

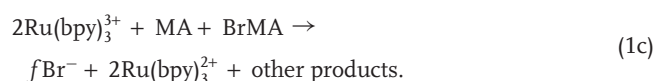
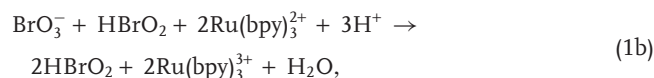
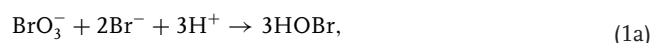
Mechanical Resuscitation of Chemical Oscillations in Belousov–Zhabotinsky Gels

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The conversion of mechanical to chemical energy is a natural phenomenon that few synthetic materials have been able to mimic robustly. The first demonstration of mechanical triggering of Belousov–Zhabotinsky (BZ) oscillations is presented in *N*-isopropylacrylamide-*co*-Ru(bpy)₃ gels for which the oscillatory nature of the BZ reaction can be visualized via periodic changes in color. It is demonstrated that BZ oscillations can be induced by the application of compressive stress to gels in which the BZ reaction has attained a steady-state upon depletion of reagents. Such macroscopic compression physically increases the volume fraction of polymer to which the Ru(bpy)₃ catalyst is grafted and triggers BZ oscillations by utilizing unreacted reagents in the aqueous solution, thus effectively resuscitating and extending the functionality of these oscillatory gels. The applied stress and the initial concentrations of malonic acid are varied to show that there is a critical stress required to trigger and restore these oscillations, and that the period and amplitude of oscillation are tunable. Leveraging this capacity to restore the functionality of the material via applied pressure, sensor applications comprising discrete BZ gels, which are capable of both visually indicating the origin of mechanical loading and transmitting this signal away from the deformation site, are demonstrated. Mechanical resuscitation of such chemical oscillations affords novel approaches to creating pressure sensors based on self-oscillating gels.

Recent developments demonstrate that synthetic materials are also capable of responding to changes in temperature, pH, and electric field.^[2–4] However, few synthetic materials are able to produce oscillating chemical signals in response to mechanical stimuli. Such synthetic material analogues could enable devices that mimic self-healing and pressure-sensitive processes where molecular mechanoreceptors enable rapid and localized transmission of chemical signals.^[5,6] Self-oscillating polymer gels that can actuate by periodically swelling and shrinking are unique candidates for such stimuli-responsive functional materials. For example, gels comprising *N*-isopropylacrylamide-*co*-Ru(bpy)₃ contain covalently bound transition metal catalyst (Ru(bpy)₃) and can respond to chemical stimuli as a result of the Belousov–Zhabotinsky (BZ) redox reaction, as demonstrated previously.^[7,8] In these NIPAAm-*co*-Ru(bpy)₃ gels, the BZ reaction proceeds via the oxidation of an organic substrate in acidic solution, which causes cyclic color changes in the oxidation state of the Ru(bpy)₃ catalyst. Although the

kinetics of the BZ reaction are quite complex, involving dozens of chemical species, the Field–Körös–Noyes (FKN) mechanism summarizes the BZ kinetics in three main processes:^[9,10]



The above system of equations was formulated originally for BZ reactions occurring in solution.^[9,10] However, the presence of chemically neutral NIPAAm chains does not change the reaction mechanism presented above. The polymer acts as a neutral diluent and affects the reaction kinetics by changing the local reactant concentrations.^[11,12] In this particular BZ gel system, the chemical state of the gel visibly fluctuates between oxidized Ru(bpy)₃ catalyst (3⁺ state), corresponding to a green hue, and a reduced catalyst (2⁺ state), corresponding to an orange hue.

1. Introduction

Biological materials such as cardiac and skin tissue exhibit the unique capacity to transduce mechanical stimuli into propagating electrical and chemical signals throughout the body.^[1]

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Changes in catalyst oxidation state affect the phase transition temperature of the thermosensitive NIPAAm polymer, resulting in periodic changes in the overall hydrophilicity of the gel for constant system temperature.^[13] Several studies have shown that the oscillatory characteristics and mechanical behavior of these BZ gels can be controlled by varying the chemistry of the reaction.^[14,15] At sufficiently small gel dimensions, color changes are accompanied by significant changes in overall gel volume.^[8,16] Further, it is well appreciated that these oscillations are indicative of a slow and cyclic approach to a monochromatic steady-state: the visible reactions cease when the concentration of reactants are sufficiently depleted.^[17] However, while BZ gels exhibit strong chemomechanical coupling, such as synchronized swelling and color change, there has been no experimental evidence demonstrating that these gels can also exhibit a chemical (or visible) reaction to mechanical stimuli.

