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Fe(bathophen)$_2$(phen)-based self-oscillating gel driven by the Belousov–Zhabotinsky reaction

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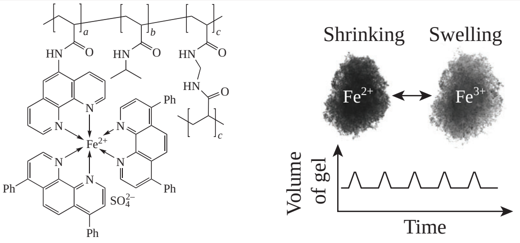
The synthesis of a new Fe(bathophen)$_2$(phen)-based self-oscillating gel driven by the Belousov–Zhabotinsky reaction is described. The gel undergoes spontaneous chemomechanical oscillations without any on–off switching by external stimuli and demonstrates the dependence of chemomechanical behavior on the concentration of the catalyst in it.



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The synthesis and investigation of autonomous self-oscillating polymer gels driven by the oscillatory Belousov–Zhabotinsky (BZ) reaction are rapidly developing areas of research.[1,2] Self-oscillating gels can be useful in a number of important applications such as the development of autonomous soft actuators, micropumps, microfluidic devices, mass transport systems and devices for signal transmission using chemical wave propagation.[3–6]

For the synthesis of such self-oscillating gels, most researchers use Ru-based complexes capable of catalyzing the BZ reaction, usually derivatives of tris(bipyridine)ruthenium(II) $[Ru(bpy)_3]^{2+}$, which are covalently bonded to polymer networks in cross-linked polyacrylamide or poly(*N*-isopropylacrylamide) gels.[7–10]

It is known[11,12] that the BZ reaction is bromination and oxidation of an organic substrate, such as malonic acid (MA), with bromate in the presence of a redox catalyst, such as ferroin or $[Ru(bpy)_3]^{2+}$, in a concentrated solution of sulfuric or nitric acid. The $Ru(bpy)_3$ complex periodically changes its oxidation state during the BZ reaction:

$$[Ru(bpy)_3]^{2+} \rightleftarrows [Ru(bpy)_3]^{3+}, \qquad (1)$$

and if it is covalently bonded to the gel polymer network, then these redox transitions lead to periodic changes in the properties (volume, transparency, *etc.*) of the entire gel. Therefore, if such a cross-linked poly(*N*-isopropylacrylamide) gel with covalently bonded $Ru(bpy)_3$ is immersed in a catalyst-free BZ solution (CFBZ), then in such a CFBZ–gel system, a chemical oscillatory reaction starts, which generates autonomous and periodic redox transitions according to equation (1). Redox alterations in the polymerized catalyst fragment change the volume phase transition temperature, as well as the degree of swelling, since the hydrophilicity of polymer chains increases in the oxidized Ru^{III} state and decreases in the reduced Ru^{II} state.[13] As a result, autonomous periodic changes in the gel volume, (that is, chemomechanical oscillations) are observed in the gel, synchronized with oscillations of the redox potential of the complex.

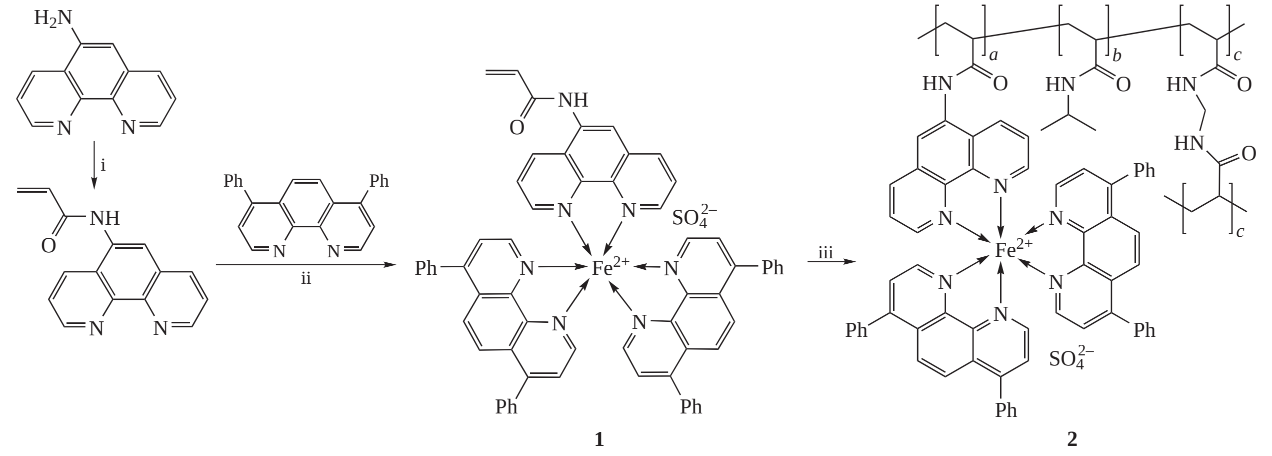
However, Ru-based complexes have significant disadvantages such as high cost, complexity of synthesis and photosensitivity. All this limits their practical application for the synthesis of self-oscillating gels. Despite this, almost all self-oscillating gels that exhibit volume oscillations (swelling/shrinking) are created on Ru-based complexes.

