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Chemical micro-oscillators based on the Belousov – Zhabotinsky reaction

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The results of studies on the development of micro-oscillators (MOs) based on the Belousov – Zhabotinsky (BZ) oscillatory chemical reaction are integrated and systematized. The mechanisms of the BZ reaction and the methods of immobilization of the catalyst of the BZ reaction in micro-volumes are briefly discussed. Methods for creating BZ MOs based on water microdroplets in the oil phase and organic and inorganic polymer microspheres are considered. Methods of control and management of the dynamics of BZ MO networks are described, including methods of MO synchronization. The prospects for the design of neural networks of MOs with intelligent-like behaviour are outlined. Such networks present a new area of nonlinear chemistry, including, in particular, the creation of a chemical 'computer'.
The bibliography includes 250 references.

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1. Introduction

In the early 1950s, Soviet chemist B.P.Belousov discovered periodic oscillations in a solution containing citric acid, sulfuric acid, potassium bromate and cerium sulfate.[1] He could not publish the results of the experiments because the journal *Kinetics and Catalysis* refused to publish the facts 'that cannot exist'. Those were the exact words characterizing the attitude of the reviewer to Belousov s discovery. However biochemist S.E.Shnoll, who was interested in oscillatory reactions, found Belousov and learned the recipe of the reaction solution. He entrusted the detailed study of the Belousov reaction to his postgraduate student A.M.Zhabotinsky, who coped brilliantly with the task. Now this reaction is known under the name of the Belousov – Zhabotinsky (BZ) reaction.†

This is how a new scientific area called nonlinear chemical dynamics or, to put it shortly and figuratively, nonlinear chemistry emerged in our country[1–5] and spread‡ all over the world having achieved the age of maturity lately.[6,7] Nonlinear chemistry is closely connected with such spheres of knowledge as cell biology,[8–13] population biology,[14–17] neurobiology,[8] materials science[19–23] as well as such a relatively new interdisciplinary scientific area as artificial intelligence.[24] Some groups of scientists from Germany,[25] the USA,[26–31] Russia,[32–37] UK,[38–41] Poland,[42] Italy[43] and Japan[44–46] direct their efforts towards the study of oscillatory chemical reactions in

† Five Soviet scientists: G.R.Ivanitsky, V.I.Krinsky, A.N.Zaikin, A.M.Zhabotinsky and B.N.Belousov were awarded in 1980 the Lenin Prize 'for the discovery of a new class of autowave processes and the study of their role in breaking the stability of excitable distributed systems'.
‡ The spread of Soviet science and, in particular, nonlinear chemistry outside the USSR accelerated in the 1990s. A.M.Zhabotinsky, for example, moved to Boston in 1991 to the laboratory of Professor I.R.Epstein and worked there until his death in 2008. The scientific work of A.M.Zhabotinsky in Boston had a great influence on research in nonlinear chemistry in the United States.

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microvolumes and micro-oscillatory ensembles (networks of MOs).§

The aim of the present review is to introduce the readers to a new field of nonlinear chemistry dealing with the development of chemical oscillators with linear sizes from tens to hundreds of microns capable of forming artificial neural networks similar to the networks which neurons form in human brain. Since neural networks of oscillators of any nature can process data in the same way as neuron networks do,[47, 48] the networks of chemical oscillators can perform something similar.

As a rule, the classic Belousov – Zhabotinsky reaction with mechanism discussed in Section 2 is used as an oscillatory reaction.[49] The role of the catalysts in this reaction is performed by metal complexes, which can be immobilized or encapsulated in microvolume thus making it possible to imagine that only this microvolume (and, probably, its nearest vicinity) will be in the oscillatory state. In relation to such microvolumes, it is convenient to introduce the term 'BZ-micro-oscillators'. Linear sizes of MOs are limited. They cannot be too small as MOs should contain all the components of the BZ reaction provided that the quantity of molecules of each intermediate inside MO should be numbered in the tens or more. When the quantity of the molecules of some intermediate is numbered in units (or less) as is the case for nano-size droplets, then high-amplitude fluctuations, large dispersion of reaction rates and, as a consequence, inability to reproduce the results become inevitable. The number N of any molecules in volume V equals $c_0 V N_A$, where c_0 is the concentration of the molecules and N_A is the Avogadro number. Simple estimation of the linear size r_m of the microvolume for $N = 10$ and $c_0 = 10^{-8}$ mol L^{-1} (the minimum concentration of some intermediates of the BZ reaction) gives

$$r_m \approx \left(\frac{N}{c_0 N_A}\right)^{1/3} \approx 100 \text{ nm} \quad (1)$$

This 'bottom limit' cuts off such a well-known system as the BZ reaction in the water-in-oil AOT microemulsion,[50] in which the linear size of reversed micelles reaches 10 nm.

The water-in-oil AOT microemultion is a thermodynamically stable microemultion in which the aqueous dispersed phase is stabilized in a hydrophobic continuous media (like saturated hydrocarbons) by AOT surfactant molecules, sodium bis(2-ethyl-1-hexyl)sulfosuccinate. If aqueous nanodroplets of AOT microemulsion contain all the components of the BZ reaction, then the system, unlike any other, is capable of producing a large number of dissipative structures such as Turing patterns, anti-waves, oscillons, segmented waves and other.[50 – 55]

At the same time, microvolumes should not be too large in order to remain homogenous and exclude the occurrence of any waves and dissipative structures. This requirement limits the upper linear size of microvolumes by 0.5 – 1 mm.[36, 56] Thus, the linear size of MOs should be from 0.1 μm to 500 μm. Note that the linear size of all living cells falls within this range, thus making the study of MOs even more interesting.

Among the peculiarities of an isolated BZ MO, we should note the following: large values of both the rate of mass exchange, k_0, between the MOs and the environment and the surface area to volume ratio (S/V) of MO. In fact, if MOs are in the aqueous phase and all (or nearly all) of the intermediates can freely diffuse into and out of them (which does not refer to aqueous microdroplets in the oil phase and to living cells), then

$$k_0 \approx \frac{D}{r_m^2} \quad (2)$$

The value of k_0 is in the range of $20 - 0.2$ s^{-1} for $r_m = 10 - 100$ μm and $D \approx 2 \times 10^{-5}$ cm^2 s^{-1} (typical value of the diffusion coefficient for small molecules). With such high values of the rate of mass exchange between the MOs and the environment (when $k_0^{-1} \ll T_0$, where T_0 is the oscillator period), the oscillations of the BZ reaction can be suppressed, though they would be reliably manifested in the closed reactor. This condition considerably narrows down the range of possible linear sizes for BZ MOs to 10 – 50 μm.

The role of the S/V ratio is not studied well enough, but at large catalyst concentration, all the main reactions can proceed only on the surface of MO. This feature should be taken into account when choosing the concentrations of immobilized catalyst. Note that this problem is not new. It arises, for instance, when an enzyme is being immobilized on the surface and in the bulk of monodisperse latex microspheres.[57]

The interest in micro-oscillators can be explained mostly by the fact that, with their help, the collective behaviour of a large number of MOs can be studied. Therefore, the individual characteristics of isolated MO given in the present review are followed by the description of their coupling. The coupling between MOs is classified by various features such as type and duration of an influence on MOs, the way of transmission of information between MOs, the direction of the influence between MOs, and some other characteristics.

Two types of coupling are specially noted. They are of inhibitory type which lengthens the period of oscillations and of excitatory type which shortens this period. According to the duration, the influence on/interaction between MOs is classified into the pulse (short) and constant (continuous) interactions. The pulse interaction is also characterized by a time delay between the emergence of a signal which causes this pulse and the moment at which this pulse affects the oscillator. In the case of two coupled neurons, the spike in one neuron provides the action potential in the axon, which runs along it to another neuron. In some time depending on the axon length, the action potential reaches a synapse and affects another neuron *via* neurotransmitters. This is an example of pulse effect with time delay which is roughly equal to the time the action potential is running along the axon. The diffusion coupling between MOs is an example of continuous interaction.

It is customary to distinguish diffusive coupling between two neighbouring MOs and an interaction between distant MOs achieved by waves, in particular the reaction-diffusion waves (an example of such a wave is a reaction-diffusion action potential running along an axon), light flashes (as in

§ Modern scientific groups are, as a rule, are international teams. For example, the authors of work Ref. 25 are include not only German scientists, but also the American professor Kenneth Showalter, who made an enormous contribution to the development of nonlinear chemical dynamics. In particular, he is a pioneer in the creation and use of micro-oscillators. The authors of Ref. 43 are not only Italians, but also a Frenchman working in this group.

fireflies), radio waves (as in cell phones), acoustic waves (as in bats and dolphins).

The interaction between MOs (or rather, the effect on MOs) can be global as well.[58 – 60] In this case, there must be another system that stands, as it were, above the MOs and can control them. This system should read and record an integral signal from all MOs. Signals from some MOs can be weak, and from others, strong, but the system of such global coupling is sensitive only to the integral signal. The stronger the integral signal, the stronger the feedback of the system on the MOs; moreover, this feedback signal is uniformly distributed over all MOs and has an inhibitory character, decreasing the activity of MOs and, accordingly, decreasing the integral signal. Note that if the global coupling had an excitatory character, then such a system would be unstable. The global inhibitory coupling occurs, for example, in the case of CO oxidation on the surface of Pt.[61] In living nature, the effect of hormones on the body can be considered as the global effect.

Finally, interactions between MOs can be unidirectional (from one MO to another one) or reciprocal. For example, diffusive interactions are mutual and cannot be unidirectional in any way. But pulse interactions (such as synaptic ones) can be unidirectional. Section 3 is devoted to characteristic features of different types of interactions between the BZ MOs.

Using a sufficiently large number of MOs, it is possible to create neural networks that perform computational tasks. Rather often, such networks are called 'chemical computers' (ChC),[62, 63] although it is necessary to clarify in each specific case what this 'computer' does exactly. In some cases, a network of chemical micro-oscillators performs logical operations such as AND or OR;[41, 64 – 67] in other cases, such a network can recognize patterns and make decisions,[63, 68, 69] and in some other cases, it can behave adaptively, adapting to external signals.[24, 70] Probably the preferred name for networks of MOs with adaptive or even cognitive behaviour should be 'chemical brain' rather than 'chemical computer', but the final name has not yet emerged. We will use the abbreviation ChC for now.

The potential scope of application of the chemical computer can be wide, ranging from the integration of systems of differential equations with any predetermined accuracy to image analyzers,[68, 69, 71] and to autonomous small devices capable of moving and behaving 'intelligently' without using electricity.[24, 70, 72] The term 'intelligent behaviour' as applied to networks of coupled chemical elements (oscillators and excitable cells) requires clarification. Usually we endow with intelligence only humans, although many mammals, as well as birds and mollusks (for example, those belonging to the families of corvids and cephalopods, respectively) behave very intelligently. Most likely, we are intruding here in the field of philosophy: what is intelligence? Is a machine that plays chess or overcomes the Turing test intelligent? If the MO network in any way behaves similarly to some living creature endowed with a nervous system, then we will say that the behaviour of the network is reasonable (or intelligent). For the initial stage of creating a 'chemical brain', such a definition is sufficient. By improving ChC, we will raise the bar of reasonability.

Of course, nowadays the chemical brain is inferior in almost everything to conventional computers; however, it fundamentally differs from them in the ability to work without electricity, using only chemical reactions (like the brain of living beings). For the functioning of the chemical brain, the creation of special mathematical programs is not required, but 'correct' architecture, proper chemical connections between the elements, and nonlinear dynamics of the elements themselves can allow this network to behave intelligently. Perhaps, the development of such networks will allow us to understand better how our own brain works.

Schemes of the ChC with adaptive behaviour are shown in Fig. 1. Light pulses were used to establish pulse coupling with a time delay between MOs.[24, 70] For proper functioning of these connections, a conventional com-

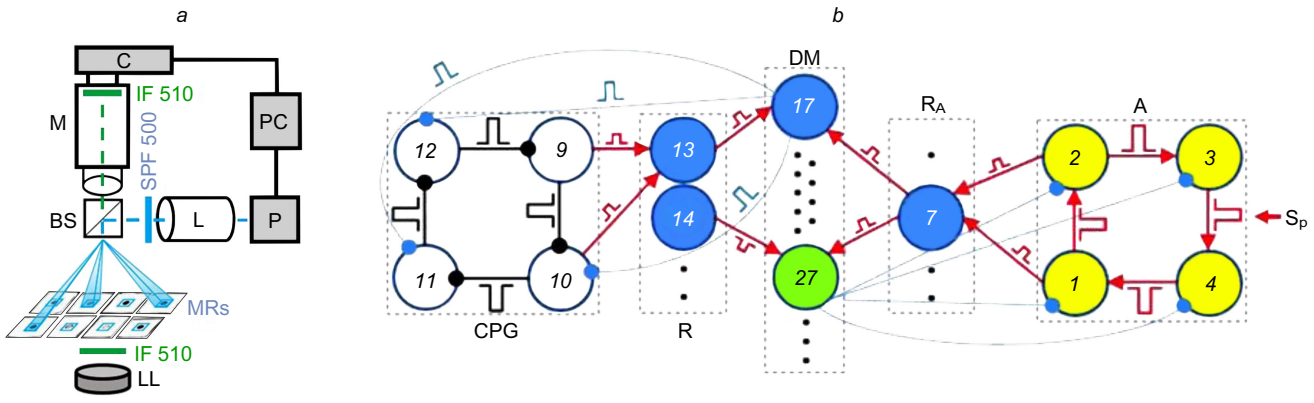


Figure 1. (*a*) Schematic diagram of a ChC and (*b*) pulse connections between its cells.[70] Legend, (*a*): M, stereo microscope; C, a CCD camera for recording the dynamics of all cells of the ChC; MRs, micro-reactors or ChC cells; PC, personal computer; P, computer projector; IF 510, interference filter with the maximum transmittance at 510 nm; LL, the source of the analyzing light; SPF 500, a cut-off filter that transmits actinic light from the computer projector with a wavelength of less than 500 nm; BS, semi-transparent (50 : 50) mirror; L, a lens that focuses the light from the computer projector onto the plane of the micro-reactors. (*b*): Cells *1 – 4* make up the antenna block, which responds to external signals (S_p) by the emergence of one or another oscillatory mode; cells *5 – 8* (only cell *7* is drawn) make up the R_A (antenna reader) block; cells *9 – 12* make up the central pattern generator (CPG) block; cells *13 – 16* (only cells *13* and *14* are drawn) make up the R (reader) block, which determines the current oscillatory mode of the CPG block; cells *17 – 30* (only cells *17* and *27* are drawn) form a decision making (DM) block, which is responsible for switching the current CPG mode to the mode corresponding to the antenna's mode.

puter and a computer projector are involved. Therefore, electricity is still required to operate this ChC. However, it is obvious that it is necessary to replace light pulses with chemical waves moving along narrow channels between the certain oscillators. Note that the lengths of all channels must correspond to the time delays in the original model with light pulses (the time delay is proportional to the channel length). Such a replacement will transform this ChC into a truly miniature device that runs only on chemical fuel.

