Soft Matter

PAPER

Structural modulation of self-oscillating gels: changing the proximity of the catalyst to the polymer backbone to tailor chemomechanical oscillation†‡

Ye Zhang,[a] Ning Li,[b] Jorge Delgado,§[a] Ning Zhou,[a] Ryo Yoshida,[c] Seth Fraden,[b] Irving R. Epstein*[a] and Bing Xu*[a]

We designed and synthesised two new polymerizable ruthenium complexes that catalyse the Belousov–Zhabotinsky (BZ) oscillating reaction and incorporated them into a copolymer to form hydrogels. The periodic oxidation and reduction of the attached ruthenium complex in the BZ reaction induces hydrating and dehydrating effects, respectively, that result in self-oscillatory volume changes of the hydrogel. We evaluated the correlation between the chemomechanical oscillation properties of the hydrogel and the proximity of the catalyst to the polymer backbone. Our results indicate that, like the change of such macroscopic parameters as temperature, reactant concentrations and pH, varying the microscopic distance between the catalyst and the polymeric chain provides a new way to tailor the chemomechanical behaviour, *e.g.*, the initiation time, the frequency of oscillation, and the volume change of BZ hydrogels. Moreover, variation of the catalysts offers a new means to control the microstructure of the copolymer by expanding the range of monomer ratios. Modulation of molecular structure appears to be an effective way to alter the reaction–diffusion profile of species within heterogeneous chemoresponsive gels, thus contributing to the development of multifunctional, active soft materials capable of converting chemical energy into controllable mechanical forces.

Introduction

Converting the energy contained in chemical bonds into mechanical force is an important process that supports life. As the result of evolution, living systems have developed thermodynamically efficient and environmentally benign ways for harnessing chemical energy to produce motion, for example, using the energy released by hydrolysis of ATP to power molecular motors.[1] Inspired by these highly efficient chemomechanical systems in nature, researchers have been striving to develop biomimetic systems to generate mechanical forces from chemical

reactions.[2,3] Among various systems developed so far, self-oscillatory gels have become an attractive system for the exploration of chemomechanical conversion,[3,4] because they allow the incorporation of structural and dynamic properties typically found in living systems into a simple molecular platform. We report here a study of the relationship between macroscopic chemomechanical behaviour and the microscopic molecular structure of polymeric networks of oscillating gels for the development of chemomechanical responsive systems.

Yoshida and coworkers first prepared an oscillating gel[3] by covalently attaching a catalyst of the Belousov–Zhabotinsky (BZ) reaction,[5–8] ruthenium(II)-tris-2,2′-bipyridyl (Ru(bpy)₃²⁺, **1a**),[9] to a copolymer of *N*-isopropyl amide[10] to form a hydrogel that expands and contracts in response to changes in the local redox potential, *i.e.*, the oxidation state of the catalyst.[3] Because the BZ reaction is able to generate oscillations in the redox state of the catalyst (*e.g.*, **1b**), the gel can pulsate in a self-sustained manner.[11,12] More importantly, millimeter-sized pieces of BZ gel can undergo self-oscillation for several hours without replenishment of reagents.[13,14] Based on these initial BZ gels, Yoshida *et al.* have explored several structural variations. For example, quaternary copolymers, which include both acidic and oxidative sites in the poly(NIPAAm-*co*-Ru(bpy)₃) chain, are able to achieve self-oscillation under acid- and oxidant-free conditions, although these gels exhibit very limited volume changes.[15–17] Until now, besides the inclusion of acidic and/or oxidative sites, few structural modifications have been explored.[18] To probe the

[a]Department of Chemistry, Brandeis University, 415 South St., Waltham, MA 02454, USA. E-mail: epstein@brandeis.edu; bxu@brandeis.edu; Fax: +1-781-736-2516; Tel: +1-781-736-5201

[b]Department of Physics, Brandeis University, 415 South St., Waltham, MA 02454, USA