Attempts to develop self-oscillating gels based on Fe complexes are few, and the resulting gels have many disadvantages. Thus, gels obtained by covalent binding of ferroin $[Fe(phen)_3]$ with polymer networks have a relatively low amplitude of chemomechanical oscillations: for the cross-linked poly[*N*-isopropylacrylamide-*co*-(5-acrylamido-ferroin)], the change in the linear dimensions of the gel during chemomechanical oscillations is 7%,[14] while for the cross-linked poly[*N*-vinylpyrrolidone-*co*-acrylic acid-*co*-(5-acrylamido-ferroin)] it is 5%.[15] The gel obtained by incorporating $Fe(phen)_3$ into a polymer network due to electrostatic interactions with a cross-linked acrylamide–sodium acrylate copolymer has a better chemomechanical amplitude up to 12% (the gel shrinks when the catalyst is oxidized and swells when reduced), but loses the catalyst during the BZ reaction and exhibits chemomechanical behavior in a narrow size range.[16,17] Although progress has been made in the development of Fe complex-based gels, their chemomechanical properties are still worse than those of Ru complex-based gels, demonstrating changes in linear dimensions of up to 18% (for gel systems that are assembled from microgels).[18]

Thus, the problem of developing a cheap, reliable and easily synthesized gel that demonstrates a significant amplitude of chemomechanical oscillations remains relevant.

In this article, we report the synthesis of a new self-oscillating gel by copolymerization of an acrylamide derivative of bis(bathophenanthroline)(1,10-phenanthroline)iron(II) sulfate [Fe(bathophen)$_2$(phen)] complex with *N*-isopropylacrylamide (IPA) and *N*,*N*′-methylenebisacrylamide (MBA). For the first time, it was found that the gel swells/shrinks synchronously with the redox oscillations of Fe(bathophen)$_2$(phen) and exhibits a 10% change in the linear size of the gel during chemomechanical oscillations.

First, for the copolymerization of the Fe(bathophen)$_2$(phen) complex with other monomers, we synthesized its derivative,



Scheme 1 *Reagents and conditions*: i, CH_2=CHCOCl, TMEDA, THF, 10 °C, 20 h; ii, $FeSO_4$, H_2O/Pr^iOH; iii, IPA, MBA, $(NH_4)_2S_2O_8$, TMEDA, H_2O/DMSO, 70 °C, 3 h.

bis(bathophenanthroline)(5-acrylamido-1,10-phenanthroline)-iron(II) sulfate [Fe(bathophen)$_2$(acphen)] **1** (Scheme 1). The synthesis is described in detail in Online Supplementary Materials. The acrylamide fragment present in the structure of the Fe(bathophen)$_2$-(acphen) complex makes it possible to copolymerize this compound with such acrylamide derivatives as IPA and MBA.