In the present review, we do not dwell on the details of the operation of ChC, which can be found in a number of publications.[24, 33, 34] For us, it is important to determine physicochemical properties that the MOs must possess to guarantee reliable functioning of MO networks with the given properties. Among such properties, we highlight the following:

(*a*) reliable and reproducible oscillatory or excitable states of isolated MO;

(*b*) homogeneity of MOs, *i.e.*, the method of MO synthesis should guarantee approximately the same properties for all MOs, including the oscillation period;

(*c*) the possibility of establishing both inhibitory and excitatory coupling between MOs;

(*d*) tuning of the coupling strength in the case of both diffusion local coupling and long-range pulsed coupling;

(*e*) controllability of the phases of MO by external pulses;

(*f*) the possibility of constant feeding of the MOs with fresh reactants so that the ChC can work as long as circumstances require;

(*g*) stability of the MOs under the conditions of the BZ reaction, that is, the ability to maintain the shape and size of the micro-oscillator for a long time, as well as the dynamics of the oscillations, which includes the period and type of oscillations (relaxation or sinusoidal).

In Sections 4 – 7 of this review, the ways of creating BZ MOs with the above properties as well as the evaluation of their suitability for the use in ChC are analyzed and summarized. As far as we know, there have been no reviews of this type, and our review is the first one, and therefore it is not devoid of flaws. For example, chemical micro-oscillators not associated with the BZ reaction remained outside the scope of this review. In the Conclusion, the current state of research in the field of development of chemical MOs based on the BZ reaction is briefly considered and the prospects for development are outlined.

Definitions of terms. A *network* is an ensemble consisting of a finite number of N nodes (vertices), between which M directed (or two-way) connections (edges) are established.[73]

Neural network is the concept used in relation to networks built on the principles of the organization and functioning of biological neural networks. In the context of this review, the nodes of such a network are micro-oscillators and/or microcells in an excitable state coupled by pulsed or diffusive connections.

Spike is a concept associated with the excitation of a neuron and the passage of an action potential along an axon. In our case, it is better to associate the spike with relaxation oscillations in nonlinear dissipative systems. Unlike harmonic oscillations, each period of relaxation oscillations can be divided into two stages: fast and slow changes in the state of the system. The stage of fast (and short) changes with a pronounced peak (which corresponds to the maximum change in the state of the system) is called a spike. In the case of the BZ reaction, the emergence and growth of the spike is due to the rapid autocatalytic increase in the concentration of the activator, $HBrO_2$, while the decay of the spike is due to the rapid reaction of the activator with the inhibitor, Br^-, in which the activator disappears.

Chemical computer is a liquid device capable of performing logical (Boolean) operations using chemical reactions. A spatially distributed homogeneous BZ reaction can serve as such a device. A heterogeneous network of microcells, for example, microdroplets, liposomes, or polymer microspheres filled with reactants of the BZ reaction or any other reaction exhibiting oscillatory dynamics and/or excitability can also serve as such a device.[74]

Chemical brain is a chemical computer with a more complex architecture that can mimic cognitive functions, such as adaptability to external signals or the ability to make decisions.

Decision making is the ability (for example, of the chemical brain) to choose between several possible actions based on the analysis of data.

Compartmentalization is related usually to living cells. This term means the division of a cell into compartments covered with a membrane of a lipid bilayer, in which certain biochemical processes are localized. In our case, this is the division of a large system into identical compartments, which are polymer microspheres or emulsion micro-droplets, in which the BZ reaction proceeds locally.

Chemical-mechanical interaction is the interaction of mechanically bound but chemically separated self-oscillating gels, in which a change in the size of one piece of gel can lead to chemical changes in another piece and *vice versa*.

2. The mechanism of the Belousov – Zhabotinsky reaction

The widely accepted mechanism of the BZ reaction is the Field – Körös – Noyes (FKN) mechanism,[75] which includes 12 reactions:

$$HBrO_2 + Br^- + H^+ \rightarrow 2\,HOBr \quad (3)$$

$$Br^- + BrO_3^- + 2\,H^+ \rightarrow HBrO_2 + HOBr \quad (4)$$

$$HBrO_2 + HBrO_2 \rightarrow HOBr + BrO_3^- + H^+ \quad (5)$$

$$HBrO_2 + BrO_3^- + H^+ \rightarrow 2\,BrO_2^\bullet \quad (6)$$

$$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O \quad (7)$$

$$Br_2 + H_2O \rightarrow Br^- + HOBr + H^+ \quad (8)$$

$$Br_2 + CH_2(COOH)_2 \rightarrow Br^- + CHBr(COOH)_2 + H^+ \quad (9)$$

$$HOBr + CH_2(COOH)_2 \rightarrow CHBr(COOH)_2 + H_2O \quad (10)$$

$$2\,BrO_2^\bullet \rightarrow HBrO_2 + BrO_3^- + H^+ \quad (11)$$

$$BrO_2^\bullet + Q + H^+ \rightarrow HBrO_2 + Z \quad (12)$$

$$Z + CHBr(COOH)_2 \rightarrow Br^- + Q + H^+ \quad (13)$$

$$Z + CH_2(COOH)_2 \rightarrow Q + H^+ \quad (14)$$

where Q is the reduced form and Z is the oxidized form of the catalyst. For example, $Q = Fe(phen)_3^{2+}$ and $Z = Fe(phen)_3^{3+}$, where phen is 1,10-phenanthroline, BrO_2 is the radical. For the photosensitive version of the BZ reaction,[76 – 78] $Q = Ru(bpy)_3^{2+}$ and $Z = Ru(bpy)_3^{3+}$, where bpy is 2,2′-bipyridine. If Ru $(bpy)_3^{2+}$ is used as a catalyst and the BZ reaction proceeds under the action of light, it is

necessary to add the following reactions for the case where the concentration of bromomalonic acid is much larger than the concentration of bromate:[79, 80]

$$Q + h\nu \rightarrow Q^* \quad (15)$$

$$Q^* + CHBr(COOH)_2 \rightarrow Z + Br^- + {}^{\bullet}CH(COOH)_2 \quad (16)$$

$$Q^* \rightarrow Q \quad (17)$$

If the concentration of bromomalonic acid is much smaller than the concentration of bromate, then reaction (18) begins to dominate instead of reaction (16):[81]

$$Q^* + BrO_3^- + 2H^+ \rightarrow Z + BrO_2^{\bullet} + H_2O \quad (18)$$

where Q* is the excited state of the catalyst. Reaction (17) is a spontaneous deactivation of an excited state. Thus, using Ru $(bpy)_3^{2+}$ as a catalyst and changing the composition of the BZ mixture, one can either suppress or initiate oscillations with the help of light.

The FKN mechanism has been stated and retold many times (see, for example,[6, 82, 83]). In total, the BZ reaction can be presented as the oxidation of malonic acid by bromate in an acidic medium:[84]

$$2BrO_3^- + 3CH_2(COOH)_2 + 2H^+ \rightarrow \quad (19)$$
$$\rightarrow 2BrCH(COOH)_2 + 3CO_2 + 4H_2O$$

Taking into account the decomposition of bromomalonic acid, the balance of the BZ reaction can be written in another way:

$$4BrO_3^- + 3CH_2(COOH)_2 \rightarrow 4Br^- + 9CO_2 + 6H_2O \quad (20)$$

The FKN mechanism (3)–(14) is sometimes subdivided into three processes:[83]

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + H_2O \quad \text{(Process A)}$$

$$BrO_3^- + 4Q + 5H^+ \rightarrow HOBr + 4Z + 4H_2O \quad \text{(Process B)}$$

$$CH_2(COOH)_2 + CHBr(COOH)_2 + 2Z \rightarrow \quad \text{(Process C)}$$
$$\rightarrow fBr^- + 2Q + PP$$

where f is the stoichiometric coefficient depending on the initial concentrations of the reactants, PP are numerous reaction products.

Note that the complete mechanism of the BZ reaction contains about 80 elementary reactions, most of which are redundant for describing the BZ oscillations.[85] It is of interest to us to depict reactions (3)–(14) graphically for the case where the catalyst is immobilized on a polymer microsphere, and all other intermediates and reactants diffuse freely. In this case, it is clearly seen which reactions are actually localized in the microsphere [these are reactions (12)–(14)] and which can occur both inside the microsphere and in the surrounding environment [these are reactions (3)–(11)], in a BZ solution without a catalyst (BZC solution) (Fig. 2). In Fig. 2, the initial reactants, bromate and malonic acid, which are present in excess, can be omitted in some reactions for simplicity. Note that Process A can take place outside the microsphere. Catalyst immobilization leads to spatial separation of elementary reactions (3)–(14).

For an approximate estimation of the distance to which the BZ reaction intermediate can diffuse from the microsphere, we use the standard expression for the diffusion length:

$$l_d \approx (D\tau)^{1/2} \quad (21)$$

where τ is the characteristic lifetime of one or another intermediate, determined by the reaction rate constants and reactant concentrations. Thus, for Br_2, the length $l_d \sim 10$ μm, and for $HBrO_2$ the length l_d can be estimated approximately as 50 μm, while for Br^-, the length l_d may turn out to be less than 1 μm due to a very fast reaction (7).

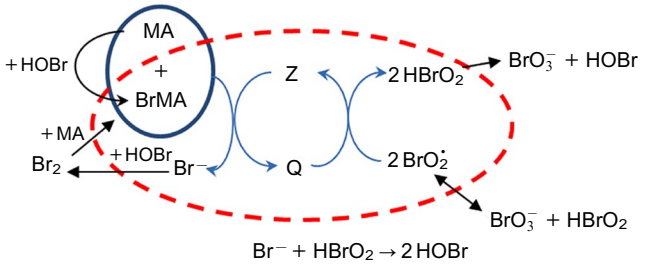


Figure 2. Scheme of the Field–Körös–Noyes mechanism. Designations: Q = $Ru(bpy)_3^{2+}$, Z = $Ru(bpy)_3^{3+}$. The conventional boundary of the polymer microsphere is indicated by the dashed red line. MA and BrMA are combined into one conditional substrate, which reduces the oxidized form of catalyst Z. The reaction between the inhibitor Br^- and the activator $HBrO_2$ is fast. This figure was created by the authors based on the data of Ref. 75.

Recall that autocatalysis in the BZ reaction [the sum of reaction (6) and two reactions (12)] begins when the concentration of the inhibitor, Br^-, decreases below the critical value.[75, 86] The $HBrO_2$ molecule is an activator, while Br^- is an inhibitor of the BZ reaction. Due to the fact that molecular bromine is almost in equilibrium with Br^- [fast reactions (7) and (8)], Br_2 is also an inhibitor.

Instead of the widely used malonic acid, the main disadvantage of which is the release of carbon dioxide bubbles during the reaction, other compounds can be used as substrates for the BZ reaction, for example, pyrogallol,[87] as well as mixed substrates, which can be the resorcinol–methyl ketone [88] or oxalic acid–acetone [89] pairs.

For the sake of completeness, note that the BZ reaction can demonstrate chaotic oscillations,[90–92] birhythmicity,[84] stationary dissipative Turing patterns,[51] anti-waves,[52] packet waves [93] and others.[50, 86]

Like the BZ reaction in macro-volume, the BZ MO can be in an oscillatory state. An example of such BZ oscillations is shown in Fig. 3 for silica gel microspheres.[94] A silica gel microsphere (with a size of about 200 μm) (see Fig. 3 *a*) with the $Ru(bpy)_3^{2+}$ catalyst immobilized in it, being immersed in the BZC solution, periodically changes colour from orange to green and *vice versa*. Figure 3 *b* shows the space–time plot of oscillations, while Fig. 3 *c* presents the same oscillations, but in the form of the dependence of the light transmission intensity of the microsphere on time.

Approximately the same oscillations are obtained for BZ microspheres made of ion-exchange resin (Fig. 4) in an aqueous BZC solution.[95] Since the initial reactants come from the BZC solution into the BZ microsphere all the time, the oscillations continue for a very long time (tens of hours or more) without noticeable signs of a change in the amplitude,[94] which is convenient for creating networks of MOs with stable modes.