Thus far, results demonstrating that a BZ signal can be mechanically triggered have been limited to membranes containing electrostatically bound ferriin catalyst. Suzuki et al. observed that local compression of an immersed, thin (approximately 200 μm) BZ Nafion membrane using a glass stick triggered a single target wave in an initially excitable but non-oscillatory system;^[18] Munuzuri et al. also demonstrated that stretching of polyacrylamide-silica gels resulted in vortex drift of BZ spirals.^[19] Computational simulations have predicted a wide variety of chemical behavior in response to the mechanical deformation of a BZ gel. These mechanical stimuli include macroscopically uniform compression, locally applied pressure, and mechanical strain. In particular, Kuksenok et al. predicted that mechanical stimuli can trigger chemical oscillations in an initially non-oscillating BZ gel; this simulated response suggests that the material can undergo transitions between oscillatory and non-oscillatory regimes.^[20–22]

In this study, we induced macroscopic compression by applying uniaxial stress to fully hydrated NIPAAm-co-Ru(bpy)₃ gels. We demonstrated that BZ oscillations can be triggered reversibly in the gel under specific conditions: a non-oscillatory gel submerged in a solution depleted of BZ reactants can be stimulated to oscillate in color under sufficiently large applied stress, and can cease to oscillate upon removal of that stress. This mechanical restoration of oscillation in an exhausted system evokes analogy to the resuscitation of a beating heart, though the mechanisms by which BZ oscillations are triggered and restored in a reactant-depleted gel are quite different than the systems-level restoration of blood flow. Furthermore, we demonstrated the tunability of BZ gel resuscitation by varying the chemical conditions of the reaction to show how the period and amplitude of mechanically triggered oscillations are affected. Finally, we designed an array of discrete BZ gels that leverages mechanical resuscitation to act either as a touch sensor sustaining an oscillatory chemical signal at the unique location of stress application, or as a touch sensor transmitting chemical signals along the array.

2. Results and Discussion

Figure 1 shows that chemical oscillations can be mechanically triggered in a BZ gel. In the present experiment, a BZ gel disc

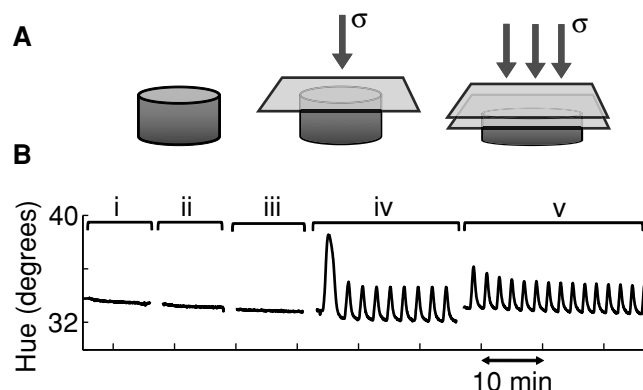


Figure 1. Mechanically triggered BZ oscillations. A) Schematic of a gel being macroscopically compressed (not to scale). B) 1.2 mm diameter BZ gel disc (0.6 mm thickness and 8.3 mm Ru(bpy)₃ catalyst) in BZ solution with initial composition: malonic acid (0.2 M), sodium bromate (0.1 M), and nitric acid (0.7 M). Increasing amounts of stress was applied to the gel throughout the experiment: i) 0.1 kPa, ii) 0.3 kPa, iii) 0.4 kPa, iv) 1.2 kPa, and v) 5.6 kPa.

of millimeter-scale dimensions and containing covalently bound Ru(bpy)₃ catalyst was submerged in the chemical reactants necessary for oscillations to occur: malonic acid, sodium bromate, and nitric acid. Experiments were conducted at 20 °C, which is below the phase transition temperature of NIPAAm (see the Experimental Section for quantification of phase transition temperature in this system); the temperature of both the external solution and BZ gel did not vary over the course of the experiment. Spontaneous BZ oscillations were initially observed in the uncompressed gel as the chemical reactants in the external BZ solution diffused into the gel disc and reacted with the confined Ru(bpy)₃ catalyst. Eventually, a non-oscillatory state was obtained, indicating the depletion of BZ reactants. The gel was monitored for 1 h to confirm that the Ru(bpy)₃ catalyst was in a uniformly reduced state. Next, increasing amounts of macroscopic, compressive stress was applied to the gel by placing glass slides of known mass on top of the disc, adding an additional slide to the current stack in 10 min intervals to increase the total applied stress (Figure 1B, i–v). As shown schematically in Figure 1A, there was no measurable change in gel thickness when relatively small amounts of stress (less than 1.2 kPa) were applied. Increasing amounts of applied stress caused the gel to expand laterally and reduce in thickness upon compression (from 600 to 589 μm). Figure 1B shows that the gel remained in a non-oscillatory state when the applied stress was between 0.1 and 0.4 kPa. When the stress was increased to 1.2 kPa, the Ru(bpy)₃ catalyst within the gel immediately changed visually from orange to green. The color change was uniform and wave patterns were not observed due to the small dimensions of the BZ gel.^[8] The applied stress was held constant for 30 min, during which the catalyst-containing gel continued to oscillate with a period of 2.3 ± 0.05 min and an amplitude of 2.6 ± 0.1 degrees. Increasing the applied stress to 5.6 kPa caused the gel to compress by 11 μm but did not qualitatively change the oscillatory characteristics (see Figure 1B, v). This experiment demonstrates that chemical oscillations can be mechanically triggered in a polymer gel, and that there may exist a critical stress required to trigger such visible oscillations in color.