Using the copolymerization of the Fe(bathophen)$_2$(acphen) complex with IPA and MBA, we synthesized poly[IPA-*co*-Fe(bathophen)$_2$(acphen)-*co*-MBA] **2** gel (see Scheme 1 and Online Supplementary Materials). In the gel, Fe(bathophen)$_2$-(acphen) is used as a catalytic fragment, while IPA and MBA are introduced as a monomer forming a polymer chain and a cross-linker, respectively. Gel **2** was synthesized as a centimeter-sized piece containing about 0.7 mol% of Fe(bathophen)$_2$(acphen) relative to IPA and then was divided into separate small pieces to study the chemomechanical properties. Pieces smaller than a millimeter were taken, since larger pieces, due to the low speed of propagation of a chemical wave, can simultaneously have both an oxidizing (expanding) and a reducing (contracting) region. Therefore, to observe the compression of the entire piece, pieces with sizes in the range of 600–800 μm were selected. Thus, it was assumed that the composition and microstructure of the gel are not changed by the division procedure. Since the gel had a complex microheterogeneous structure similar to a sponge, when cut, it formed pieces of irregular shape.

To test the chemomechanical properties of gel **2**, a piece of gel [Figure 1(*a*)] was immersed in an aqueous CFBZ solution. The concentrations of BZ reagents in the CFBZ solution were almost the same as in the testing of gels based on the Fe(phen)$_3$ complex: 0.063 M MA, 0.084 M $NaBrO_3$ and 0.25 M H_2SO_4.[14]

The piece of gel **2** [see Figure 1(*a*)] showed self-oscillating behavior in the CFBZ solution [Figure 1(*d*)], becoming lighter (darker) in the oxidized (reduced) state of the catalyst. The length of the piece increased when the catalyst was in the oxidized state and decreased when it was in the reduced state; the mechanical oscillations of the gel coincided with the chemical ones. The amplitude of mechanical oscillations (changes in the linear size of the gel) was 8 ± 1%. During oscillations, the pieces of gel freely located in the reactor with the CFBZ mixture slightly moved along the bottom, which made it difficult to observe them and obtain the space–time plots of their dynamics. To avoid this shift, we attached one of the surfaces of the piece to a rough glass surface. Figure 1(*a*) shows snapshots of the shrunken (snapshot *1*) and swollen (snapshot *2*) states of the attached piece of gel **2**.

Figure 1(*d*) shows a space–time plot of the oscillations of an attached piece of gel **2**. The space–time plot demonstrates the size and color of the piece as a function of time.

Online Supplementary Materials provide an experimental setup for recording snapshots of gel pieces and measuring their sizes, as well as a procedure for constructing space–time plots. As we mentioned above, a piece of gel **2** was attached to the surface of the glass. This localized the pieces, but did not allow their chemomechanical properties to be fully manifested. To study the oscillations of an incompletely attached piece of gel **2**, we placed