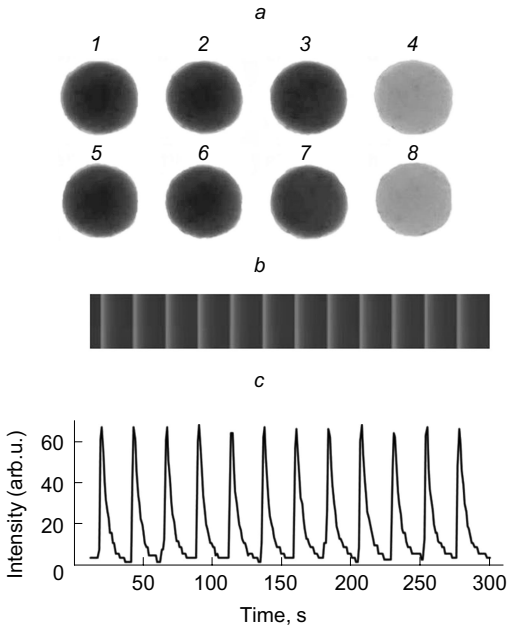


Figure 3. Oscillations of a BZ silica gel microsphere with a $Ru(bpy)_3^{2+}$ catalyst immobilized in it.[94] (*a*) Snapshots of the BZ microsphere taken with an interval of about 6 s, the period of oscillations is about 23.5 s, the diameter of the microsphere is 219 μm, $[Ru(bpy)_3^{2+}] = 3$ μmol g^{-1}. Concentrations of reactants in the BZC mixture (M): [MA] = 0.36, $[NaBrO_3] = 0.27$, [NaBr] = 0.07, and $[H_2SO_4] = 1.0$. (*b*) BZ oscillations of a microsphere presented in the form of a space – time plot. Light stripes correspond to the predominance of the oxidized form of the catalyst, and dark stripes correspond to the predominance of the reduced one. The recording was carried out through an interference filter with the maximum transmission at 450 nm, where $Ru(bpy)_3^{2+}$ has the maximum absorption. (*c*) The same oscillations as in panel (*b*), but presented as kinetics of the intensity of light transmitted through the microsphere. This figure is reproduced with permission from the American Chemical Society.

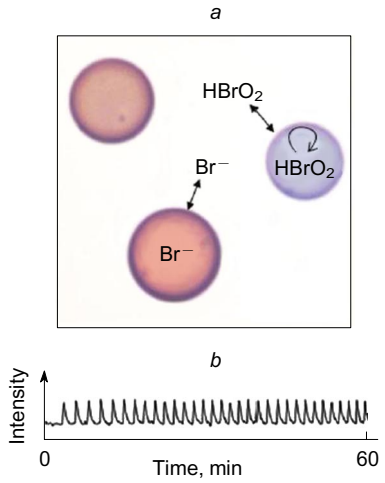


Figure 4. (*a*) Images of ion-exchange resin microspheres loaded with a catalyst (ferroin) of the BZ reaction in a BZC solution and (*b*) kinetics of BZ oscillations in the form of changes in the intensity of light transmitted through the microsphere.[95] The field of view is approximately 1 mm × 1 mm. In panel *b*, the reduced (oxidized) catalyst in microspheres is red (blue); a semicircular arrow in a blue microsphere symbolizes autocatalysis. Drawing is published with permission from the Royal Society of Chemistry.

3. Types of interactions and dynamic modes of BZ micro-oscillators

Before proceeding to a description of the methods for creating BZ MOs with the required properties, let us consider the types of interactions that are possible between chemical oscillators and possible patterns and dynamic modes to which these interactions lead. Note that if a macroreactor (with a linear size of about 1 centimetre or more) is intensively stirred, then its behaviour should be the same as dynamics of closed microreactor with the same reactant concentrations. Therefore, we will consider in this chapter some classical experiments on the study of dynamics of coupled macroreactors.

As we have already noted in the Introduction, the interaction of two chemical oscillators can be both local (diffusive type)[96] and of the long-range type, which is realized, for example, with the help of electrodes and wires,[97,98] or by mass exchange controlled by peristaltic pumps,[99–104] or by means of light pulses.[105,106] The following types of coupling are often used: excitatory and inhibitory, unidirectional and reciprocal, with and without delay. The synchronization of two BZ oscillators was first demonstrated experimentally in 1975.[107] Depending on the strength of coupling and differences in the initial frequencies of oscillators, such phenomena as synchronization of oscillators at a common frequency and synchronization at frequencies that are multiples of the common frequency were observed.

Using controllable mass exchange between two BZ oscillators, it was found (Fig. 5) that two oscillators can be in three stable states:[99] antiphase oscillations at a relatively low rate of mass exchange, in-phase oscillations at high rates of mass exchange, and a heterogeneous stationary state (SS), again at high rates of mass exchange, when the SSs in the two reactors are different, namely, the catalyst in one reactor is predominantly in the oxidized state, and in the other, predominantly in the reduced state. Bistability was also discovered, that is, the coexistence of two different dynamic modes at the same parameters.

In fact, this study[99] was an experimental proof of the previously obtained theoretical result,[108] according to

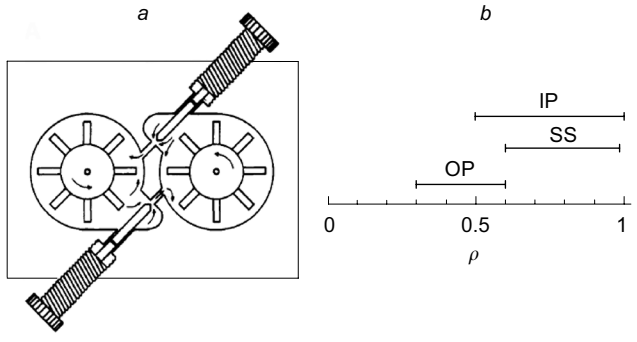


Figure 5. (*a*) Configurations of two BZ reactors coupled by mass exchange and (*b*) experimentally obtained diagram of the dependence of the stability of three dynamic modes, IP, SS, and OP, on the coupling strength ρ, where ρ is the ratio of the rate of mass transfer between reactors to the rate of supply of fresh reactants to the reactors;[99] IP, in-phase oscillations; SS, stationary heterogeneous state; OP, antiphase oscillations. This figure is reproduced with permission from the American Chemical Society.

which an inhomogeneous stationary state can occur in a system of two oscillators of any nature coupled by mass transfer which is proportional to the difference in the concentrations of the reactants in the reactors. This result looked pretty unexpected, since it was believed among chemists that diffusion between reactors should lead to an equalization or blurring of differences between different parts of the total system. Nevertheless, the ability of coupled oscillators to generate stable stationary dissipative patterns was already known by that time from theoretical works.[109, 110]

Since then, many theoretical and experimental works have appeared, the authors of which have investigated systems of coupled chemical oscillators (see reviews [29, 73, 111 – 116]). Among them, the studies on the coupling of only two chemical oscillators should be outlined, since they are the basis for the analysis and design of networks with a large number of oscillators.¶

Recently, more subtle methods than the mass exchange for reactor coupling have emerged. In these methods, only inhibitor molecules or only activator molecules act as information carriers between reactors. The most important innovation in the methods of the coupling of two oscillators was the introduction of pulse coupling with a delay, which, like a diffusion coupling, can be either of pure inhibitory or pure excitatory nature (Fig. 6).[105, 118, 119] This type of coupling mimics a synaptic connection between two neurons, in which two oscillators (or two neurons) do not exchange their material contents, but affect each other due to reagents (or neurotransmitters) stored in separate reservoirs (in the case of synapses, these reservoirs are vesicles). The time delay between a spike in one oscillator and the moment of time when it affects another oscillator is similar to the time it takes for an action potential to travel along an axon connecting two neurons.

For BZ MOs, such pulse coupling is realized *via* light pulses [when $Ru(bpy)_3^{2+}$ is used as a catalyst]. Two BZ MOs, being located close to each other, can interact through the diffusion of the intermediates of the BZ reaction as well.[120 – 122] For BZ micro-reactors, diffusive and pulse coupling are the two main types of coupling. Therefore, we will consider what dynamic modes they lead to.

Diffusive type of coupling between BZ MOs is realized most evidently for BZ micro-droplets obtained by the microfluidic method (Fig. 7).[96, 122 – 124] These micro-droplets, which are an aqueous BZ solution in a continuous oil phase, the so-called BZ droplets, are formed in a microfluidic chip when the aqueous phase is mixed with an immiscible liquid, oil. The size of BZ droplets can be varied in the range from several tens to hundreds of microns. An ensemble of BZ droplets (in both one-dimensional and two-dimensional configurations) is ideal for studying synchronous regimes of a large number of coupled MOs.[125]

Such BZ droplets (Fig. 8) are separated by an oil medium, in which mainly hydrophobic molecules and the inhibitor Br_2 can diffuse in the case of the BZ reaction. If only the inhibitor diffuses between the BZ droplets, then stationary Turing patterns emerge at a small length g of the gap between droplets (*i.e.*, when the coupling strength is large). Turing patterns in this case look like an inhomogeneous stationary state of the system with completely different values of the variables in the left and right droplets.[120] If the gap is large enough (but not excessively large), then high-amplitude in-phase relaxation oscillations can occur at symmetric excitation of the initial homogeneous stationary state. In this case, the gap of a moderate length plays the role of a time delay line, at which in-phase oscillations with a period depending on g are possible.

Turing patterns, antiphase oscillations in a capillary, complex oscillatory spatial patterns, as well as more com-

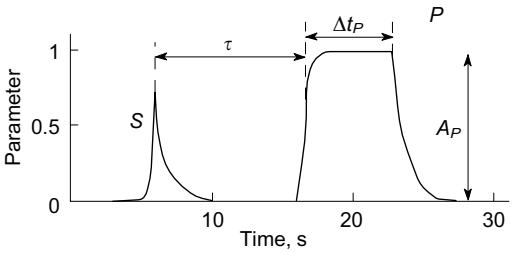


Figure 6. Scheme illustrating the emergence of pulse P after τ seconds since the emergence of spike S in reactor i. The variable S in the reactor i must reach a certain critical value for the emergence of pulse P. An almost rectangular pulse P is characterized by a duration Δt_p and an amplitude A_p. The drawing was created by the authors based on the data from Ref. 116.

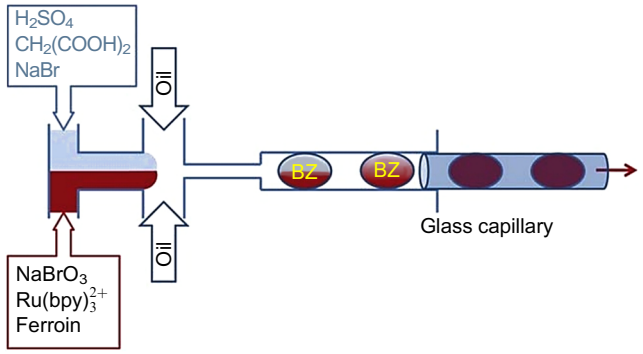


Figure 7. Scheme of a microfluidic droplet generator made of polydimethylsiloxane (PDMS).[124] On the left, two water streams are introduced into the droplet generator; blue and red streams which contain different reactants of the BZ solution. The streams mix and flow together through the central channel until they meet two perpendicular oil streams. Oil jets divide the water flow into portions that form BZ droplets in the nozzle. A glass capillary (inner diameter of 100 μm) is inserted into the PDMS chip a few millimetres downstream to collect BZ droplets. To stabilize the BZ droplets, a surfactant is added to the oil. The scheme is published with permission from the Royal Society of Chemistry.

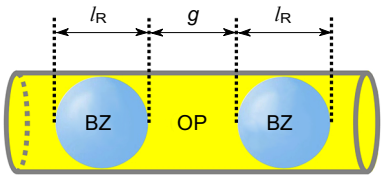


Figure 8. In the water droplets in the capillary, a hypothetical reaction proceeds which is described, for example, by the Brusselator or Oregonator model. The droplets are separated by the organic phase (OP). The length of the droplets is l_R, and the length of the gap between them is g. The drawing was created by the authors based on the data of Ref. 120.

¶ Note that the study of two coupled oscillators began with Christiaan Huygens, who described synchronous oscillations of two clock pendulums suspended side by side on a common wooden support.[117]

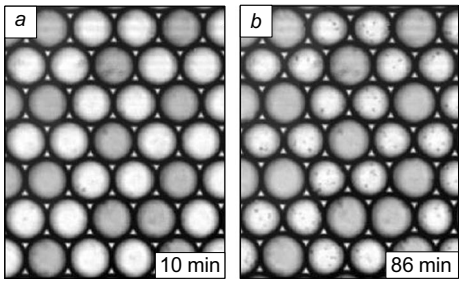


Figure 9. Hexagonal Turing patterns formed from BZ micro-droplets in the continuous oil phase (*a*) after 10 minutes and (*b*) after 86 minutes after mixing.[27] Over time, oxidized (light) droplets shrink, while reduced (dark) droplets swell. The initial droplet diameter is 66 μm. Initial concentrations of BZ reactants in droplets: [MA] = 0.2 M, [$NaBrO_3$] = 0.3 M, [H_2SO_4] = 0.08 M, [ferroin] = 3 mM, [$Ru(bpy)_3$] = 0.4 mM. Drawing is published with permission from Proceedings of the National Academy of Sciences USA.

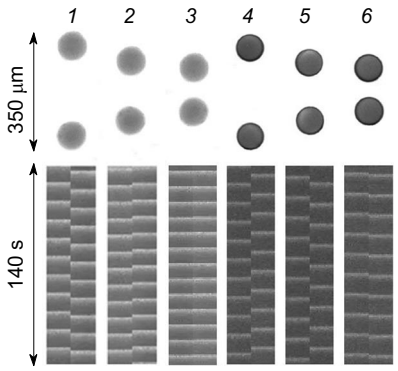


Figure 11. The emergence of in-phase synchronization when two BZ MOs with diffusive excitatory coupling approach each other; microspheres (*1–3*) are made of silica gel, while (*4–6*) are Dowex 50WX2 microspheres.[94] Microspheres *1*, *2*, *4*, and *5*, no synchronization; *3* and *6*, in-phase synchronization. The Figure is reproduced with permission from the American Chemical Society.

plex (hexagonal) Turing patterns in a plane were obtained (see Fig. 9) in large ensembles of BZ droplets.[27, 96, 123]

If BZ MOs made of solid microspheres with an immobilized catalyst and saturated with all BZ reactants are placed in the oil phase, then, like BZ micro-droplets, they give antiphase oscillations, as should be the case for purely inhibitory coupling.[94] An example of such oscillations in the form of space–time plots is shown in Fig. 10. Located initially at a large distance from each other, the BZ MOs are not synchronized and oscillate with slightly different periods and phase shift. However, as they approach each other, a diffusive inhibitory coupling begins to emerge between them, which leads to lengthening and aligning of the MO periods and ultimately leads to antiphase oscillations.