[c]Department of Materials Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

role of molecular structure for developing chemomechanical soft materials, we examine here the influence of the distance between the catalyst and the polymeric backbone on the chemomechanical behaviour of BZ gels.
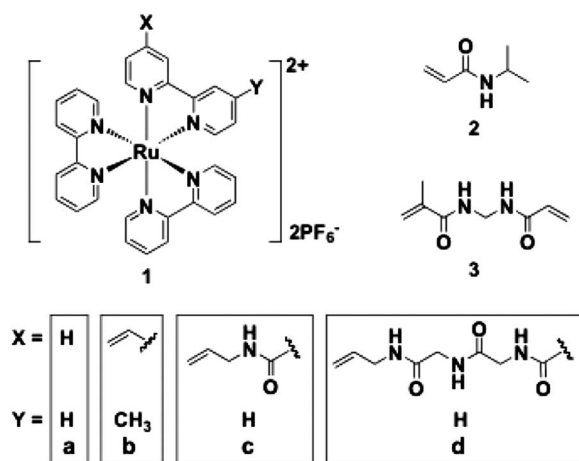
We find that varying the distance between the catalyst and the polymeric chain provides a new way to tailor the chemomechanical behaviour of a hydrogel. For example, increasing this distance reduces the initiation time, preserves the volume change of the hydrogel during chemical oscillation, and broadens the accessible range of monomer ratios in the gel-forming copolymer. Our work suggests that such modulation of molecular structure is an effective way to design the properties of heterogeneous chemoresponsive gels, a key challenge in the development of multifunctional soft materials that convert chemical energy into controllable mechanical forces.
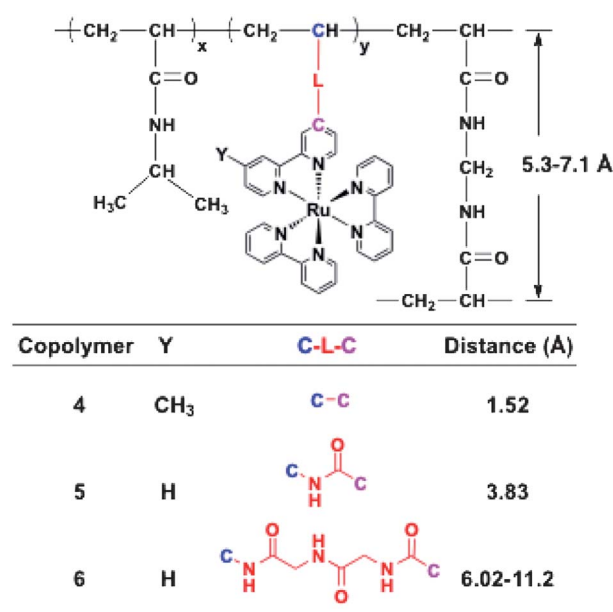
Results and discussion

Synthesis of catalysts and copolymers

Starting from the structure of the classic BZ catalyst, ruthenium(II)-tris-2,2′-bipyridyl (1a),[19,20] we designed and synthesised three catalysts 1b, 1c, and 1d (Scheme 1) with longer distances between the ruthenium metal center and the olefin group on the catalysts. Based on the synthesis of 1a,[21–23] we obtained 1b in a fair yield (40%) according to an earlier procedure that uses 4-vinyl-4′-methyl-bipyridine as one of the bidentate ligands.[24] The synthesis of 1c relies on the synthesis of 4-carboxylbipyridine, which couples with allylamine to provide N-allyl-[2,2′-bipyridine]-4-carboxamide as one of the bidentate ligands in 1c.[25] The total yield of the synthesis of 1c is 76%, which is much higher than that of 1b. The preparation of 1d is similar to 1c, except that two glycine residues connect the allylamine and the 4-carboxylbipyridine. The total yield of 1d is 16%. Then, we prepared three series of copolymers (4, 5, and 6) using 1 (b, c, or d) and 2 as the monomers and 3 as the crosslinker.

Scheme 2 shows the resulting copolymer networks that serve as the matrices of the BZ gels. We designate the polymers made of 1b, 1c, and 1d as polymers 4, 5, and 6, respectively. The major difference among these three polymers is the distance between

Scheme 2 Molecular structures of the polymer networks of the BZ gels.

the BZ catalyst (i.e., Ru(bpy)$_3^{2+}$) and the backbone of the polymer. For example, according to the bond length, the estimated distances[26] are 1.52, 3.83, and >6.02 Å in polymers 4, 5, and 6, respectively. The BZ gel consisting of polymer 4 has been extensively studied,[3,4,27,28] so it serves as a useful reference for the BZ gels made of polymers 5 and 6. While we chose the optimised ratio of monomers and amount of crosslinker for making 4,[4] we varied the ratios of monomers and the amounts of crosslinkers for making copolymers 5 and 6. We distinguish the various combinations by Roman numerals after the type of copolymer in the labels of the BZ gels (Table 1).

Formation of BZ hydrogels

Table 1 shows the ratios of the monomers and crosslinkers, and images of the corresponding BZ gels. For example, to make Gel 4, we mixed 1b, 2, and 3 in the molar ratio of 0.012 : 1.0 : 0.0124 and added azobisisobutyronitrile (AIBN) as the initiator of radical polymerization to form the crosslinked copolymer in methanol solution. After dialysis to remove the unreacted monomers, we obtained Gel 4. A mixture of 1c, 2 and 3 at the

Scheme 1 Molecular structures of the monomers and crosslinker used to form the polymer networks of the BZ gels.