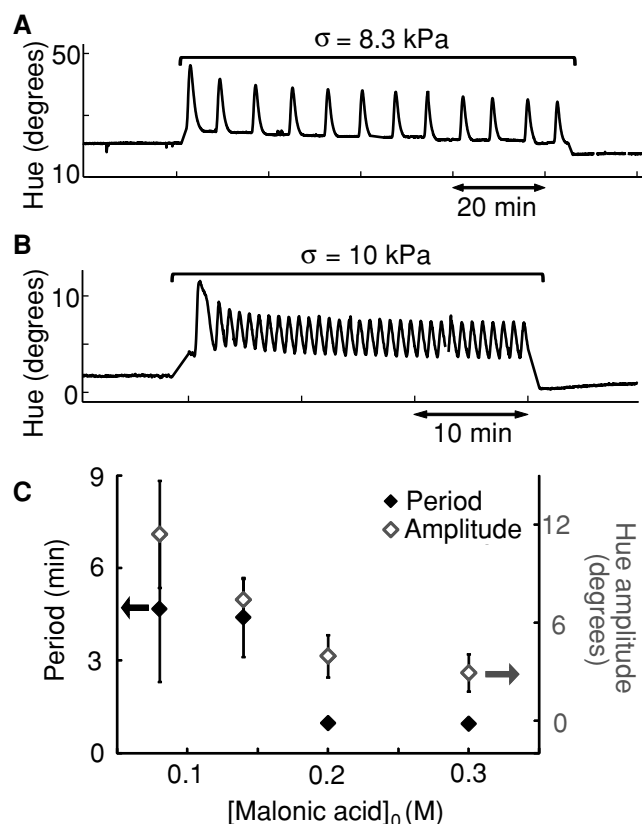


Figure 2. Triggered oscillations versus malonic acid concentration in BZ gel discs of 0.7–0.9 mm diameter (0.6 mm thickness and 8.3 mM Ru(bpy)₃ catalyst). A) Triggered oscillations in a BZ gel after 20 h in a solution containing malonic acid (0.08 M), sodium bromate (0.1 M), and nitric acid (0.7 M). B) Triggered oscillations in a BZ gel after 20 h in a solution containing malonic acid (0.3 M), sodium bromate (0.1 M), and nitric acid (0.7 M). C) Triggered period and amplitude of oscillations for gels submerged in BZ solutions with different initial concentrations of malonic acid. Applied stress was between 0.7 and 11.3 kPa. Error bars represent standard deviation for replicate experiments in different gel samples.

It is important to note that the mechanically triggered oscillations illustrated in Figure 1 were achieved after a specific history of exposing the gel to BZ reagents. The reaction conditions for which non-oscillating gels can be mechanically triggered to oscillate were achieved for a range of chemical conditions by submerging BZ gels in the necessary reactants and exhausting the system via reactant depletion over many hours. **Figure 2** summarizes a set of experiments in which unused, freshly cut BZ gel discs of 0.7–0.9 mm diameter and 0.6 mm thickness were submerged in 5 mL of BZ solution at time zero. Samples were cut from the same source of polymer gel via a biopsy punch, and consistent catalyst distribution among replicate gel samples was confirmed prior to the experiment by quantifying the hue of each gel in water (see the Supporting Information). The gels remained immersed in the BZ solution bath for 20 h. This immersion interval was required in order to achieve a consistent, non-oscillatory state within the gel, regardless of the initial BZ conditions such as acid concentration. During this time, the BZ gel was allowed to self-oscillate to the point of exhaustion, meaning that reactant molecules were consumed

while inhibitor species were produced until the gel eventually stopped oscillating. After 20 h, the non-oscillatory state of the gel was quantified and confirmed by monitoring the sample hue under an optical microscope in the BZ bath for at least 1 h. Compressive stress was applied to the gel, sufficient to trigger BZ oscillations, and maintained constant for 40–80 min. The critical stress required to trigger oscillations varied between 0.7 and 1.2 kPa. We note that slight differences in gel composition and thickness may affect these results. See the Experimental Section and the Supporting Information for specific details, including calculations of color in terms of hue. We applied a range of compressive stresses to the gels, varying between 0.7 and 11.3 kPa, and found that the oscillatory period and amplitude for a gel at a given acid concentration was unaffected by the magnitude of applied stress (beyond the critical stress for a specific gel). Although periodic swelling and shrinking of the gel was observed in freely self-oscillating BZ gels (not shown here, but similar to observations by Chen et al.),^[8] such volumetric changes were negligible for mechanically triggered gels oscillating at low amplitude under applied compression.