Purely excitatory or predominantly excitatory diffusive coupling between MOs leads to the in-phase oscillations. As an example of such oscillations, the dynamics of two identical BZ MOs of two types, silica gel microspheres and Dowex 50X2 cation exchanger, is presented in Fig. 11. BZ microspheres containing an immobilized catalyst are placed in an aqueous medium (BZC solution), which allows activator molecules ($HBrO_2$) to diffuse freely.[94] The oscillators are not synchronized initially, but when they approach each other, a sufficiently strong excitatory coupling arises between them, which equalizes the frequencies of the MO oscillations and ultimately leads to the in-phase oscillations.

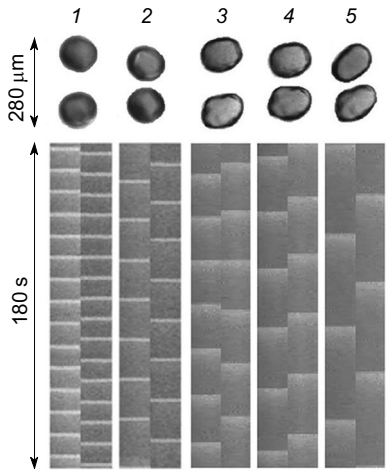


Figure 10. The emergence of antiphase synchronization when two BZ MOs with diffusive inhibitory coupling approach each other.[94] BZ MOs are obtained by immobilization of $Ru(bpy_3)^{2+}$ on silica gel microspheres. Microspheres *1*, *3*, and *4*, no synchronization; *2* and *5*, antiphase synchronization at a small gap. The Figure is reprinted with permission from the American Chemical Society.

Consider now the dynamic modes of two pulse-coupled BZ oscillators.[105, 126–128] In contrast to diffusion-coupled oscillators, a short-term effect of one oscillator on another one is brought about only by a spike in one of them (see Fig. 6). If the BZ reaction is in a stationary state, then there can be no pulse coupling between the oscillators. Qualitatively, we can say that the driving force of the pulse coupling is the excited state of the oscillator (spike), while for diffusive coupling, a state close to stationary state is more important, since the relaxation (spike) oscillator spends most of its time precisely near this state. These distinctions lead to the fact that the dynamic modes of two oscillators coupled by either pulse or diffusive coupling are qualitatively different, both in the case of excitatory and inhibitory coupling. Note also that pulse-coupled oscillators cannot generate Turing patterns.

Pulse coupling can be unidirectional, that is, asymmetrical, but for comparison with diffusive coupling, let us consider the case of two identical oscillators coupled by the same (symmetric) pulses. Diffusive inhibitory coupling leads to antiphase oscillations (see Fig. 10), while pulsed inhibitory coupling with a relatively long time delay τ leads to the in-phase oscillations.[105] The antiphase mode is also possible, but at relatively short times τ.

Diffusive excitatory coupling generates in-phase oscillations (see Fig. 11), while pulsed excitatory coupling at relatively long times τ causes fast antiphase oscillations. Almost in-phase oscillations are observed only at short times τ. The word 'almost' means that the time shift between the near in-phase spikes equals the delay time τ, which is, although small, but finite.

Examples of experimental setups for pulsed (long-range) coupling between oscillators can be found in a number of publications.[33, 105, 106, 128, 129]

BZ MOs based on vesicles, micro-droplets, and microspheres make it possible to create complex neural-like MO networks with both diffusive and pulse coupling.

4. Compartmentalization of BZ MOs in micro-droplets and liposomes

4.1. BZ micro-droplets

The development of the technique of mixing microflows in micro-channels (tens of microns in diameter) and advances in the field of nonlinear chemistry † gave rise to a method for creating BZ MOs in capillaries.[27, 96, 115, 124, 132] The scheme of the generator of BZ micro-droplets stabilized with surfactants in the organic phase is shown in Fig. 7. The surfactant prevents sticking and coalescence of micro-droplets dispersed in the organic phase. The droplet size is determined by the geometric characteristics of the device (chip) and the flow rates of the aqueous and organic phases.

BZ droplets formed at the junction of micro-channels can be stored for further studies in similar (100 – 200 μm in diameter) hydrophobic capillaries. In this case, a researcher investigates the dynamics of a one-dimensional ensemble of BZ droplets. However, droplets can also be collected in a plane in a 'flat capillary', forming a two-dimensional, usually hexagonal, arrangement of droplets.[123]

It was shown that the coupling between neighbouring BZ droplets separated by a hydrophobic medium is due to the diffusion of non-polar molecules, mainly Br_2. First, the experimental results were consistent with theoretical calculations for diffusive coupling through Br_2.[120] Second, when a Br_2 trap (for example, molecules with double bonds) was added to the organic phase, the coupling between the droplets was broken: the droplets began to oscillate independently of each other.[96]

For effective coupling, the gap between neighbouring BZ droplets should be so small that the characteristic diffusion time of the BZ reaction intermediates (Br_2) through it should be shorter than the period of the BZ oscillations.[115] It was also found that the strength of the inhibitory coupling between adjacent BZ droplets depends on the concentration of malonic acid (MA): the lower the [MA], the greater the coupling strength.[124] In all cases of using BZ droplets with a sufficiently large diameter (about 0.2 mm), antiphase oscillations were observed between neighbouring droplets. Stationary Turing patterns were formed at a small diameter of droplets (less than 0.1 mm), a low concentration of MA (less than 0.1 M), and at a narrow gap between droplets when droplets were almost touching.[96, 121]

In such a one-dimensional system of BZ micro-droplets separated by narrow hydrophobic gaps, propagating BZ waves and large clusters (in which BZ droplets oscillated in-phase) were also observed.[133] This occurred at an increased concentration of bromate and a decreased concentration of MA. Presumably, under such conditions, an excitatory coupling plays a significant role due to the diffusion of the activator $HBrO_2$, which can dissolve in the oil phase in small amounts (perfluorinated oil was used).

One of the disadvantages of BZ micro-droplets in a continuous hydrophobic medium is the impossibility (at present) of feeding BZ droplets with fresh BZ reactants. Consequently, this system is closed and can function only for a limited time (several hours).

4.2. BZ vesicles (liposomes)

Unlike BZ droplets, which are usually stabilized by a surfactant monolayer (simple emulsion) and are stable only in an organic hydrophobic medium, BZ liposomes are BZ drops surrounded by a bilayer phospholipid membrane. They are able to be in both the continuous oil and continuous aqueous phase, retaining their shape. The contents of liposomes are isolated from the external environment by a bilayer membrane.

It is known that the microfluidic method makes it possible to obtain a double emulsion, which is an emulsion with small droplets of some third liquid (water, for example) inside large droplets filled with another (medium) water-immiscible liquid; in its turn, large droplets are dispersed in an external continuous liquid (phase) immiscible with the middle liquid.[134] Using the technique of coaxial microfluidic mixing (Fig. 12), BZ liposomes surrounded by a double phospholipid bilayer were fabricated.[135]

Since it is always possible to modify a double bilayer with various additives, it is possible to change its permeability with respect to different intermediates of the BZ reaction.[136] This makes it possible to control the diffusive coupling between neighbouring BZ MOs. As a rule, BZ liposomes placed in a capillary or in a plane are in contact by their membranes. Therefore, diffusive mass exchange proceeds through two adjacent bilayers. In this case, the wave propagation along the contacts between the BZ MOs is observed, which indicates the excitatory nature of the coupling due to diffusion of $HBrO_2$.

Interesting results were obtained using liposomes dispersed in the organic phase and containing a BZ solution.[43] Liposomes were formed using a microfluidic generator (Fig. 13). The liposome shells were composed of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) and modified with various additives. For example, myristic acid, posi-

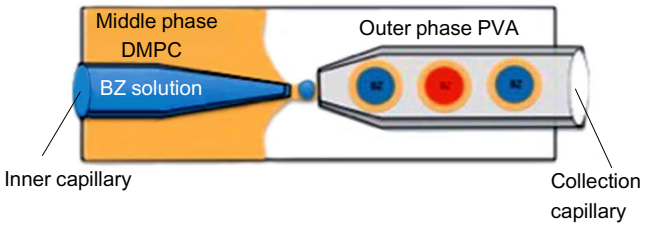


Figure 12. Scheme of a coaxial microfluidic generator of BZ liposomes.[135] BZ solution from the inner capillary is dispersed in the form of droplets into the middle phase, consisting of a solution of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) in a mixture of chloroform and cyclohexane, and from it into the outer phase, consisting of an aqueous solution of polyvinyl alcohol (PVA). Then, the obtained BZ liposomes are collected in a collection capillary of a larger diameter. This process affords liposomes containing a BZ solution inside. This BZ solution is separated from the external aqueous medium by a bilayer membrane. The Figure is reproduced with permission from the Royal Society of Chemistry.

† The technique of microflow mixing in microchannels was developed at Harvard University in the group of Professor Whitesides.[130] A great contribution to the development of nonlinear chemistry was made by the group led by Professor I.R.Epstein from Brandeis University.[29, 131] The fact that these two universities are close to each other in Boston, and the professors communicate with each other, had a beneficial effect on the development of studies of BZ MOs in capillaries.

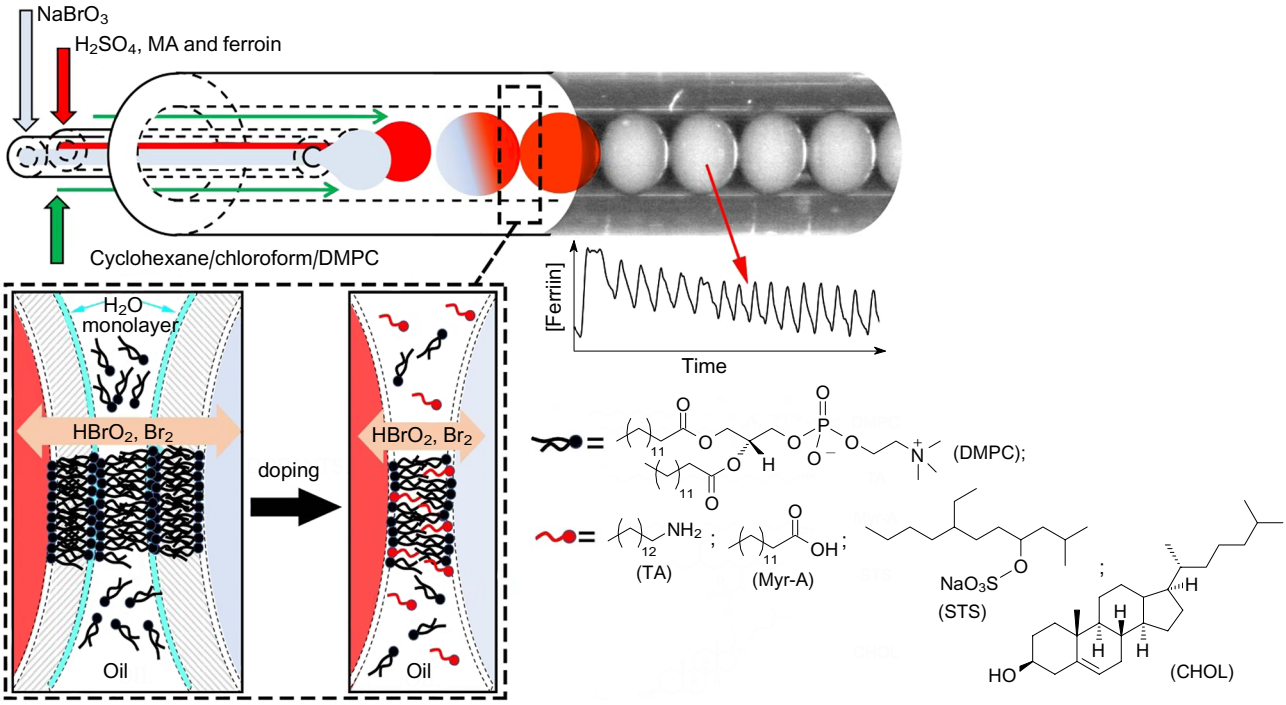


Figure 13. Scheme of a microfluidic device used to create arrays of droplets (loaded with components of the oscillatory BZ reaction) with multi- and monolayer shells (in the upper part of the Figure); structure of a multilayer (multilamellar) membrane of a BZ droplet obtained using pure DMPC and a monolayer (monolamellar) membrane of a droplet obtained using DMPC with additives (in the lower part of the Figure).[43] The droplets are dispersed in the organic phase. On the right, there is kinetics of oscillations of the BZ reaction inside the drop and the formulae of additives for modifying the membrane. Designations: TA, tetradecylamine; Myr-A, myristic acid; STS, sodium tetradecyl sulfate (sodium 2-methyl-7-ethyl-4-undecyl sulfate); CHOL, cholesterol. The Figure is published with permission from the American Chemical Society.

tively charged tetradecylamine, and negatively charged tetradecyl sulfate in the form of sodium salt were used as additives. These substances have the same hydrophobic tail R ($R = C_{14}H_{29}$) as DMPC, but different polar heads. Cholesterol has also been studied as an additive. When using pure DMPC, the liposomes had a multilayer (multilamellar) membrane and were in contact with each other by lipid multilayers (see Fig. 13 bottom left). These liposomes showed a weak inhibitory coupling, leading to the formation of two populations of liposomes with different oscillation periods, T_1 and T_2. Over time, the T_1/T_2 ratio tended to two, with neighbouring liposomes alternately falling into one or another population.