Table 1 Ratios of monomers and crosslinkers used for making the BZ gels and their appearances in the reduced and the oxidised states

Gel	4	5-I	5-II	5-III	6-I	6-II	6-III
Catalyst (mol%)	1.20	1.20	1.20	0.60	1.20	1.20	0.60
2 (mol)	1	1	1	1	1	1	1
3 (mol%)	1.24	1.24	0.62	1.24	1.24	0.62	1.24
Ru(II)							
Ru(III)							

molar ratio of 0.012 : 1.0 : 0.0124 with the same initiator and a similar dialysis procedure gave Gel **5-I**. Using the same components and procedure for making Gel **5-I**, but reducing the amount of the crosslinker **3** to half of that in Gel **5-I**, we obtained Gel **5-II**. Similarly, by decreasing the amount of catalyst **1b** to half of that in Gel **5-I**, we got Gel **5-III**. Replacing **1c** by **1d** and following the procedure for making Gels **5**, we obtained Gels **6-I**, **6-II**, and **6-III**.

Redox behaviour of BZ gels

Table 1 also shows optical images of the BZ gels in their reduced and oxidised states. Immediately after synthesis of the gels, the catalysts are in the reduced state (Ru(II)), and the gels appear yellow, orange or red depending on the type of catalyst and thickness of the gels. Using $Ce(SO_4)_2$ as the oxidant, it is possible to oxidise the metal center from the Ru(II) to the Ru(III) state. If a gel appears transparent green upon oxidization, it is able to oscillate under the conditions of the BZ reaction. According to this criterion, Gels **4**, **5-I**, **5-II**, **5-III**, **6-II**, and **6-III** should behave as oscillatory BZ gels. Gel **6-I**, however, remains deep orange after immersion in the $Ce(SO_4)_2$ solution; it also fails to behave as a BZ gel. Though it is unclear why Gel **6-I** remains in the reduced state, one plausible cause is that Gel **6-I** is too crowed to allow the oxidant to diffuse towards the Ru metal center. These results demonstrate that the synthesis of the copolymer controls the redox behaviour of the BZ gel, which correlates with its ability to oscillate under the BZ reaction conditions.

Fig. 1 Equilibrium swelling ratio of (A) Gel **4** and (B) Gel **5-I** as a function of temperature in reduced state Ru(II) and oxidised state Ru(III).

Temperature profiles of BZ Gels 4 and 5-I

To determine how the distance between the catalyst and the polymer backbone affects the maximum volume change of the BZ gels, we compared the temperature profiles of Gels **4** and **5-I**. Fig. 1 shows the temperature dependence of the equilibrium swelling ratio, obtained by immersion of the gels in $Ce(SO_4)_2$ and $Ce(NO_3)_3$ solutions. The use of $Ce(NO_3)_3$ ensures that the reduced state of $[Ru(bpy)_3](PF_6)_2$ is in the same ionic conditions as the oxidised state. Having the same thickness (0.4 mm) and size (square of edge 1.0 cm), Gels **4** and **5-I** were immersed in $Ce(SO_4)_2$ or $Ce(NO_3)_3$ solution. The circumference of each gel was measured at different temperatures. The relative circumference of the gel was defined by dividing the circumference of the gel at each temperature by the circumference of the gel in its initial state at 18 °C in $Ce(SO_4)_2$ or $Ce(NO_3)_3$ solution. Due to the thermoresponsive character of the poly-NIPAAm component,[29] the swelling ratios of the gels change with temperature and exhibit clear phase transitions. The gels swell at low temperature and gradually deswell upon increasing the temperature. As shown in Fig. 1, the gels remain in the shrunken (de-swollen) state above the transition temperature (defined as the midpoint of the sigmoidal relative circumference *versus* temperature curve). Gel **4** exhibits a phase transition at 30.5 °C in the reduced state and at 32.0 °C in the oxidised state. Gel **5-I** exhibits a similar trend with phase transitions at 30.8 and 31.5 °C in the reduced and oxidised states, respectively. In both gels, the phase transition temperature of the gel occurs at a higher temperature in the oxidised state, and the temperature range of the phase transition is broader for the oxidised state. The difference in volume between the reduced and oxidised states of the gels is smaller for Gel **5-I** than for Gel **4**. According to the curves in Fig. 1, the maximum circumference change of Gel **5-I** is 15%, which is smaller than that of Gel **4** (22%) at a constant temperature. In theory, if the gel were a cube and swelled or deswelled isotropically the maximum volume change would be 52% and 82% for Gel **5-I** and Gel **4**, respectively.