As shown in Figure 2A and B, removal of the applied stress caused oscillations to cease. These results suggest that the action of applying compressive stress to the gel effectively changes the local concentrations of chemical reactants in the BZ reaction. In particular, macroscopic compression physically increases the volume fraction of polymer to which the Ru(bpy)₃ catalyst is grafted. Such changes result in a transition to an oscillatory regime in which the mechanism of oscillation is the same kinetic process summarized by Equations 1a–c: reactant species periodically oxidize and reduce the transition metal catalyst. This mechanism is consistent with past observations of a BZ membrane,^[18] and with simulations on BZ gels that have characterized the effect of an increase in polymer volume fraction due to compression on BZ kinetics and oscillatory response.^[20,21] When the compressive stress is removed, the gel reverts back to a state in which the balance of reactant molecules to inhibitor species is insufficient for oscillation to occur. Note that the reversible triggering of oscillations via mechanical compression is consistent with Equations 1a–c, by which compression effectively increases the relative concentration of Ru(bpy)₃, and thus stimulates production of the HBrO₂ activator species. Likewise, addition of sodium bromate (BrO₃[−]) to uncompressed gels submerged in a reactant-depleted solution also induced oscillations by driving Equation 1b forward (data not shown). Further evidence for this concentration-mediated triggering is given by a separate experiment, in which we also observed that physical contact of the gel with a silver wire could be used to trigger oscillations in a non-oscillating gel (see the Supporting Information for details). Here, the silver wire was not used to apply mechanical load, but facilitated the reduction of bromate ions and simultaneous oxidation of metal catalyst to confirm that an external stimulus is required to trigger oscillations and overcome the presence of inhibitor species. Thus, together these data support the interpretation that adding or removing compressive stress to BZ gels can effectively – and reversibly – trigger oscillations by changing the local concentration of dissolved reactant species and covalently bound catalyst. To strain the analogy of cardiac resuscitation further, the mechanical compression is required to restore and extend

the functionality of oscillatory behavior in these exhausted BZ gels.

By varying the initial conditions of the reaction, we found that the oscillatory behavior of a mechanically triggered gel was tunable. Specifically, the period and amplitude of oscillation depended on the initial concentration of malonic acid in solution. A relatively large amplitude ($14.4^\circ \pm 0.8^\circ$) and longer period (7.3 ± 0.6 min) was observed when the gel was placed in an initial solution containing 0.08 M malonic acid (see Figure 2A), as compared with a gel placed in 0.3 M malonic acid that oscillated with an amplitude of $3.7^\circ \pm 0.1^\circ$ every 0.9 ± 0.04 min (see Figure 2B). As noted, catalyst concentration and reaction conditions were maintained as similar as possible among all experiments, in that initial reduced catalyst concentration was verified through correlations with hue prior to the BZ reaction (i.e., in water) and was consistently $0.21^\circ \pm 0.01^\circ$; further, all samples were punched to uniform diameter from a single polymerization batch reaction for which initial catalyst concentration was measured via UV spectroscopy and gel thickness was approximately constant at 0.6 mm. However, we note that the hue of the gel in the non-oscillating steady-state, attained after exposure of each gel sample to BZ acid reagents for 20 h, was not identical in separate experiments (see the Supporting Information). This may be related to slight differences in sample diameter and defects at the sample perimeter. The hue after exhausting the BZ self-oscillations was considered a small perturbation, in that while variable hue prior to compression affected the minimum hue observed in a particular experiment, we found no correlation between minimum hue and the magnitude of the triggered period or amplitude. In total, four different malonic acid conditions were tested with two to four replicate samples and experiments at each condition. In all of the experiments, the oscillations were reversibly triggered by adding and removing compressive stress to the gel. These results, summarized in Figure 2C, demonstrate that the period and amplitude of the mechanically triggered oscillation can be tuned by changing the composition of the initial BZ reactants.

The error bars shown in Figure 2C represent the standard deviation for period and amplitude across replicate experiments in different gel samples. When the initial concentration of malonic acid was 0.2 M or greater, the triggered oscillations were relatively consistent across replicate experiments in different gel samples. When the initial malonic acid concentration was lower, however, the triggered period and amplitude varied over several minutes and degrees, respectively, across different gel samples. We note that the period and amplitude of triggered oscillations were highly consistent for a given gel sample. To understand the inconsistent oscillatory behavior across different gel samples at low malonic acid concentrations, it is important to quantify the self-oscillatory behavior of BZ gels because the triggered oscillations are influenced by these initial conditions.

In fact, the dependence of period and amplitude on malonic acid concentration in triggered BZ gels is anticipated, because this trend is also observed in self-oscillating gels (see Figure 3). Here, we use the term “self-oscillatory” to refer to BZ gels that spontaneously oscillate at time zero when submerged in a fresh BZ solution comprising malonic acid, sodium bromate, and nitric acid. Not all BZ gels spontaneously self-oscillate immediately when submerged in BZ reactants, because the chemistry