The addition of myristic acid or positively charged tetradecylamine led to the formation of liposomes with an oligolamellar membrane. These liposomes also showed a weak inhibitory coupling and formed two populations of liposomes with different oscillation periods. However, the addition of tetradecyl sulfate resulted in droplets with a monolamellar (single-layer) membrane. These liposomes exhibited strong inhibitory coupling and synchronized out of phase like usual BZ droplets (see Section 4.1). When cholesterol was used as an additive, the coupling between liposomes was not observed due to the reaction of bromine molecules with cholesterol; recall that Br_2 molecules are carriers of the inhibitory interaction.

Thus, by changing the physicochemical properties of BZ liposome membranes, it is possible to change the type of molecules diffusing through the membrane and, consequently, the strength and type of coupling, which makes it possible to control the collective behaviour of these BZ MO.

BZ liposomes[132] are used in neural-like networks to solve certain mathematical problems, for example, to perform simple logical operations, or more complex tasks such as pattern recognition.[42, 68, 69] Theoretical problems of pattern recognition using MO networks are being solved in the group of Professor J.Gorecki.[63, 69, 137, 138]

The use of liquid-based BZ MOs has proven to be an important and versatile method for modelling neural-like networks. The chemicals responsible for coupling in these systems are mainly inhibitor Br_2 and activator $HBrO_2$. Membranes can determine a dominant type of coupling or act as special traps for carrier molecules, which allows fine tuning of the general dynamic properties of chemical MO networks, while the size, composition, and structure of liquid BZ MOs can be fine-tuned using microfluidic devices. However, the problem of the feeding of such MOs with fresh BZ reactants still needs to be solved.

5. BZ MOs based on organic polymer microspheres

5.1. Polymeric gels

Usually convection is observed when the BZ reaction proceeds in purely aqueous solutions (due to evaporation from the surface or due to CO_2 bubbles). This hydrodynamic effect perturbs the dissipative structures formed during the BZ reaction and leads to their complication.[139] Since hydrodynamic convection within gels is suppressed, the gels began to be used to conduct precision experiments to study BZ waves. As a rule, the BZ reaction catalyst is immobilized in a gel, after which such a gel can be stored for

a long time in a chemically inert medium. When it is immersed in a BZC solution, BZ oscillations or waves emerge in the gel.

Recall that 'a gel is a solid consisting of at least two components, one of which (polymer) forms a three-dimensional network due to covalent bonds or non-covalent interactions (chemical and physical gels, respectively). This 3D network is in the environment of another component, which is a liquid, and the amount of the latter is at least sufficient to ensure the elastic properties of the gel, but can exceed the amount of polymer by tens or hundreds of times'.[140] Such gels are capable of absorbing and retaining a significant amount of an aqueous BZ solution. Theoretical studies of the characteristics of gels and the principle of their swelling in aqueous solutions, based on thermodynamics, were carried out in the mid-20th century[141] and were intensively continued after the works of Shibayama and Tanaka.[142]

For the first time, the catalyst of the BZ reaction, ferroin, was immobilized on a colloidal film, in which BZ waves appeared when it was immersed in a BZC solution.[143] Since then, different types of gels have been tried to immobilize BZ reaction catalysts: organic polymer gels and inorganic silica gels.[139] In both cases, sorption (immobilization) of the BZ reaction catalyst molecules, for example, ferroin or $Ru(bpy)_3^{2+}$, in the gel took place. Thus, the immobilization of ferroin derivatives [for example, iron(II) tris(bathophenanthroline disulfonate)complex] on polyacrylamide, partially cross-linked with *N*,*N*′-methylenebis(acrylamide), led to the formation of a gel with a catalyst concentration of 1 mmol L^{-1}, which is sufficient for monitoring waves in a thin layer of the gel. However, ferroin immobilized in gels that do not contain charged functional groups, such as polyacrylamide gel, is washed out with time.[144]

5.2. Polymer microspheres

Ferroin and Ru $(bpy)_3^{2+}$ complex were successfully immobilized on ion-exchange resins made of a polystyrene matrix containing strongly acidic sulfo groups.[45, 56, 145 – 149] Before proceeding directly to resin microspheres, let us briefly describe the basic properties of these resins, which can affect the efficiency and duration of retention (immobilization) of catalyst molecules on the resin under conditions of the BZ reaction.

A systematic description of ion-exchange resins and their classification are presented in a number of works.[150 – 153] As a rule, ion-exchange resins used for fabrication of BZ MOs are made of cross-linked copolymers of polystyrene and divinylbenzene containing ion-exchange functional groups (Structure **1**).[154 – 156] Ion exchange resins are generally classified[155] into four main groups:‡

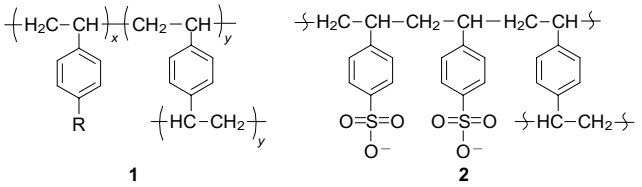
(*a*) strongly acidic cation exchangers (for example, Dowex 50WX2) containing strongly dissociated acidic groups, for example, sulfonic acid groups ($R = SO_3H$);

(*b*) weakly acidic cation exchangers containing weakly dissociated acidic groups, for example, carboxyl groups ($R = CO_2Na$);

(*c*) strongly basic anion exchangers containing strongly basic groups, for example, quaternary ammonium groups ($R = NR'_3Cl$);

‡ There are other types of ion exchange resins, but they are usually not used to immobilize BZ catalysts.

Structures 1, 2



(*d*) weakly basic anion exchangers containing weakly basic groups, for example, ammonium ones ($R = NH_3OH$).

Cross-linking of polystyrene with divinylbenzene (usually from 0.5 to 20%) affects the porosity of the resulting ion exchange resin.[157] Depending on the structure of the polymer framework, ion-exchange resins are subdivided into gel, macroporous, and isoporous resins.[150,156] There are no pores in gel resins, so they are capable of ion exchange only after swelling, that is, when solvent molecules have penetrated between polymer units. Macroporous resins have through- and dead-end pores of different sizes, swell little, but they are very active in sorption and exchange reactions due to the initially developed pore surface. Isoporous resins have pores of more or less the same size. Porosity affects such resin properties as swelling, capacity, and selectivity. Resins with a low content of cross-links have a gel structure, while those with a high content have a macroporous structure. Typically, the lower the cross-linking percentage, the higher the moisture content, ion exchange capacity (typically 1.5 to 10 mEq per gram on dry basis) and the ability to adsorb large ions.

Since the catalysts of the BZ reaction are mainly positively charged metal ions or metal complex cations, they are immobilized using cation exchangers with negatively charged functional groups (Structure **2**). Attempts have been made to immobilize negatively charged iron(II) tris(bathophenatroline disulfonate) complexes on an anion exchanger.[139] However, since only 0.9% of the total positive charge on the anion resin was used to immobilize the catalyst, the resin retained a high positive charge density and the immobilized catalyst was surrounded by positively charged groups. Anions of the BZ solution, such as Br^- and BrO_3^-, concentrated near the catalyst, while the protons were repelled from it. As a result, an electric double layer was formed at the resin surface, and such a gel required a significantly higher concentration of protons in the BZ mixture in order to have the same BZ dynamics as neutral gels. This fact, as well as the lower prevalence of negatively charged metal complexes catalyzing the BZ reaction, led to the predominant use of cation exchangers for the immobilization of the BZ catalysts.

Dowex 50, made of a gel-like macroporous strongly acidic cation exchange resin with high mechanical durability, is widely used for immobilization of BZ reaction catalyst molecules. Typically, this resin is produced in the form of microspheres with diameters ranging from several tens to several hundred micrometers. Dowex 50 resin is based on a polystyrene – divinylbenzene matrix containing sulfonic acid groups, which can firmly hold metal cations and their complexes.[158] Depending on the method of fabrication, Dowex 50 resins (WX2, WX4, and WX8) can differ in granule size, swelling capacity and exchange capacity, while all the types of Dowex 50 maintain the ability to retain BZ catalysts.

Dowex 50 microspheres containing ferroin [45, 147, 159, 160] or tris(2,2′-bipyridyl)ruthenium(II) complexes,[161] and also their derivatives [for example, tris(4,4′-dimethyl-2,2′-bipyridyl) ruthenium(II)] [25] are especially popular as BZ MOs. This resin is characterized by an excellent ability to firmly hold large metal complex cations. Depending on the size of the BZ microspheres and the composition of the BZ mixture, homogeneous regular oscillations, irregular wave behaviour, and the propagation of regular BZ waves on the surface of Dowex 50WX4 microspheres were observed when the microspheres were immersed in a BZC solution.[56,145]

Since each single BZ microsphere of a sufficiently small size can be considered as a BZ MO, an ensemble of such BZ MOs allows one to study the collective behaviour of micro-oscillators. In the population of BZ MOs based on ion-exchange resins, collective modes such as global [162] and cluster synchronization [160, 163, 164] were observed, as well as stochastic synchronization, which implies statistical phase matching of the oscillators due to the presence of an overall noise signal.[165] The collective response of BZ MOs with an increase in their concentration, an effect called 'quorum sensing', has been extensively studied.[166, 167] The 'chimera' mode, in which part of the BZ MOs is synchronized in phase (one in-phase cluster) and the remaining oscillators behave chaotically, has become very famous.[168, 169] Note that the chimera regime arises in a system where all oscillators are identical and the coupling between them is the same (described by the same equations).[168, 169]

In large populations of BZ MOs, two types of transitions to the 'quorum sensing' state are found:[38]

(*a*) gradual synchronization of oscillations in the population of BZ MOs;

(*b*) threshold switching on of the in-phase oscillatory mode.

Despite the numerous advantages of BZ microspheres based on ion-exchange resins, they also have disadvantages. First, since the sorption of positively charged catalyst molecules on the SO_3^- groups of microspheres occurs due to electrostatic forces, then in the case when such BZ MOs are immersed in a BZC solution with a pH below 1, positively charged protons can replace positively charged catalyst molecules in the microsphere, which leads to the washing out of the catalyst into the BZC solution. Using $Ru(bpy)_3^{2+}$ as an example, it was shown that the rate of its washing out from microspheres directly correlated with the acid concentration in the BZC solution.[94]

Second, the diffusive interaction between Dowex 50W microspheres bearing an immobilized catalyst of the BZ reaction is predominantly of an excitatory type in an aqueous medium, which leads to the in-phase synchronization between the BZ MOs. Inhibitory diffusive coupling between these BZ microspheres was not found in an aqueous medium. If Dowex 50WX2 BZ microspheres are removed from the aqueous BZC solution and placed in an organic or organofluorine medium, then the BZ oscillations damp quickly.

Finally, Dowex microspheres are not always chemically stable under BZ conditions. The effect of strong oxidants and acids (as in the BZ reaction) on an ion-exchange resin can lead to its destruction due to oxidation reactions and rupture of cross-links between polymer chains.[170–172] Since chlorine has a destructive effect on the resin and shortens its service life,[172] it is reasonable to assume that the bromine formed during the BZ reaction can also destroy MO based on ion-exchange resins.

6. BZ Micro-oscillators based on inorganic polymer microspheres

6.1. Silica gels

The first inorganic materials resistant to the action of the BZ medium that began to be used for the immobilization of the catalyst of the BZ reaction were thin layers of silica gel.[139, 173] A layer of silica gel with an immobilized catalyst was immersed into a BZC solution, from which fresh BZ reactants diffused into the silica gel, thus initiating a BZ reaction.

Optically transparent SiO_2 hydrogels with immobilized metal complexes are inert matrices for BZ reactants. The diffusion coefficients of low molecular weight substances in silica gels with low silicon dioxide content are comparable to their diffusion coefficients in pure solutions.[174] However, the density of silica gel is important for the speed of the BZ wave propagation: an increase in the concentration of silicate from 6.2% to 12.4% leads to a decrease in the speed of the BZ waves by approximately 1.5 times.[175] With the help of scanning electron microscopy, it was found that the structure of the diluted gel can be characterized as a loosely bound three-dimensional network with pore sizes up to 0.15 μm, while in denser gels, microscopic structures are not a network, but rather a compact aggregation of particles without visible pores.[175]

Probably a 6.2% silicate gel is the best matrix for the BZ reaction. The BZ solution is sufficiently well retained in the pores of such a gel, and chemical reactions and diffusion proceed without any significant interaction with the structure of the gel. In denser silica gels, the microstructure is heterogeneous, and in some areas of the gel, small molecules are able to pass the silicate structure better than in others, that is, diffusion is not uniform. Such gels are not suitable as matrices for the BZ reaction, but, possibly, they can be used for special studies on the formation of inhomogeneous structures.