Chemical oscillation of BZ gels

After confirming that the volume difference between the oxidised and reduced states is preserved when the distance between the catalyst and the polymer backbone is increased, we evaluated the chemical oscillation of the gels in a closed system consisting of an optical cell (1 mL) equipped with temperature control. We performed the chemical oscillation experiments under different conditions based on the temperature profiles of Gels **4** and **5-I** and the previously optimised conditions for Gel **4**.[4,30] The solution for the BZ reaction consisted of nitric acid (HNO_3), sodium bromate ($NaBrO_3$), and malonic acid (MA). The three conditions chosen were: (A) $[HNO_3]_0 = 0.8$ M, $[NaBrO_3]_0 = 0.2$ M, $[MA]_0 = 0.08$ M, and $T = 293$ K; (B) $[HNO_3]_0 = 0.8$ M, $[NaBrO_3]_0 = 0.08$ M, $[MA]_0 = 0.06$ M, and $T = 293$ K; (C) $[HNO_3]_0 = 0.8$ M, $[NaBrO_3]_0 = 0.08$ M, $[MA]_0 = 0.06$ M, and $T = 298$ K. Condition B is the optimised condition reported for the detection of chemomechanical oscillation of Gel **4**,[3] which served as a reference condition for the new gels, allowing assessment of the volume changes of Gels **5** and **6** during chemical oscillation. The only difference between conditions B
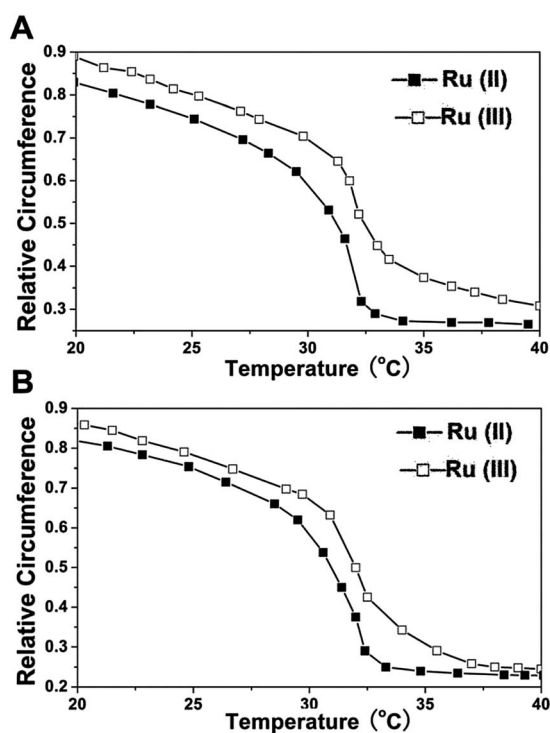
and C is the temperature. We chose a temperature away from the phase transition to exclude the possibility that the volume change originated from local temperature fluctuations in the gels.

Typically, we filled the optical cell with fully mixed BZ solution. After equilibrating the temperature, we put the gel (cut into a cube of edge length ~0.4 mm) into the cell and recorded the optical image of the gel with a CCD camera at 10 s intervals. Analysis of each video gave the time of initiation, the change of colour, the frequency of oscillation, the change of volume, and the stability of oscillation of the gel. Although the test setup was a closed system, the volume of the gel was considerably smaller than that of the BZ solution in the cell ($V_{gel} : V_{BZsolution}$ < 1 : 15 000). For the first few hours, it is reasonable to assume that the chemical environment of the gel is constant.

Fig. S1‡ shows traces of the transmittance, and Table 2 summarises the test results under condition A. For example, Gel 4 begins to oscillate after 44 000 s, reaches relatively stable oscillation at about 54 000 s, and exhibits an initial oscillation period of 80 s. The oscillation gradually speeds up and reaches a period of 60–70 s after another 10 000 s (Fig. S1A‡).

The results in Table 2 indicate that lengthening the distance between the catalyst and the polymer backbone significantly reduces the time needed to initiate chemical oscillation, probably because Gels 5-I, 5-II, 5-III, 6-II, and 6-III are more permeable to the BZ reagents than Gel 4. The traces for Gels 5-I, 5-II, and 5-III suggest that decreasing the amount of crosslinker in Gels 5 leads to an increase in the initiation time and the time for reaching stable oscillation. We found that, under strong acidic condition (*i.e.*, BZ reaction conditions), the gels with less crosslinker shrink more than those with more crosslinker. Such shrinkage may result in the long initiation periods. Fig. S1‡ shows that Gels 5-I and 5-III have similar oscillatory characteristics, implying that the amount of the catalyst 1c attached to the polymer is less critical than the amount of the crosslinker in determining the oscillatory characteristics of these gels. Catalyst 1c results in gels with intermediate distance between Ru(bipy)$_3^{2+}$ and the polymer backbone among the copolymers 4, 5 and 6. The oscillatory behaviours of Gels 5 suggest that the amount of crosslinker 3 directly affects the microstructure of the gel to dictate the oscillation of the gel. In the case of Gels 6, the use of catalyst 1d results in copolymers with the longest catalyst–backbone distance. Both the amount of catalyst 1d and crosslinker 3 affect the behaviours of these gels. Among the three Gels 6, Gel 6-I has the most crosslinker and the most catalyst, and it fails to oscillate under conditions A, B, and C. Decreasing the amount of either the catalyst or the crosslinker results in gels that oscillate under these conditions.