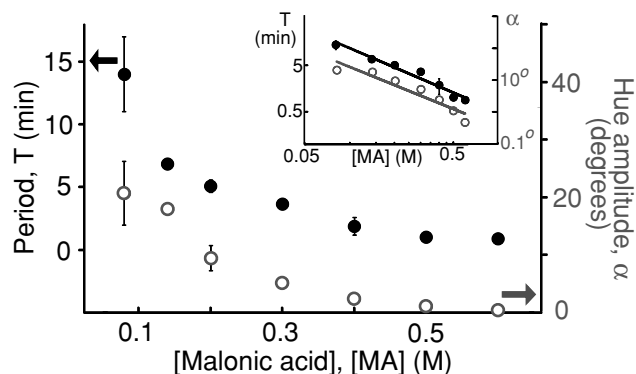


Figure 3. Period and amplitude versus malonic acid concentration for spontaneously self-oscillating BZ gels (0.7–0.9 mm diameter and 0.6 mm thickness) containing 8.3 mM Ru(bpy)₃ catalyst. Inset shows these data on a log-log scale. Error bars represent standard deviation for replicate experiments in different gel samples. Constant 0.1 M sodium bromate and 0.7 M nitric acid.

of the reaction is quite sensitive to initial conditions that include low concentrations of reactants. Small differences in gel diameter, thickness, and catalyst distribution can sufficiently perturb these initial conditions. While similar dependence of oscillation period on acid concentration have been recorded in other BZ gel studies,^[15,23] our BZ gels self-oscillated over a relatively wide range of conditions. As in previous work, the period and amplitude of oscillation decreased with increasing malonic acid concentration. In contrast to the findings of Yoshida et al.,^[15,23] however, our gels oscillated at relatively high concentrations of malonic acid (0.6 M). Under this condition, the low-amplitude oscillations were not visibly discernable; the oscillations were also not detectable when average RGB or a blue-filtered gray value of the gel was quantified through image analysis. Our method of quantifying the hue^[24] of the gel is robust, and detects low-amplitude oscillations in which a low number of catalyst molecules are oscillating within the gel (see the Supporting Information and the Experimental Section for definitions of hue). At 0.08 and 0.14 M malonic acid, we observed the largest standard deviation for period and amplitude across different gel samples. In some instances at these conditions, the gel did not spontaneously self-oscillate at all. Thus, it is not unexpected that the mechanically triggered responses quantified in Figure 2C exhibit larger variation at 0.08 and 0.14 M malonic acid. The conditions necessary to mechanically trigger oscillations depend on the initial conditions and BZ oscillations at time zero. In general, at lower malonic acid concentrations, both spontaneous self-oscillations and mechanically triggered oscillations in BZ gels are remarkably sensitive to the initial conditions of the experiment.

In Figure 4, we present the comparison between the period of oscillation and the estimated characteristic diffusion time for the system. The period of oscillation was quantified as a function of malonic acid concentration for two BZ gels containing different concentrations of Ru(bpy)₃ catalyst: 5.8 and 8.3 mM. While similar trends were observed for the different gels, the magnitude of the period differed quantitatively. Specifically, the parameters in a power law fit of the data were dependent on the catalyst concentration (see insets in Figure 3,4). In the absence

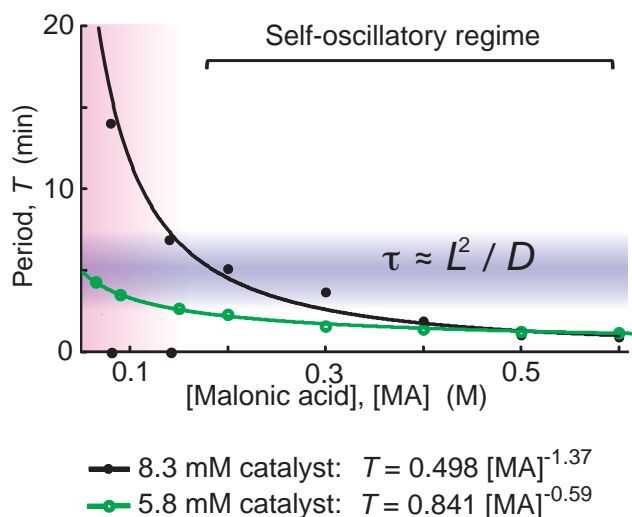


Figure 4. Oscillatory regimes in BZ gels in relation to estimated diffusion time for 0.6–0.9 mm sized gels. The blue, shaded region corresponds to the estimated diffusion time τ . When the experimental period of oscillation exceeds the diffusion time, the system becomes sensitive to initial conditions (pink shaded region) and can exhibit either oscillations or a steady-state (note black points on horizontal axis indicating gels that did not self-oscillate).

of any chemical reaction, the diffusion time τ for the system can be estimated as:

$$\tau \approx \frac{L^2}{D} \quad (2)$$

where L is the characteristic length and D is the diffusion coefficient for the system. Here, the characteristic length L is defined by the BZ gel dimensions; the present gels exhibited diameters ranging between 0.7 and 0.9 mm and thicknesses of 0.6 mm. As these dimensions are comparable, and as there may be differences between axial and radial diffusion through the gel due to details of the experiments (e.g., the gel rests on a Petri dish), we estimated the diffusion time for a range of length scales (0.6–0.9 mm). Accounting for the low polymer volume fraction in our gels (0.08), the diffusivity D of reactant molecules through the BZ gel was similar to that through aqueous solution,^[18,25] and the resulting estimated diffusion time for our experiments ranged between 3.3 and 7.5 min.