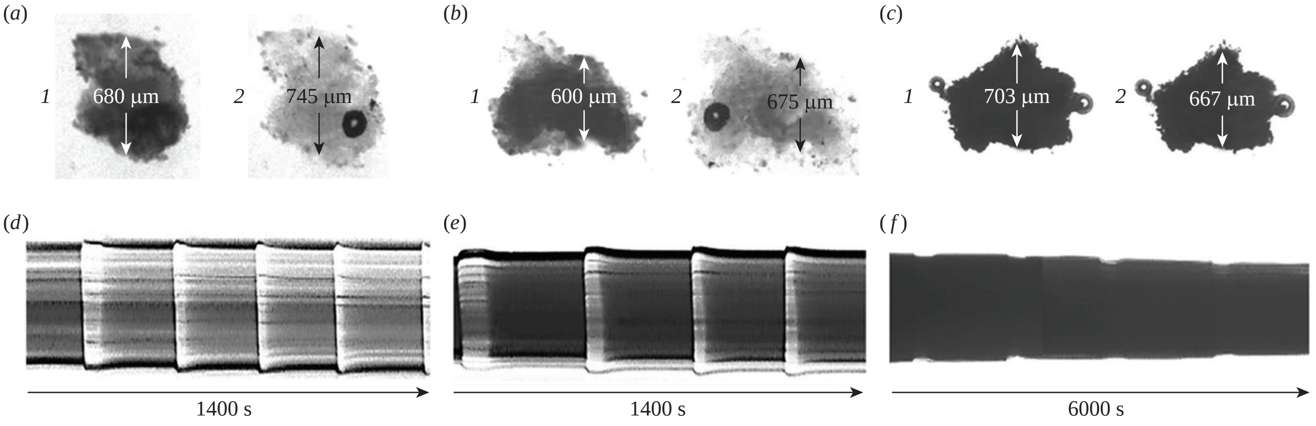


Figure 1 Oscillations of gel pieces in a CFBZ solution containing 0.063 M MA, 0.084 M $NaBrO_3$ and 0.25 M H_2SO_4. (*a*)–(*c*) Snapshots and (*d*)–(*f*) space–time plots of oscillations of (*a*),(*d*) attached and (*b*),(*e*) partially attached pieces of gel **2**, as well as (*c*),(*f*) attached piece of gel **5** with the catalyst in (*1*) reduced and (*2*) oxidized state. Space–time plots were obtained along the lines indicated by white arrows in the snapshots at 525 nm, near the absorption maximum of Fe(bathophen)$_2$(acphen). The average oscillation period was (*d*) ~290, (*e*) ~330 and (*f*) ~1500 s. Vertical light (dark) bands on the space–time plots correspond to the oxidized (reduced) state of the catalyst. Rounded dark areas in the snapshots are CO_2 bubbles that arise during the BZ reaction.

it in the CPBZ mixture, only partially attaching the piece to the bottom using a small branch.

Figure 1(*b*) shows snapshots of this piece of gel, and Figure 1(*e*) shows a space–time plot of its dynamics. As can be seen, the partially attached gel demonstrates a greater amplitude of mechanical oscillations than the fully attached one. Changes in the linear size of the piece were 10 ± 1%. We assume that the reason for the difference in the amplitude of mechanical oscillations between attached and partially attached gel pieces can be explained by the difference in the diffusion of BZ reagents and reaction products in the pieces.

The oscillating behavior of attached and partially attached gel pieces is demonstrated in the videos accelerated by 64 times (Figures S3 and S4, see Online Supplementary Materials).

It seems that the self-oscillating behavior of gel **2** is due to the same reasons as the behavior of cross-linked polyisopropylacrylamide gels based on Ru complexes.[13,19] When gel **2** is immersed in the CFBZ solution, the BZ reaction starts in the gel, since $\mathrm{Fe(bathophen)_2(acphen)}$ is a catalyst for this reaction. Redox processes in the complex,

$$\mathrm{Fe(bathophen)_2(acphen)^{2+}} \rightleftarrows \mathrm{Fe(bathophen)_2(acphen)^{3+}}, \qquad (2)$$

change the volume phase transition temperature and the swelling ratio of gel **2**, because the hydrophilicity of polymer chains increases in the oxidized $\mathrm{Fe^{III}}$ state and decreases in the reduced $\mathrm{Fe^{II}}$ state. As a result, the gel exhibits autonomous swelling–shrinking oscillations coinciding with the redox oscillations of the complex.

To study the effect of the amount of incorporated catalyst on the chemomechanical behavior of the gel, gels **3**, **4** and **5** were synthesized, having the same structure as gel **2**, but containing about 0.5, 1.0 and 1.2 mol% $\mathrm{Fe(bathophen)_2(acphen)}$, respectively, relative to IPA. The pieces of gels **3**, **4** and **5** were tested in the same way as a fully attached piece of gel **2**. It has been found that gel **3**, which contains less catalyst than gel **2**, also changes its linear dimensions less (about 5%) during chemomechanical oscillations. However, gel **4**, although containing more catalyst than gel **2**, exhibits a reduced amplitude of mechanical oscillations (5%) compared to gel **2**. Gel **5**, containing about 1.2 mol% catalyst, shows chemomechanical properties opposite to those of gels **2**, **3** and **4** with less catalyst. Gel **5** [Figure 1(*c*)] shrinks as the catalyst oxidizes and swells as it is reduced [Figure 1(*f*)], which resembles the behavior of acrylamide-based gels[16,17] rather than IPA-based gels. It should be noted that such a variation in the chemomechanical behavior of the gel with an increase in the concentration of the catalyst in it can be called a ‘reversal’ of the chemomechanical properties of the gel. This phenomenon requires further detailed study.

Thus, we have synthesized a novel BZ type $\mathrm{Fe(bathophen)_2}$-(phen)-based self-oscillating gel, which demonstrates high-amplitude chemomechanical oscillations under the conditions of the BZ reaction. Changes in the linear dimensions of gel pieces during oscillations reached 10%. We have shown that the gel can react to catalyst oxidation by both swelling and shrinking, depending on the content of the catalyst in the gel. Such a self-oscillating gel could potentially be used as a material for the development of chemomechanical devices.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.09.030.

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