Comparison of gel pairs (Gels 4 and 5-I, Gels 5-II and 6-II, and Gels 5-III and 6-III) that contain different catalysts but have the same ratio of monomers demonstrates that the identity of the catalyst plays a significant role in determining the frequency of oscillation. For example, the oscillation periods I and II of Gel 4 are both 30 s shorter than those of Gel 5-I. The distance between the catalyst and the polymer backbone also affects the frequency. Oscillation periods I and II of Gel 5-III are both 40 s longer than those of Gel 6-III. While similar to those of Gel 5-III, oscillation periods I and II of Gel 5-I are both 30 s longer than those of Gel 5-II. Apparently, the concentration of catalyst 1c barely affects the oscillation frequency of Gels 5 under condition A, but the concentration of crosslinker does influence the oscillation frequency of these gels. Though the relatively small size of the gels should allow complete oxidation of all the catalysts in the gels, it is possible that in some cases not all the catalyst is oxidised during oscillation.

Condition B is the typical condition for testing the chemomechanical behaviours of oscillating gels.[4,30] Besides examining the chemomechanical oscillation properties of the gels, we also collected data for the analysis of chemical oscillation. Fig. S2‡ shows the traces of chemical oscillation under condition B, and Table 3 summarises the test results under this condition. Unlike Gel 5-I, Gel 5-II is unable to oscillate under condition B even after being immersed in BZ solution for 24 hours (86 400 s), which is consistent with our observation that decreasing the amount of crosslinker results in longer initiation times (Table 2). Considering that fewer crosslinkers result in a less rigid matrix in Gel 5-II, we decided to rigidify the microstructure of the gel by raising the reaction temperature to deswell the gel. We increased the temperature in 1 °C steps from condition B, and monitored the gel in BZ solution for about 4 hours (15 000 s). After observing no oscillation from 21 to 23 °C during 12 h, we increased the temperature in 0.5 °C steps and found that a temperature of 24.5 °C clearly caused Gel 5-II to oscillate (Fig. 2). With Gel 6-III, after a long period of stable oscillation, an unstable, slower oscillation period appears between 25 000 s and 35 000 s (Fig. S2E‡). After that, Gel 6-III oscillates quite stably with a period of about 200 s.

As shown in Fig. 2, increasing the temperature is an efficient way to perturb the gel microstructure.[29] We therefore performed experiments under condition C, which has the same concentrations as condition B, but a higher temperature (25 °C). Fig. S3‡ and Table 4 summarise the results under condition C.

Table 2 Oscillation characteristics of gels under condition A

Gel[a]	4	5-I	5-II	5-III	6-II	6-III
Initiation (s)	44 000	0	1000	0	2000	1500
Stabilisation (s)	54 000	7500	38 000	6000	4000	11 000
Oscillation period I[b] (s)	80	110	80	110	60	70
Oscillation period II[c] (s)	70	100	70	90	60	50

[a] Gel 6-I does not oscillate. [b] Oscillation period I is measured at the beginning of relatively stable oscillation. [c] Oscillation period II is measured during the stable oscillation stage, 10 000 s after the beginning of relatively stable oscillation.

Table 3 Oscillation characteristics of gels under condition B

Gel[a]	4	5-I	5-III	6-II	6-III
Initiation (s)	51 500	11 500	16 000	0	3500
Stabilisation (s)	52 500	27 500	34 500	0	8000
Oscillation period I[b] (s)	240	210	200	600	210
Oscillation period II[c] (s)	170	180	180	/	190
Max. volume change[d] (%)	8.0%	3.3%	/	20.1%	2.6%