The diffusion time is set by L and D for a given gel, whereas the period of BZ oscillation is related to both L ^[8] and the concentration of catalyst and reagents. If the period of oscillation is comparable or less than τ (i.e., below the shaded blue region in Figure 4), then the typical BZ self-oscillatory state is achieved robustly. If instead the period of oscillation exceeds the diffusion time, a quasi-equilibrium distribution of chemical reagents within the gel can be reached and self-oscillation is not assured. Figure 4 demonstrates that this quasi-equilibrium can be achieved at sufficiently low concentrations of malonic acid and sufficiently high catalyst concentrations (i.e., within the shaded pink region for gels containing 8.3 mM catalyst). We found that above some critical malonic acid concentration, gels of this higher catalyst concentration always spontaneously

self-oscillated, but below this malonic acid concentration some gels would self-oscillate and others would not. It is important to emphasize that we did not observe a strictly non-oscillatory region for these gels comprising 8.3 mM catalyst. Rather, we report that out of 13 total experiments conducted at 0.08 and 0.14 M malonic acid, only five gels were self-oscillatory at time zero. In contrast, all six experiments conducted above 0.14 M were self-oscillating gels. The behavior observed at lower malonic acid concentrations (≤ 0.14 M) for gels containing 8.3 mM catalyst indicates access to a bistable state, in which the self-oscillatory and steady-states co-exist. Clear demonstration of this coexistence would require a high number of replicate experiments that is beyond the scope of this work. In the gel comprising 5.8 mM catalyst, we always observed that the gel self-oscillated over the conditions shown in Figure 4, in which the period of oscillation did not exceed 5 min and was thus comparable to or below τ . However, in the gel with 8.3 mM catalyst, we observed two regimes that describe oscillations in BZ gels: a robust regime in which self-oscillation is consistently attained, and a chemically sensitive regime in which the sample can either oscillate or attain a steady-state.

Furthermore, we note that if a non-oscillatory state is achieved at time zero when the gel is submerged in fresh BZ reagents, mechanical triggering of the BZ oscillations can be

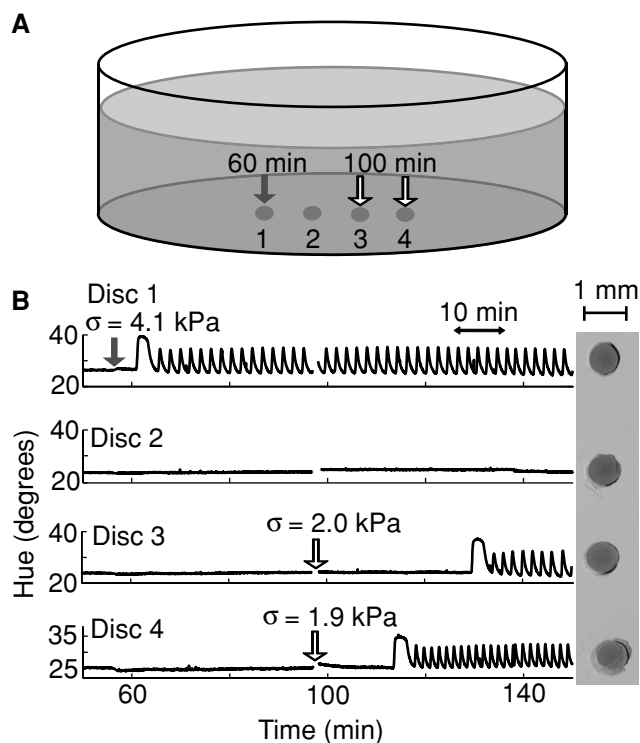


Figure 5. BZ gel discs as pressure sensors. A) Schematic of experiment, indicating the times at which discs 1, 3, and 4 were mechanically compressed (not to scale). B) Hue of discs 1–4, indicating that oscillations were triggered in discs 1, 3, and 4. BZ gel discs were 0.7–0.8 mm in diameter (0.6 mm thickness and 8.3 mM Ru(bpy)₃ catalyst) in a solution bath with initial composition: malonic acid (0.08 M), sodium bromate (0.1 M), and nitric acid (0.7 M). The gap distances between discs were 1.8 mm (disc 1 and 2), 1.3 mm (disc 2 and 3), and 1.5 mm (disc 3 and 4).

achieved almost immediately. In other words, a 20 h immersion interval in the BZ solution to exhaust the self-oscillations is not required. In contrast, for the initially self-oscillating gels, the observed mechanical sensitivity can be achieved only after sufficient time has elapsed (i.e., 20 h) to ensure that reactant molecules have been consumed and self-oscillations have ceased (see the Supporting Information for discussion of effects when immersion intervals of are less than 20 h.) Thus, this condition corresponds to a steady-state after exhaustion of the BZ reaction, for which subsequent mechanical compression can cause transition from a steady-state to the oscillatory state. Figure 4 represents a suggested method for determining the conditions required to achieve a non-oscillatory but mechanically triggerable BZ gel; the exact conditions required to achieve this state will depend on details of gel chemistry.