Besides the case of BZ SiO_2 microspheres and the case of a thin layer of SiO_2 with a homogeneously immobilized catalyst, there is a case when a network of BZ oscillators was obtained by dropping a ferroin solution in the form of

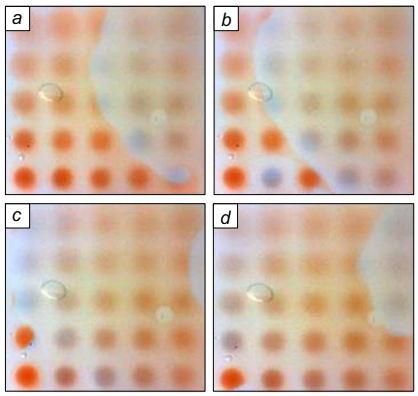


Figure 14. Silica gel matrix with ferroin spots immobilized on it immersed in a BZC solution.[176] Panels *a*–*d* demonstrate the propagation of BZ waves for four successive points of time separated by an interval of 112.5 s. To avoid boundary effects, the distance to the boundaries of the Petri dish from the extreme ferroin spots is made larger than the size of the entire array of spots. The image is reproduced with permission from the American Physical Society.

small spots on a flat layer of silica gel containing a copolymer of 4-styrenesulfonic and maleic acids as a catalyst retention additive (Fig. 14).[176] Spots with a diameter of about 0.9 mm were formed in such a way that a square lattice with a size of 5×5 spots was obtained. The distance between the spots varied from 0.2 mm to 1.4 mm. The diffusive coupling between the spots was of excitatory type. According to the theory, nothing but propagating waves or synchronous oscillations should exist in such a system. However, with a weak diffusive coupling, which is achieved by increasing the distance between the spots to values of more than 1 mm, the complex oscillatory modes are also observed. Note that the blue waves in Fig. 14 in places where there are no spots of the ferroin indicate that ferroin is washed out from these spots into the silica gel layer, which further enhances the excitatory coupling (but already due to waves, not diffusion) between the spots.

Monodisperse BZ SiO_2 microspheres with a catalyst immobilized in them (Fig. 15 *a*,*b*) were synthesized in a microfluidic droplet generator by first mixing solutions of sodium metasilicate, acids, and catalyst and then dispersing the resulting mixture (sol) in the fluorinated oil.[94] The synthesis of microspheres without the use of microfluidic technique, that is, by simple dispersion of a similar sol of silicic acid in the organofluorine phase, led to the production of polydispersed BZ SiO_2 microspheres (see Fig. 15 *c*). By varying the composition of silica gel, it was possible to achieve satisfactory retention (immobilization) of the catalyst inside the BZ microspheres, which made it possible to use the latter as BZ MOs in a BZC solution, where they exhibited oscillations for several hours. The dependence of the oscillation period (T, s) on the diameter of the microspheres (d, μm) is as follows:

$$T = 0.069\,d \qquad (22)$$

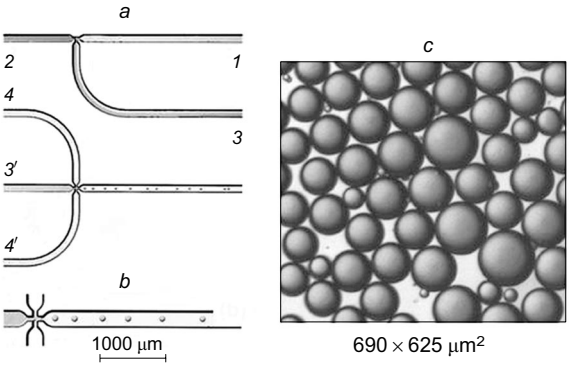


Figure 15. (*a*) General scheme for the formation of monodisperse silica gel microspheres in a microfluidic droplet generator, (*b*) enlarged snapshot of the crosshair of the droplet generator and the monodisperse droplets formed therein.[94] The sodium metasilicate solution in channel *1* is mixed with the solution in channel *2*, which contains acid and $Ru(bpy)_3^{2+}$; the sol obtained in channel *3* (channel *3* is a continuation of channel *3*) is directed into the crosshair of the droplet generator, where it is dispersed in the perfluorinated oil coming from channels *4* and *4* (the oil contains fluorinated surfactant). After a while, silica gel microspheres with an immobilized catalyst are formed in the droplets. (*c*) Snapshot of polydisperse silica gel microspheres with immobilized $Ru(bpy)_3^{2+}$ obtained by conventional shaking of the sol in perfluorinated oil.[94] The figure is reproduced with permission from the American Chemical Society.

In aqueous BZC solutions, a diffusive excitatory coupling between BZ SiO_2 microspheres is established, which leads to the in-phase synchronization of oscillations in these microspheres.[94] In addition, BZ SiO_2 microspheres are able to exhibit oscillations in the hydrophobic phase (in organic oils). After the SiO_2 microspheres were impregnated with the components of the BZ reaction and immersed in the organic phase, they showed oscillations for 3 hours. In the hydrophobic phase, an inhibitory diffusive coupling between SiO_2 microspheres is established, which leads to antiphase synchronization of their oscillations.[94]

6.2. Mesoporous glass

Information about attempts to develop a BZ MOs based on mesoporous glasses has not been found in the literature, but, nevertheless, we present here a brief description of such glasses as interesting materials suitable for the propagation of chemical waves in them, including anisotropic propagation and, hence, media in which computing processes of ChC could take place, including those characterized by massive parallelism.[177]

Mesoporous glass is a glassy porous material with a spongy structure obtained as a result of thermal and chemical treatment of glasses of a special composition. Usually, for the production of porous glasses, alkaline borosilicate glasses are used, in which one of the phases is capable of through washing out when exposed to alkali or acid. Due to the extensive surface, mesoporous glasses are capable of absorbing many substances including catalysts for the BZ reaction. For example, Vycor 7930 glass (trade name Corning) has a porosity of about 28%, an average pore diameter of 4 to 6 nm, and a surface area of 90 to 200 $m^2\ g^{-1}$,[178] which makes it possible to efficiently adsorb BZ reaction catalysts.

Amemiya *et al.*[179] immobilized the catalyst $[Ru(bpy)_3^{2+}]$ on Vycor 7930 mesoporous glass with a thickness of about 1 mm by keeping it in a catalyst solution. Then this glass was placed into a BZC solution. The velocity of the chemical waves arising in the glass was equal to about a third of that in aqueous systems. However, with this immobilization method, it was difficult to determine the actual concentration of $Ru(bpy)_3^{2+}$ in the glass, since the catalyst was adsorbed on the glass non uniformly.

Anisotropic mesoporous glass with a pore diameter of 30 nm with immobilized ferroin was obtained by mechanical stretching of a heated initial borosilicate glass with subsequent treatment.[180] The chemical waves arising when it was placed in a BZC solution were also anisotropic, which manifested itself in unusual wave profiles that differed from the usual profiles in isotropic mesoporous glasses. The anisotropy of the wave profile is explained by the different diffusion coefficients of the activator $HBrO_2$ along the X and Y (and, probably, Z) axes in the anisotropic glass.

Mesoporous glasses with immobilized ferroin have found application as elements of a chemical diode, a device demonstrating the unidirectional propagation of chemical waves.[177] The unidirectional chemical waves at their propagation from plate to plate were observed when the plates were located so that the corner of one plate was close to the flat side of the other plate, and there was a necessary gap between the plates.

6.3. Aluminosilicates

As sorbents for the immobilization of the catalyst of the BZ reaction, it is possible to use aluminosilicates (clays), which exhibit cation exchange properties [181, 182] and, therefore, can retain cations of metal complexes. Clay particles have a very small size of the order of 1 to 2 μm, which is on the border between nano and micro scales. This makes it possible to form agglomerates of various size clay particles with an immobilized catalyst and to study them as objects for studying cooperative phenomena in networks of BZ MOs.[183] Thus ferroin was immobilized on particles of kaolinite and montmorillonite, clays with different sorption and cation exchange properties.[183] Among many different types of clays, only kaolinite proved to be stable in the BZ medium (containing a strong acid and an oxidizing agent). Other clays (montmorillonites) showed a short service life in the BZ environment, although they demonstrated catalytic properties.

The resulting clay particles with an immobilized catalyst were used to create a small MO network in a plane (Fig. 16). The elements of this network were not single sub-micron clay particles, but their millimetre-sized agglomerates immersed in the BZC solution. With an increase in the stirring rate of the BZC solution, the degree of in-phase synchronization of the network elements also increased,[183] as it should be in the case of the excitatory coupling. Isolated sub-micron clay particles should not exhibit oscillatory dynamics due to a very high rate of mass exchange with the BZC solution.

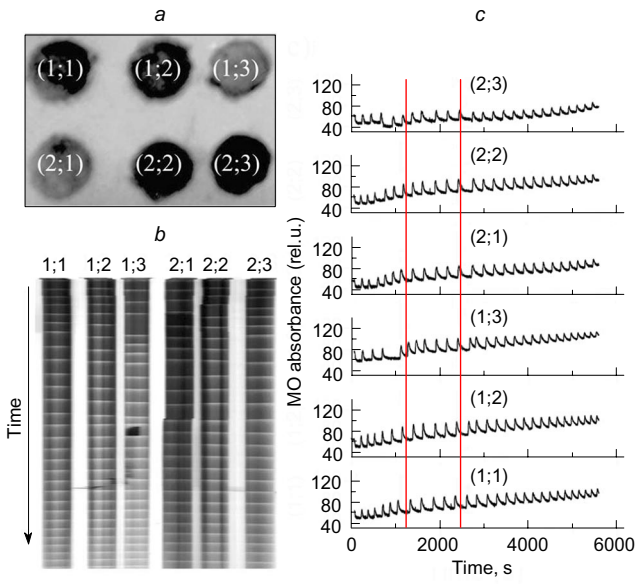


Figure 16. Behaviour of a network of six MOs in which single oscillators are coupled through a BZC solution.[183] The coupling is of purely diffusive type in the absence of stirring and of diffusive-global type at a moderate stirring rate. (*a*) Arrangement of six network elements (*i*; *j*); each element is a hole with a diameter of 1 mm, filled with 'clay' with immobilized ferroin, with the 'clay' particles being no more than 2 μm in size. Oscillators (1;3) and (2;1) are in the oxidized state, the rest are in the reduced state. (*b*) Space – time plot of each element of the network, the total time is 5500 s. (*c*) Time series of oscillatory dynamics for each element obtained from the space – time plot. The vertical red lines indicate the points of time at which the stirring rate changed from zero to low stirring rate (left line) and finally to high stirring rate (right line). The Figure is reproduced with permission from the American Chemical Society.

7. BZ MOs based on self-oscillating gels

7.1. Self-oscillating BZ gels obtained by sorption of the catalyst on gel materials

Interesting results were obtained by Russian scientists,[36, 37] who synthesized composite gels of polyacrylamide and silica gel and also gels based on a copolymer of acrylamide and sodium acrylate. After absorption of ferroin, such gels exhibited periodic colour changes and chemical-mechanical oscillations when immersed in a BZC solution. It was shown that the redox transitions of the catalyst lead to oscillations in the bulk of the gel if the diameter of a sample of this gel exceeds a certain threshold value ($\sim 0.7-0.95$ mm). It was also found that the period of chemical oscillations of the gel particles increases with decreasing their size (particles with a size from 0.6 mm to 2 mm were studied).

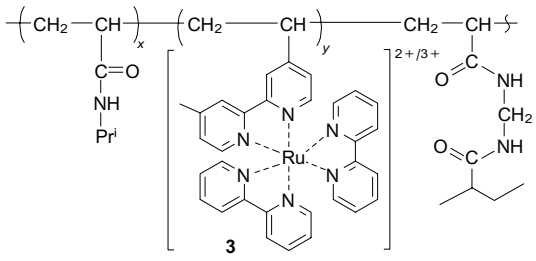
The authors compared the degree of swelling of the polymer gel in equilibrium states in which the catalyst is either in oxidized or reduced form at the same acidity of the medium and proposed the mechanism for chemical-mechanical oscillations. According to this mechanism, the oscillations are the result of the reversible formation of additional bonds between the negatively charged components of the gel (possibly SiO for one gel or COO for another gel) and the catalyst during the redox transformations of the latter.

7.2. Self-oscillating BZ gels obtained by covalent bonding of a catalyst to polymers

The use of the BZ MOs obtained by sorption of the catalyst of the BZ reaction on polymer materials (microspheres, for example) has one, but a significant drawback: the immobilized catalyst is washed out from the microspheres immersed in a strongly acidic BZC solution.[37, 94] This disadvantage was overcome by creating a gel in which the catalyst was covalently linked to the polymer network. This was achieved by copolymerization of a complex of bis(2,2′-bipyridine)(4-vinyl-4′-methyl-2,2′-bipyridine)ruthenium(II) with *N*-isopropylacrylamide and *N*,*N*′-methylenebis(acrylamide) (Structure **3**).[184, 185] In an aqueous medium, the resulting gel formed an analogue of polyisopropylacrylamide (PNIPAAm) gel, a thermosensitive polymer that was first synthesized in the 1950s.[186] *N*-Isopropylacrylamide copolymerized with *N*,*N*′-methylenebis(acrylamide) forms a three-dimensional (PNIPAAm) gel, which, when heated in water above 32 °C, undergoes a reversible phase transition from a swollen hydrated state to a tightly compressed dehydrated state, losing about 90% of its volume.

In contrast to the PNIPAAm gel, which responds to temperature change, synthesized gel **3** changed its volume in response to changes in the oxidized (reduced) state of the

Structure 3



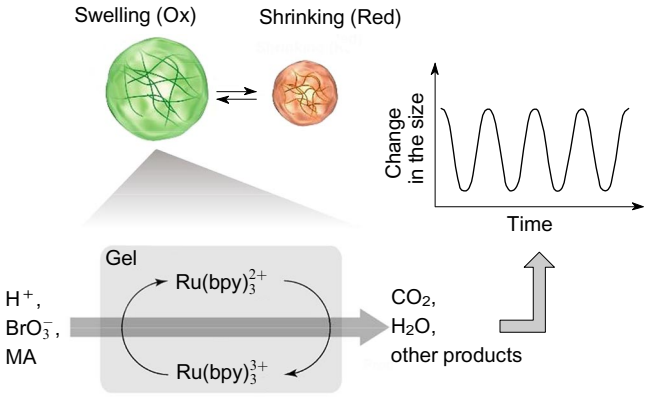


Figure 17. Scheme of self-oscillations of gel **3** and time dependence of the change in its size during swelling and shrinking as the catalyst is converted from the reduced to the oxidized state in the BZC solution.[185] A gel bead placed in a BZC solution periodically swells and shrinks during the transition of the catalyst from the oxidized state (Ox) to the reduced state (Red). During the reaction, the gel consumes malonic acid and bromate from the BZC solution, emitting the reaction products into the solution. The drawing is published with permission from the Royal Society of Chemistry.

metal complex, but now at a constant temperature. When immersed in the BZC solution, the gel periodically changed its volume, expanding during the oxidation of Ru $(bpy)_3^{2+}$ and shrinking during the reduction of Ru $(bpy)_3^{2+}$ (Fig. 17), *i.e.*, it showed chemomechanical oscillations.