[a] Gels 5-II and 6-I do not oscillate. [b] Oscillation period I is measured at the beginning of relatively stable oscillation. [c] Oscillation period II is measured during the stable oscillation stage. [d] The maximum volume change is calculated from a single oscillation period (reduced state–oxidised state–reduced state) based on volume changes in Fig. 3.
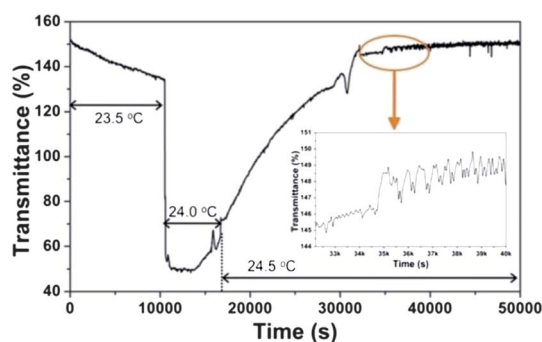
Fig. 2 Temperature-dependent oscillation profile of Gel **5-II** in BZ solution: [HNO$_3$] = 0.8 M, [NaBrO$_3$] = 0.08 M, [MA] = 0.06 M.

The behaviours of Gels **5-I**, **5-II** and **5-III** at this slightly higher temperature further confirm that increasing the distance between the catalyst and the polymer backbone helps to reduce the initiation time of oscillation. However, Gel **4** requires a longer time to initiate oscillation at the higher temperature (condition C) than at the lower temperature (condition B). As noted above, Gel **4** is much less permeable than Gels **5** and Gels **6**. When Gel **4** becomes more rigid at higher temperature, the diffusion of the BZ reactants into Gel **4** becomes slower, which results in an even longer initiation time. As shown in Scheme 2, the distance between the catalyst and the polymer backbone in Gels **6** is similar to or longer than the length of the crosslinker, which makes Gels **6** quite different from Gel **4** and Gels **5**. This difference may result in Gels **6** exhibiting different oscillatory behaviours compared to those of Gels **5**. For example, Gel **6-II** requires a longer initiation time than Gel **6-III** under condition C, but Gel **6-III** needs a longer time for initiation under condition B. Both Gels **6-II** and **6-III** require longer time to reach stable chemical oscillation under condition C than under condition B, a trend that is opposite to the behaviour of Gels **5**, which require longer time to reach stable oscillation under condition B than under condition C. A plausible explanation for Gels **6** taking longer to reach stable oscillation at the higher temperature is the longer time required to rearrange the position of the catalyst in the more rigid structures of Gels **6**. These results suggest that the effect of increasing the distance between the polymer backbone and the catalyst differs from that of increasing the temperature, likely because they result in different changes in the microstructures of the gels.

Analysis of the results for Gels **5-I**, **5-II**, and **5-III** suggests that decreasing the amount of the crosslinker or the catalyst in Gels **5**

leads to longer duration of self-sustained oscillation. Increasing the temperature fails to promote oscillation in Gel **6-I**, probably because it contains too many crosslinkers. There are more crosslinkers in Gel **6-III** than in Gel **6-II**, which likely contributes to the longer time for Gel **6-III** to reach stable oscillation.

Under condition C, the oscillation periods I and II of Gel **4** are both shorter than those of Gel **5-I**. The oscillation periods I and II of Gels **5-II** and **5-III** are longer than those of Gels **6-II** and **6-III**, respectively. These results are consistent with the behaviours of the gels under condition A. In addition, the similarity between the stabilised oscillation periods of Gels **5-I** and **5-II** indicates that the increase of temperature rigidifies the gels, thus minimizing the influence of the crosslinker concentration on the oscillation period.

Chemomechanical properties

Because milder reaction conditions lead to slower oscillation, condition B, as the mildest condition among the three BZ reaction conditions tested in the work, allows the most convenient detection of the volume changes of the gels. According to Yoshida *et al.*,[4] the size of the gel needs to be smaller than the intrinsic wavelength of the pattern associated with the chemical oscillation in order for the redox changes to occur homogeneously within the gel. Aihara and Yoshikawa estimated this critical length at about 0.6 mm for a BZ gel.[31] Thus, we cut the gel into tiny cube with edges of about 0.4 mm and immerse the gels into the BZ solution to observe the swelling–deswelling oscillation under a microscope equipped with a CCD camera able to take video images every 10 s. Analysis of the video confirms that the active swelling–deswelling oscillation of the gel correlates with its chemical oscillation, *i.e.*, the gel reversibly swells and deswells in the oxidised and reduced states, respectively. Fig. 3 shows the chemomechanical behaviours of the gels. The volume change of the gel is calculated by comparing the surface area of the cube to its size at the beginning of the oscillations. The maximum volume changes in Table 3 are calculated by comparing the volume changes of the gels in one

Fig. 3 Synchronised chemical and mechanical oscillations of Gels **4** (A), **5-I** (B), **6-II** (C) and **6-III** (D) under condition B. Swelling and deswelling of the gels (blue circles and line) are coupled to chemical oscillations (black line).