Next, we incorporated our knowledge of chemomechanical transduction in BZ gels to design a pressure sensor. In this experiment, a row of four nearly identical BZ gel discs, spaced more than 1 mm apart from each other, were placed in a Petri dish containing a BZ solution bath. After 20 h of immersion, self-oscillations in all four discs were exhausted and a non-oscillatory state was achieved. After monitoring the non-oscillatory state for 1 h, disc 1 was mechanically compressed, triggering oscillations in only that disc. Forty min later, discs 3 and 4 were simultaneously compressed. Again, the applied stress triggered oscillations in both discs, although the induction time elapsed between the application of stress and the observation of oscillations varied due to slight differences in disc thickness. Disc 2 was a control region that was uncompressed and remained in the non-oscillatory state. The periods of oscillation for discs 1, 3, and 4 were approximately 2.1, 2.0, and 1.5 min, respectively. The amplitudes were 10.0°, 9.4°, and 6.9°, respectively. Thus, we have demonstrated an application in which the BZ gel discs function as a touch-sensitive material, oscillating only when each disc is mechanically triggered.

In a separate experiment, we demonstrated that the gel discs can communicate with each other via chemical diffusion, after only one gel is mechanically triggered to oscillate. Figure 6 shows two BZ gel discs, with an edge-edge spacing (gap distance) of 0.23 mm as measured while submerged in BZ solution. Again, the gels were submerged in a BZ solution bath for 20 h to achieve non-oscillatory states. Disc 1 was mechanically compressed, triggering oscillations, as expected. Interestingly, despite remaining uncompressed, disc 2 also began to oscillate. This result indicates that intermediate, activator species that were generated by the BZ reaction in disc 1 diffused across the gap within seconds, triggering an oscillatory response in disc 2. At these experimental conditions, the gels oscillated at low amplitudes such that the gap distance of 0.23 mm was constant. Although the discs exhibited similar hues in water (0.2°), the steady-state hue of the gels prior to compression differed. As noted previously and in the Supporting Information (see Table S1), the steady-state hue of the gel does not affect the magnitude of the triggered period or amplitude. The period of oscillation for disc 1 was 1.5 min with an amplitude in hue of 8.9°, while the period of oscillation for disc 2 was 1.8 min with an amplitude of 6.7°. Physically, these results indicate that there is a critical gap distance between discs for communicative chemical diffusion to occur. As noted by Tateyama et al. and

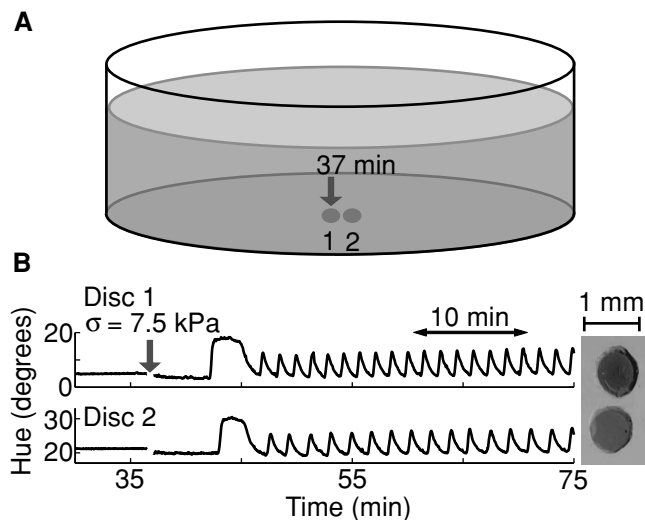


Figure 6. BZ gel discs as a pressure sensor with signaling capacity. A) Schematic of experiment, indicating the time at which only disc 1 was mechanically compressed. B) Hue of discs 1 and 2, indicating that both discs oscillate in response to mechanical triggering of disc 1. BZ gel discs were 0.7 mm in diameter (0.6 mm thickness and 8.3 mm Ru(bpy)₃ catalyst) in a solution bath with initial composition: malonic acid (0.08 M), sodium bromate (0.1 M), and nitric acid (0.7 M). The gap distance between discs was 0.23 mm.

Fukuda et al., the critical gap length between chemically communicating BZ oscillators depends on the detailed conditions of the experiment.^[26,27] At these specific chemical conditions, a gap distance of 0.31 mm was too large, and the uncompressed gel did not oscillate (data not shown). In summary, we have demonstrated that a BZ gel array of sufficiently small gap distances can sense mechanical loading and transmit oscillating, chemical signals away from the affected area.