Due to the redox transitions of the metal complex embedded in the polymer chain, the degree of gel swelling changes, since the hydrophilicity of the polymer chains increases upon oxidation and decreases upon reduction of the metal complex.[187] As a result, the gel which has received the name 'self-oscillating gel'§ exhibits autonomous 'expansion – contraction' oscillations under constant environmental conditions.[188]

Modification of self-oscillating BZ gels based on ruthenium complexes proceeds in many directions. For example, an increase in the degree of swelling of gel **3** was achieved by introducing 2-acrylamido-2′-methylpropanesulfonic acid into its structure.[189, 190] As a result, gel **4** was obtained, which changed its thickness by 10% when immersed in the BZC solution; such change in thickness is about 10 times greater than that for a gel with a homogeneous network structure.[190] The increase in the degree of swelling is due to the microphase-separated structure of the obtained gel, that is, the structure containing spontaneously formed micro- and nanoscale regions with a predominant content of domains of only one type. When such a gel is immersed in the BZC solution, chemical BZ waves emerge in it leading to a significant peristaltic movement of the gel fragments. Note that the linear size of the gel in this case must greatly exceed 1 mm.

The behaviour of such copolymers in the BZC solution (that is, under conditions when the redox state of the catalyst changes) depends on their structure and size. In the case of an uncross-linked linear copolymer containing metal complex BZ catalyst, periodic changes in the transparency and viscosity of the entire mixture of the BZC solution and copolymer are observed. These changes are due to spontaneous cyclic transitions of the copolymer between soluble and insoluble forms (Fig. 18).[20, 187]

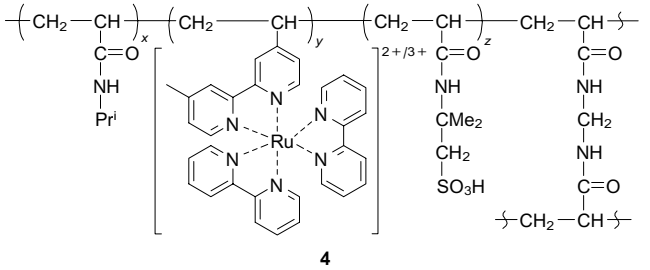
In the case of incorporation of the BZ catalyst into a cross-linked copolymer with a network structure (for example, gel **3**), periodic oscillations of the size (volume) of the gel pieces occur if these pieces are sufficiently small (less than 1 mm). If the gel has the form of elongated pieces of a centimetre length, then BZ waves emerge in it and, accordingly, the regions of the oxidized and reduced states of the catalyst coexist; these regions differ in the degree of swelling. This gives rise to peristalsis-like contractions of the gel (this feature is inherent in gel **4**). In other words, if the size of the gel is larger than the chemical wavelength, then spatial heterogeneities arise in it, which spontaneously propagate, leading to peristalsis-like movements of the gel.[191, 192]

If the size of a piece of the BZ gel is much smaller than the BZ wavelength (usually several millimetres), then redox changes occur homogeneously in the gel without the formation of spatial heterogeneities.[193] It was also found that the oscillation period increases (2.3-fold) with a decrease in the diameter of cylindrical gel pieces from 1.88 mm to 0.65 mm.[194 – 196] The authors attribute this phenomenon to an increase in the rate of washing out of bromomalonic acid.

Further modification of self-oscillating gels has led to the creation of copolymer **5**, in which all substrates of the BZ reaction, except for malonic acid, were included in the polymer chain.[197] The synthesized copolymer contains both pH control centres (SO_3^- groups) and sites with tetraalkylammonium groups which bind the oxidizing agent BrO_3^- by ionic bonds. A solution of this polymer periodically changed its optical properties with the addition of only one reactant of the BZ reaction, malonic acid.

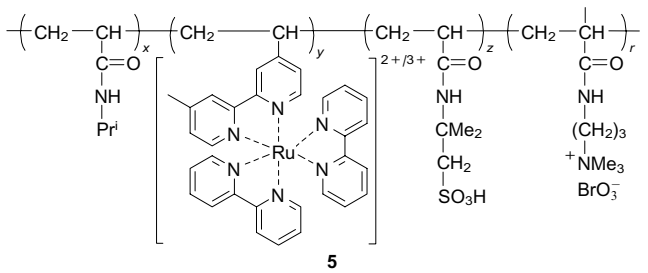
Subsequently, comb-type self-oscillating gel **6** was synthesized.[198] The term 'comb' means that the polymer matrix of the gel contains side polymer chains with free movable ends grafted to the main polymer network. In contrast to the usual type of self-oscillating gels, in which $Ru(bpy)_3^{2+}$ is immobilized only on the main chains, gels with a comb-type

Structure 4



4

Structure 5



5

§ BZ gels with similar properties are sometimes called Yoshida gels.

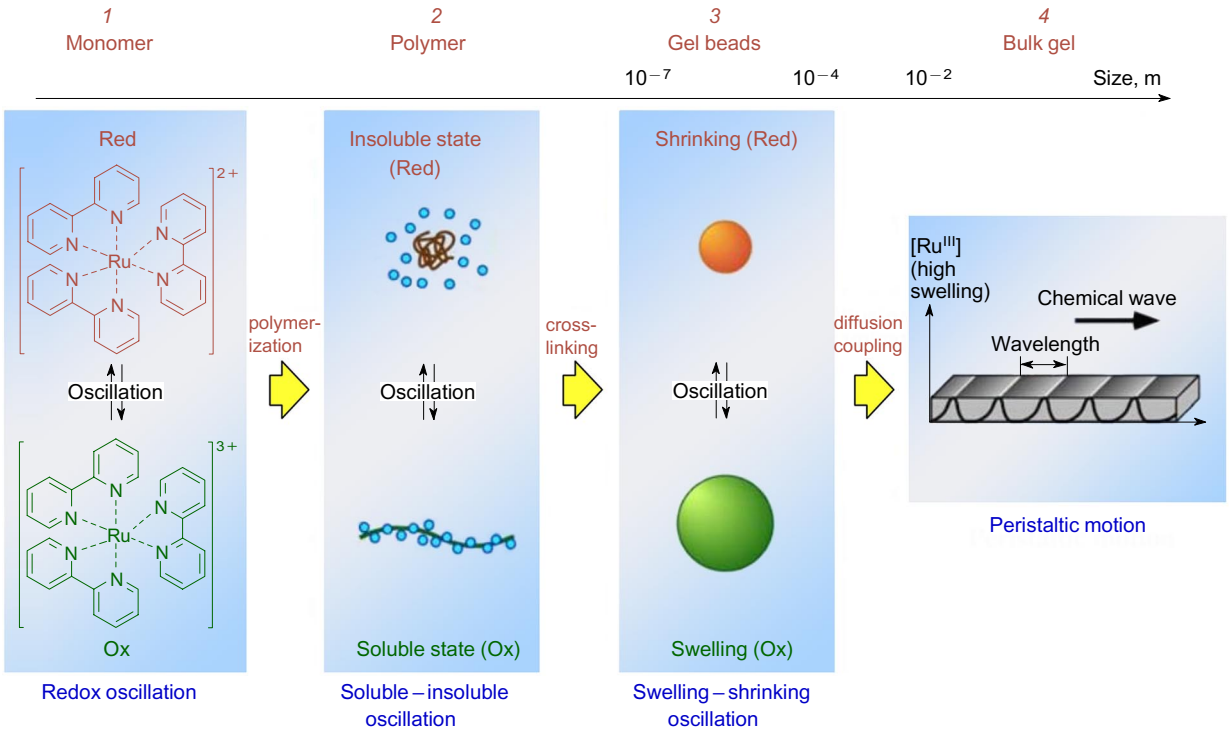


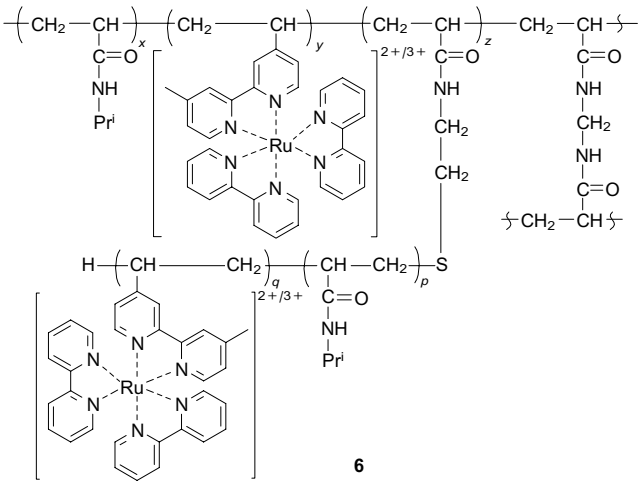
Figure 18. Self-oscillations of the gel in the BZC solution presented at different spatial scales.[20] Panel *1*, redox oscillations of the $Ru(bpy)_3^{2+/3+}$ catalyst. Panel *2*, periodic transitions of a copolymer with a catalyst embedded in the linear chain from insoluble state to soluble state during the transition of a catalyst from a reduced to an oxidized state. Panel *3*, small gel beads (less than 1 mm) immersed in the BZC solution change their size periodically. The green and orange colours correspond to the oxidized and reduced states of the catalyst. Panel *4*, mechanical peristaltic waves caused by chemical waves are observed in a gel of several centimetres in size when it is immersed in the BZC solution.

polymer matrix exhibit more significant and rapid periodic changes in size (volume) in the BZC solution, because the grafted side chains can respond to the redox change of $Ru(bpy)_3$ faster than the main chains.

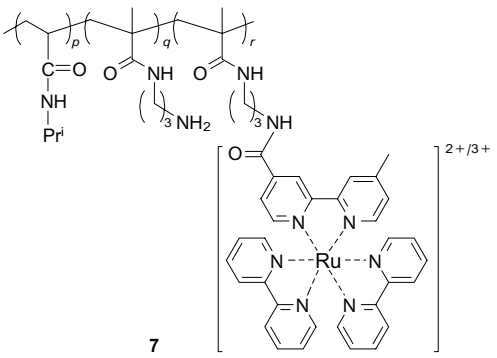
In all the above works, the complex bis(2,2′-bipyridine)(4-vinyl-4′-methyl-2,2′-bipyridine)ruthenium(II) with a vinyl group was used, with the help of which it was copolymerized with other monomers forming linear and reticulated polymers. A different approach was used to synthesize self-oscillating gels with a grafted catalyst.[199, 200] First, a linear copolymer of *N*-isopropylacrylamide and *N*-(3-aminopropyl)methacrylamide was synthesized, to the amino groups of which the following derivative of $Ru(bpy)_3^{2+}$ was grafted in different ratios: bis(2,2′-bipyridine)(1-(4′-methyl-2,2′-bipyridine-4-carbonyloxy)-2,5-pyrrolidinedione)ruthenium(II) complex. The resulting copolymer **7** demonstrated oscillations of optical density when placed in a BZC solution (Fig. 19). If *N*-methylenebisacrylamide was additionally introduced into the copolymer (as a cross-link), then a three-dimensional polymer network was obtained, which, after grafting of the catalyst, formed a self-oscillating gel. Pieces of this gel exhibited chemomechanical behaviour (see Fig. 19).

Depending on the reaction conditions and the monomer ratio, gels with different properties were obtained. By varying the ratio of free amino groups and amino groups that have reacted with Ru $(bpy)_3^{2+}$, it is possible to regulate the hydrophilic – hydrophobic balance of the gel by changing the amplitude and period of the BZ oscillations, and also to ensure that the BZ oscillations will occur in a wide temperature range, including at 37 °C.[199]

Structures 6, 7



6



7

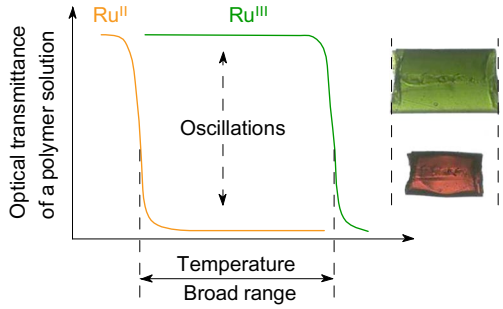


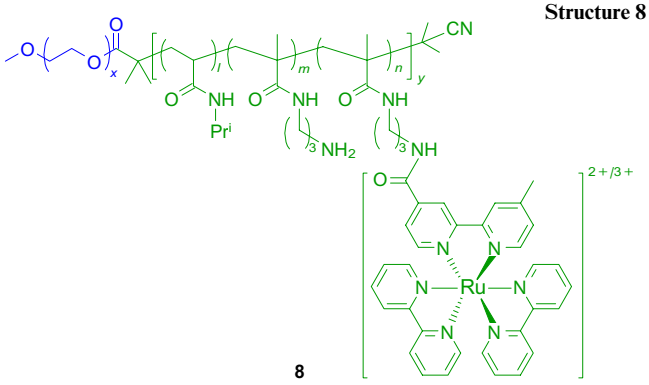
Figure 19. Dependence of the optical transmittance of a solution of copolymer **7** on temperature during the transition of the catalyst from the reduced state (Ru^{II}) to the oxidized state (Ru^{III}) at oscillations (*a*) and change in the volume of the gel obtained by cross-linking of the copolymer with *N*-methylenebis(acrylamide) during the transition from the reduced (red) to the oxidized (green) state.[199] The drawing is published with permission from the Royal Society of Chemistry.