Table 4 Oscillation characteristics of gels under condition C

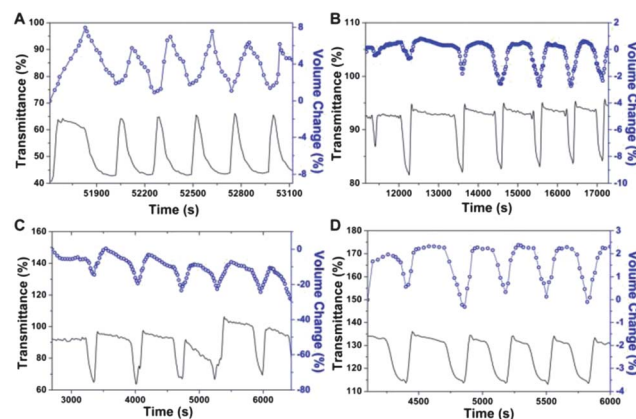| Gel[a]	4	5-I	5-II	5-III	6-II	6-III
Initiation (s)	76 000	0	0	0	6500	0
Stabilisation (s)	78 000	16 000	40 000	22 000	30 000	53 000
Oscillation period I[b] (s)	90	130	140	130	150	80
Oscillation period II[c] (s)	60	140	130	110	140	60

[a] Gel **6-I** does not oscillate. [b] Oscillation period I is measured at the beginning of relatively stable oscillation. [c] Oscillation period II is measured during stable oscillation stage.

oscillation period that starts from a reduced state, reaches the oxidised state, and returns to reduced state. The magnitude of the volume change declines with time after the start of oscillation, probably because of the increased rigidity of the gel in the strongly acidic BZ solution. Thus, we calculated the maximum volume change from the first several oscillations of each gel. As shown in Table 3, the maximum volume change of Gel **5-I** is 3.3%. Gel **5-III** shows negligible volume change. This result suggests that increasing the concentration of the catalyst leads to larger volume change for Gels **5**. The maximum volume change of Gel **6-II** is 20.1% (see Video‡), which is much higher than that of Gel **6-III** (2.6%). In this case, both the concentrations of catalyst and of crosslinker affect the volume change of the gel. For Gels **6**, higher concentrations of the catalyst and lower concentrations of the crosslinker favor larger volume change under condition B.

Conclusions

By designing and synthesizing new catalysts for BZ reactions, we produced six new copolymers that act as matrices of BZ gels. This is the first time that BZ catalysts, other than **1b**, have been incorporated in poly-NIPAAM-based copolymers. By testing these gels (including a control, Gel **4**) under different BZ reaction conditions, we found that modifying the distance between the catalyst and the polymer backbone significantly changes the oscillatory behaviours of the gels. Increasing the distance between the catalyst and the polymer backbone results in a shorter initiation time for oscillations. Intermediate distances (*i.e.*, in Gels **5**) lead to faster stabilised oscillation. Further extension of the distance (*e.g.*, replacing catalyst **1c** by **1d**) slows the oscillations of the Gels **6**. Whereas comparison of Gels **4** and **5-I** suggests that lengthening the distance between the catalyst and the polymer backbone leads to a decrease of the volume change during oscillation, comparison of Gels **5-III** and **6-III** indicates the opposite. Thus there is no simple correlation between the chemomechanical behaviour and catalyst–backbone distance. Nevertheless, this work confirms that tailoring the catalyst incorporated in a BZ gel should be a powerful approach to manipulate the performance of such gels. Although the manipulation is far from precise at present, it is a promising start for scientists interested in controlling the performance of self-oscillatory materials. Meanwhile, our results provide useful clues for understanding the link between macroscopic oscillation properties and the gel microstructure, which should aid in designing and fabricating BZ gels for improved performance. Moreover, more detailed correlation between the chemical structure and the mechanism of BZ reactions[32] and the chemistry during the induction period[33] will also help to optimize the chemomechanical behaviour of these gels. While this work presents the relation between the chemical properties and the chemomechanical oscillation of the gels, it also suggests that forces generated by chemomechanical reaction are different with different gels, which warrants further study in the future.