3. Conclusions

Together, these studies have demonstrated that visible reactions within a non-oscillating, depleted BZ gel sample can be resuscitated. Specifically, chemical oscillations can be triggered by mechanically compressing the BZ hydrogel beyond a critical stress. These findings have important implications for restoring the functionality and, thus, extending the lifetime of devices that exploit BZ gels. We have shown that the triggered oscillatory response is markedly sensitive to initial physical and chemical conditions, but can be rendered robust via consideration of the initial acid composition and exhaustion of self-oscillatory behavior prior to compression. Furthermore, we have developed a method for eliciting robust chemomechanical responses in BZ gels. We anticipate that these results will enable future studies that explore the effects of localized impact and tensile strain on BZ gel oscillations. Finally, we have designed BZ gel sensors that detect the location of mechanical stress and have the capacity to transmit chemical signals away from the area of deformation. While these proof-of-principle demonstrations confirm novel functionality and design versatility of BZ gels, we foresee a wide range of new applications with additional

heterostructured and compositional complexities that are able to sense mechanical stimuli and respond chemically.

4. Experimental Section

Synthesis of Poly(NIPAAm-co-Ru(bpy)₃): The monomer catalyst, ruthenium (4-vinyl-4-methyl-2,2-bipyridine)bis(2,2-bipyridine) bis(hexafluorophosphate) (Ru(bpy)₃) was synthesized from commercially available 4,4'-dimethyl-2,2'-bipyridine and Ru(bpy)₂Cl₂.^[28,29] NIPAAm monomer (125 mg), Ru(bpy)₃ monomer (6.6 mg for the 8.3 mm gel and 4.8 mg for the 5.8 mm gel), *N,N*-methylenebisacrylamide (MBAAm) (2.2 mg) crosslinker, and 2,2-azobis(isobutyronitrile) (AIBN) (5.3 mg) initiator were dissolved in methanol (0.8 mL) and degassed with nitrogen for 5 min. The solution was polymerized between polystyrene petri dishes for 18 h at 60 °C. The resulting gel was soaked in methanol for 1 week to remove unreacted monomers and gradually hydrated.^[30] To determine catalyst concentration within the gel, absorption at $\lambda = 457$ nm was measured via UV/Vis spectrophotometry to quantify unreacted Ru(bpy)₃ monomer. The approximate yield of polymerized Ru(bpy)₃ monomer was 91% for the 8.3 mm gel and 88% for the 5.8 mm gel. The phase transition temperature of the gel was characterized by measuring decreasing gel size as a function of increasing temperature. Measurements were collected when the gel was fully submerged in cerium(III) sulfate or cerium(IV) sulfate, corresponding to either the fully reduced or oxidized catalyst states, respectively. When the catalyst was in the uniformly reduced state, the transition temperature of the gel was approximately 33 °C, similar to the LCST of NIPAAm. When the catalyst was in the uniformly oxidized state, the transition temperature of the gel was approximately 36 °C. Therefore, the phase transition temperatures, and thus, the hydrophilic properties of the gel, depend on the catalyst oxidation state. All reagents were obtained from Sigma-Aldrich, except for the Ru(bpy)₂Cl₂ which was obtained from Acros Organics.

Initiation and Imaging of BZ Reaction: The BZ solution was prepared using nitric acid, malonic acid, and sodium bromate. Before adding the BZ reactants to the gel, the solution was vortexed under vacuum. To prepare the BZ gel sample, storage water was aspirated from the gel. The sample remained hydrated but the surrounding petri dish did not contain excess water. To initiate the BZ reaction, 5 mL of filtered BZ solution was pipetted directly on top of the gel such that the gel was well-submerged in an unstirred, BZ solution. Time-lapse imaging at room temperature was recorded under a stereomicroscope (Olympus, SZX7) with an LED light and camera (Olympus, DP25) to record any initial, spontaneous oscillations in the gel.

Mechanical Induction of BZ Oscillations: After the gel remained submerged in the BZ solution for 20 h, the non-oscillatory state was confirmed by recording the uniformly reduced state (orange hue) of the sample for 1 h using time-lapse imaging. A glass slide of known mass was gently placed on top of the gel sample, compressing the gel. Applied stress was increased by placing additional glass slides on top of the sample. Time-lapse imaging was used to record the compressed, oscillating gel. The projected area of the gel was recorded to calculate the lateral expansion and change in thickness of the sample. The applied stress varied between 0.7 and 11.3 kPa, and the compressive displacement of the gel varied between 0 and 60 μ m. Glass slides were carefully removed from the gel to terminate oscillations.

Characterization of BZ Reaction in Gels: Images of the gel were analyzed via ImageJ to quantify hue as defined with cylindrical coordinates on the RGB color space.^[24] Gels were analyzed by averaging hue over a representative area (5–15% of the total gel area) at each frame. The period of oscillation was quantified by calculating the elapsed time between hue peaks corresponding to oxidized ruthenium. Five to ten oscillations in each gel were quantified, and the average \pm standard deviation among replicate experiments in different gels reported. To calculate the theoretical diffusion time, the diffusion coefficient for small molecules through aqueous solution (D_0) was used, correcting for the experimental polymer volume fraction ϕ as:

$$D = D_0 (1 - \phi) \quad (3)$$

ϕ was approximately 0.08, resulting in a diffusion coefficient of $1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

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