy)$_3$ remains reduced. In the solution, the gel undergoes a phase transition in the vicinity of 33 °C. The phase transition temperature is the same as that for poly(IPAAm) gel in 0.3 M nitric acid, and the effects of the redox moiety are not obtained. This result may be attributed to both increases in hydrophilicity due to the charge of Ru and hydrophobicity due to coordination of bipyridine. In the Ce(IV) solution, which is a powerful oxidizing agent, however, the gel quickly turns from orange to green, suggesting that Ru(II) is oxidized to Ru(III). The phase transition temperature shifts to a higher region around 36 °C because the hydrophilicity of the polymer increases due to the increase in the charge of the redox moiety.[24-26] This deviation of the phase transition temperatures between Ru(II) and Ru(III) states results in remarkable swelling and deswelling changes with redox changes of Ru(bpy)$_3$ at constant temperature.

In the reaction solution, the chemical wave generated by the periodic redox changes of Ru(bpy)$_3$ propagates in the poly(IPAAm-*co*-Ru(bpy)$_3$) gel. The redox pattern and the following swelling−deswelling changes of the gel are demonstrated in Figure 2 ((a) the spatio−temporal diagram constructed from digitized sequential images and (b) the supplementary illustration). The redox state in the gel is presented in gray scale (dark; reduced state, light; oxidized state). In the gel, the period of chemical oscillation is about 6 min and the chemical wave propagates with the velocity of approximately 0.03 mm/s. With the propagation of the chemical wave, the gel boundary fluctuates with the periodical changes of the gel length with an amplitude of several tens of micrometers. The two vertical lines in the picture are the tracks of the marker showing a certain position in the gel. The markers move into the interior at the initial stage, which means the oscillation of the gel occurs with

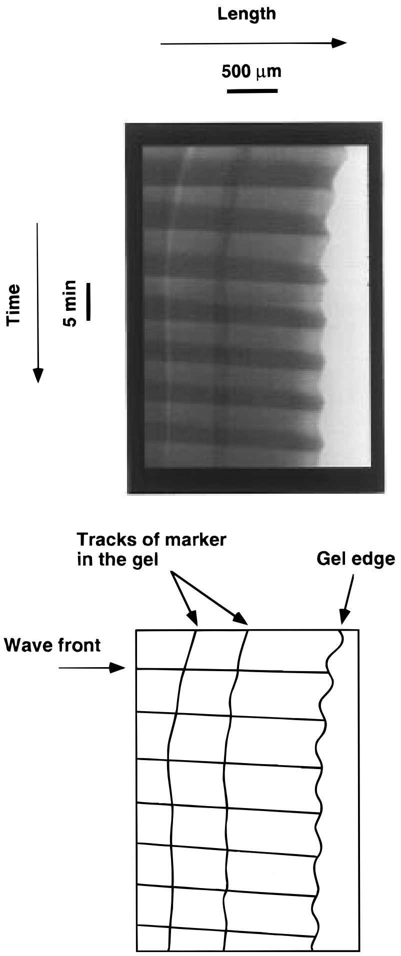

Figure 2. (a) Spatio−temporal pattern of gel oscillation. The rectangular poly(IPAAm-*co*-Ru(bpy)$_3$) gel (1 mm × 1 mm × 20 mm) was immersed in 8 mL of the aqueous solution containing malonic acid (0.0625 M), sodium bromate (0.084 M), and nitric acid (0.3 M) in a petri dish at 20 °C . The time course of the pattern formed on the gel was recorded on a VTR through a CCD camera. One-line images along the gel length were sampled every 3 s, and a time series of 880 frames (44 min) was pictured by a personal computer. In general, sulfuric acid is used as an acidic medium in the BZ reaction. However, since the swelling difference between Ru(II) and 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. (b) Schematic illustration of 2a.

a decrease in the total length. This total deswelling is due to an increase in ionic strength after the gel is transferred from the store solution (pure water) to the reaction solution. In the steady state, the gel oscillation exhibits contraction at the oxidized state and expansion at the reduced state. These results are opposite to the equilibrium swelling behavior of the gel demonstrating higher swelling at the oxidized state. The characteristic delay of gel swelling and deswelling in response to the chemical oscillation may generate such a mechanical oscillation with a phase shift. Probably, the mechanical changes of the gel reversely effect the chemical oscillation because the solute diffusivity varies in the gel, which may also contribute to the observed phase differences between mechanical and chemical oscillations. The details are under investigation.

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