References

1 R. K. Soong, G. D. Bachand, H. P. Neves, A. G. Olkhovets, H. G. Craighead and C. D. Montemagno, *Science*, 2000, **290**, 1555–1558.
2 V. H. Ebron, Z. W. Yang, D. J. Seyer, M. E. Kozlov, J. Y. Oh, H. Xie, J. Razal, L. J. Hall, J. P. Ferraris, A. G. MacDiarmid and R. H. Baughman, *Science*, 2006, **311**, 1580–1583.
3 R. Yoshida, T. Takahashi, T. Yamaguchi and H. Ichijo, *J. Am. Chem. Soc.*, 1996, **118**, 5134–5135.
4 R. Yoshida, T. Takahashi, T. Yamaguchi and H. Ichijo, *Adv. Mater.*, 1997, **9**, 175–178.
5 V. K. Vanag and I. R. Epstein, *Science*, 2001, **294**, 835–837.
6 I. R. Epstein and K. Showalter, *J. Phys. Chem.*, 1996, **100**, 13132–13147.
7 T. Bánsági, Jr, V. K. Vanag and I. R. Epstein, *Science*, 2011, **331**, 1309–1312.
8 A. M. Zhabotinsky, F. Buchholtz, A. B. Kiyatkin and I. R. Epstein, *J. Phys. Chem.*, 1993, **97**, 7578–7584.
9 B. Durham, J. V. Caspar, J. K. Nagle and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4803–4810.
10 G. H. Chen and A. S. Hoffman, *Nature*, 1995, **373**, 49–52.
11 A. N. Zaikin and A. M. Zhabotinsky, *Nature*, 1970, **225**, 535.
12 Z. Nosczticzius, W. Horsthemke, W. D. McCormick, H. L. Swinney and W. Y. Tam, *Nature*, 1987, **329**, 619–620.
13 K. Miyakawa, F. Sakamoto, R. Yoshida, E. Kokufuta and T. Yamaguchi, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2000, **62**, 793–798.
14 S. Sasaki, R. Koga, R. Yoshida and T. Yamaguchi, *Langmuir*, 2003, **19**, 5595–5600.
15 Y. Hara and R. Yoshida, *J. Phys. Chem. B*, 2005, **109**, 9451–9454.
16 Y. Hara and R. Yoshida, *Langmuir*, 2005, **21**, 9773–9776.
17 Y. Hara and R. Yoshida, *J. Phys. Chem. B*, 2008, **112**, 8427–8429.
18 Y. Zhang, N. Li, J. Delgado, Y. Gao, Y. Kuang, S. Fraden, I. R. Epstein and B. Xu, *Langmuir*, 2012, **28**, 3063–3066.
19 J. N. Younathan, W. E. Jones and T. J. Meyer, *J. Phys. Chem.*, 1991, **95**, 488–492.
20 K. P. Zeyer and F. W. Schneider, *J. Phys. Chem. A*, 1998, **102**, 9702–9709.
21 P. A. Anderson, G. B. Deacon, K. H. Haarmann, F. R. Keene, T. J. Meyer, D. A. Reitsma, B. W. Skelton, G. F. Strouse, N. C. Thomas, J. A. Treadway and A. H. White, *Inorg. Chem.*, 1995, **34**, 6145–6157.
22 P. Belser, A. Vonzelewsky, M. Frank, C. Seel, F. Vogtle, L. Decola, F. Barigelletti and V. Balzani, *J. Am. Chem. Soc.*, 1993, **115**, 4076–4086.
23 G. Denti, S. Campagna, S. Serroni, M. Ciano and V. Balzani, *J. Am. Chem. Soc.*, 1992, **114**, 2944–2950.
24 H. D. Abruna, A. I. Breikss and D. B. Collum, *Inorg. Chem.*, 1985, **24**, 987–988.
25 J. Delgado, Y. Zhang, B. Xu and I. R. Epstein, *J. Phys. Chem. A*, 2011, **115**, 2208–2215.
26 The distance between the BZ catalyst and the backbone of the polymer was estimated based on calculating the length of the C–C bond by model simulation in Chem3D. Once there is more than one possible structure, the estimated distance varies in a range.
27 T. Sakai and R. Yoshida, *Langmuir*, 2004, **20**, 1036–1038.
28 R. Yoshida, M. Tanaka, S. Onodera, T. Yamaguchi and E. Kokufuta, *J. Phys. Chem. A*, 2000, **104**, 7549–7555.
29 H. G. Schild, *Prog. Polym. Sci.*, 1992, **17**, 163–249.
30 I. C. Chen, O. Kuksenok, V. V. Yashin, R. M. Moslin, A. C. Balazs and K. J. Van Vliet, *Soft Matter*, 2011, **7**, 3141–3146.
31 R. Aihara and K. Yoshikawa, *J. Phys. Chem. A*, 2001, **105**, 8445–8448.
32 L. Hegedus, M. Wittmann, Z. Nosczticzius, S. H. Yan, A. Sirimungkala, H. D. Forsterling and R. J. Field, *Faraday Discuss.*, 2001, **120**, 21–38.
33 A. Cadena, N. Perez, J. S. Agreda and D. Barragan, *J. Braz. Chem. Soc.*, 2005, **16**, 214–219.

Addition and correction

Note from RSC Publishing

This article was originally published with incorrect page numbers. This is the corrected, final version.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.