By copolymerizing *N*-isopropylacrylamide and *N*-(3-aminopropyl)methacrylamide with polyethylene oxide, a diblock copolymer was obtained, to the amino groups of which, as in the previous case, the following derivative of $Ru(bpy)_3^{2+}$ was grafted: bis(2,2′-bipyridine)(1-(4′-methyl-2,2′-bipyridine-4-carbonyloxy)-2,5-pyrrolidinedione)ruthenium(II) complex. As a result, copolymer **8** was obtained,[200] which, when placed in the BZC solution, demonstrated self-assembly into vesicles upon reduction of the metal complex and the disintegration of vesicles to single polymer chains upon oxidation of the metal complex (Fig. 20). When $Ru(bpy)_3^{3+}$ is reduced to Ru $(bpy)_3^{2+}$, the polymer chains in the BZC solution become more hydrophobic, which leads to their association and the formation of vesicles, in which polymer chains with shorter hydrophilic regions are located inside the vesicles, and chains with longer hydrophilic moieties are located outside. Upon oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$, the polymer chains again become hydrophilic and the associate decomposes into single polymer chains (unimers).

To study the mechanisms of vesicle formation under equilibrium and non-equilibrium conditions during the BZ reaction, diblock copolymers with different block lengths were synthesized. It turned out that the length of the hydrophilic segment significantly affects the size of the vesicles, which is explained by the difference in their thermodynamic stability.

In all of the above examples, the catalyst of the BZ reaction is embedded either in the main or in the side chains

Structure 8



8

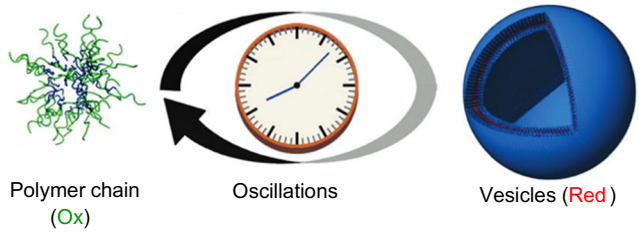
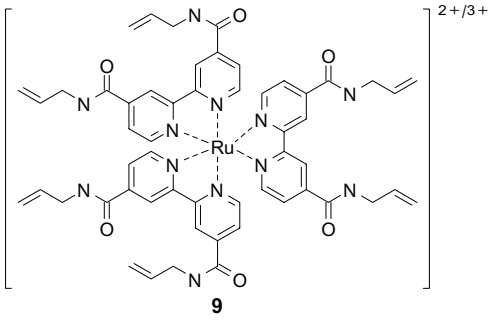


Figure 20. Oscillations of copolymer **8** when it is immersed in the BZC solution. During the transition of a catalytically active metal complex from the oxidized state to the reduced one, oscillations are accompanied by periodic self-assembly of vesicles from single polymer chains (unimers).[200] Drawing published with permission from the Royal Society of Chemistry.

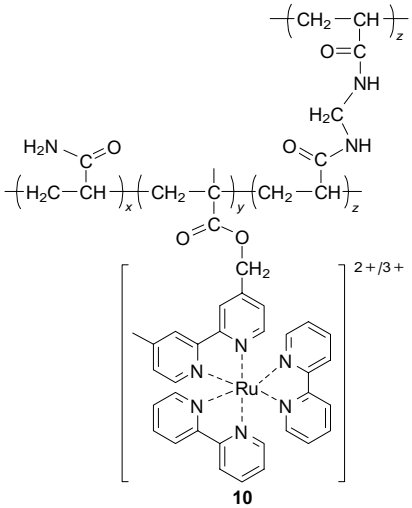
of self-oscillating gels. However, the catalytically active metal complex can also play the role of cross-linker between polymer chains. As such a metal complex, complex **9** was synthesized, the so-called 'hypercross-linker',[201] which, upon copolymerization with acrylamide or allylamine, formed gels capable of changing their size when the oxidation state of the metal complex changes and of demonstrating periodic mechanochemical oscillations when immersed in the BZC solution. The main difference of this gel from other self-oscillating gels with a covalently bonded metal complex catalyst is that the gel contracts during catalyst oxidation, and expands upon reduction.

Gel **10** with similar dynamics of chemomechanical oscillations was synthesized by copolymerization of acrylamide, bis(2,2′-bipyridine)-(4-methacryloylmethyl-4-

Structures 9, 10



9



10

methyl-2,2′-bipyridine)ruthenium(II) complex, and *N*,*N*′-methylenebis(acrylamide).[202] When the catalyst was oxidized, the size of the resulting gel decreased. The rate of chemomechanical oscillations of gel **10** (the oscillation period is about 12 s) differs significantly from that for the majority of self-oscillating gels based on *N*-isopropylacrylamide (for example, gels **3** and **4**, for which the oscillation period is about 5 minutes).

The synthesis of gels based on ruthenium complexes is rather expensive. Therefore, the efforts of chemists were aimed at synthesis of gels containing, in the polymer chain, iron complexes (which are catalytically active in the BZ reaction) instead of the ruthenium complex.[203, 204] As a result, gel **11** was synthesized,[203] which demonstrated periodic changes in colour when immersed in the BZC solution, but the authors did not report on the chemomechanical properties of the gel.

Gel **12** containing in the chain a catalytically active derivative of ferroin, (5-acrylamido-1,10-phenanthroline)bis(1,10-phenanthroline)iron(II) complex, was also synthesized.[204] When a piece of this gel (0.2 mm in size) was placed in a BZC solution, it periodically changed colour and size during the redox transitions of the metal complex.

The authors of the above experimental studies do not provide data on the stability of gels in harsh BZ media; however, it can be assumed that the gels are subject to destruction due to hydrolysis in an acidic medium of the amide groups of acrylamide and *N*,*N*-methylenebis(acrylamide) derivatives. It should be noted that the process of destruction of gels and gel microspheres can be controllable. Experiments are being carried out[205] and theories of this process are being developed[206] with the aim of making practical use of the controlled destruction of gels.

The process of changing the volume (size) of gels during the transition of a catalyst from the reduced state to the oxidized state and *vice versa* is interesting from the point of view of creating actuators, artificial analogues of muscles,[188] capable of converting chemical energy into mechanical energy.

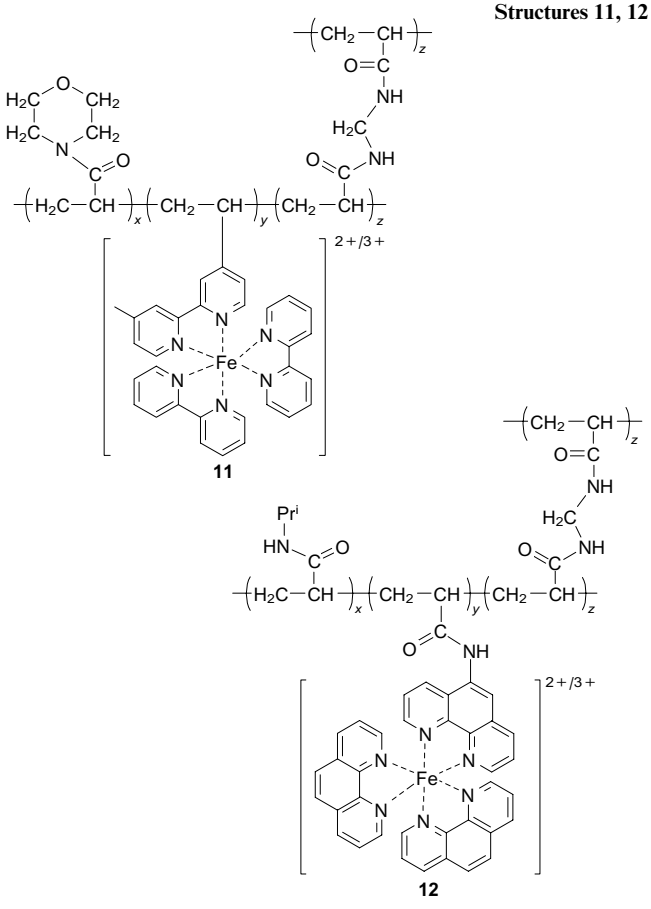
There is also a large block of theoretical studies on gels that change shape during the BZ reaction, in particular, studies on the displacement of pieces of self-oscillating gels in space.[207 – 214] The encourager of these works is Professor Anna Balazs.

Recently, a new trend has emerged in the development of chemical devices (often fabricated from self-oscillating gels) capable of performing operations on pattern recognition. These devices are a kind of 'soft' chemical computer.[31, 215 – 223] To develop such devices, it is necessary to be able to control an ensemble of single small pieces of gel (or micro-oscillators).

There are works in which the catalyst of the BZ reaction, $Ru(bpy)_3^{2+}$, was covalently bound to gelatin through the amino groups of the amino acid lysine, which is part of the gelatin.[224, 225] In this case, the remaining free lysine amino groups were subsequently cross-linked with glutaraldehyde. The gels obtained in this way, when immersed in the BZC solution, increase (decrease) their volume upon oxidation (reduction) of the catalyst.[225]

However, gelatin-based gels are not sufficiently stable under the BZ reaction conditions. The samples remain functional for 4 to 7 hours, but mechanical integrity is lost after 12 hours or slightly more, and the gel effectively dissolves in the BZC solution after 24 hours.[224, 225] In this regard, we believe that gelatin-based gels are not very suitable for the production of micro-oscillators which should work for a long time.

Structures 11, 12



7.3. Ensembles of self-oscillating BZ micro-oscillators

The simplest way to control pieces of self-oscillating gel is to synchronize their oscillations. For example, self-oscillating gel **3** was synthesized in the form of submillimetre-sized disks (BZ disks) separated by a non-reactive polyacrylamide gel.[226] The resulting disks could be of different sizes and contain different amounts of the metal complex catalyst. In Fig. 21, we present the oscillatory behaviour of four such BZ disks of the same size, but with different concentrations of the $Ru(bpy)_3^{2+}$ catalyst. The distance between the gel disks with the highest and lowest catalyst concentrations was large enough to exclude their interaction, and the other three gaps between the BZ disks were selected in such a way that synchronization was possible between them. Adding the BZC solution to such an ensemble of the disks, one can observe that stable in-phase synchronization occurs between the four BZ disks after a while, provided that the BZ waves propagate from the BZ disk with the lowest catalyst concentration to the disk with the highest catalyst concentration.

Using gel **7** immobilized on the glass surface,[218] Japanese scientists reproduced the famous work of Russian and Japanese scientists on the creation of a chemical diode.[177] Being shaped like pentagons with a thickness of 114 nm and located as shown in Fig. 22, pieces of gel immersed in the BZC solution generated chemical BZ waves, capable of propagating unidirectionally through the gap, from the flat face of one pentagon to the sharp corner of the other.

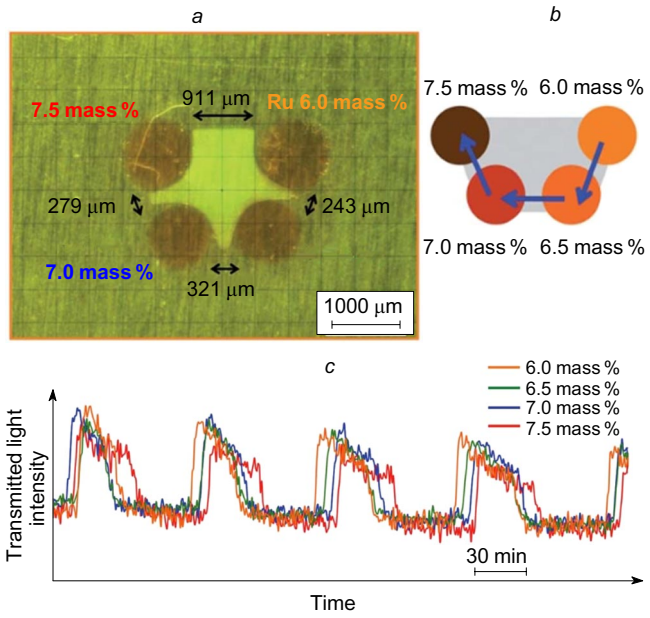


Figure 21. Synchronization of oscillations of four disks of gel **3**.[226] (*a*) Photograph of gel disks arranged in a trapezoidal shape and separated by polyacrylamide gel; concentrations of the catalyst $Ru(bpy)_3^{2+/3+}$ are expressed in mass %. (*b*) Propagation of the BZ wave along the gel disks. (*c*) BZ oscillations in the disks presented as time dependences of the intensity of light transmitted through the disks. The drawing is published with the permission from the Royal Society of Chemistry.

The asymmetric arrangement of small, rectangular gel pieces with an immobilized catalyst in the plane also makes it possible to create unidirectional propagation of the BZ waves when these pieces are immersed in the BZC solution.[227, 228]

Investigation of the interaction of pieces of gelatin gels containing a chemically bound $Ru(bpy)_3^{2+}$ catalyst is also worth mentioning.[224] When two such pieces were placed in the BZC solution, they showed chemical oscillations and types of synchronization depending on the distance between the pieces of gel. At small distances, the in-phase oscillations emerged, and at large distances, when the BZ waves were observed between the pieces of gel, antiphase oscillations were detected.

In addition to the chemical coupling of the pieces of BZ gel, chemical-mechanical interaction is also possible, leading to a change in the course of the BZ reaction in the gel.[229]

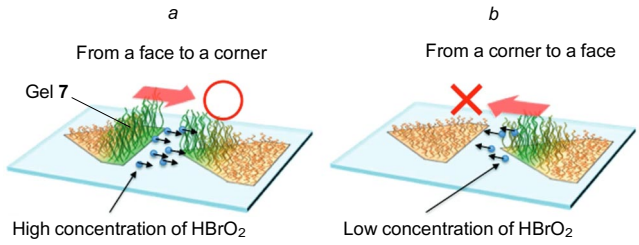
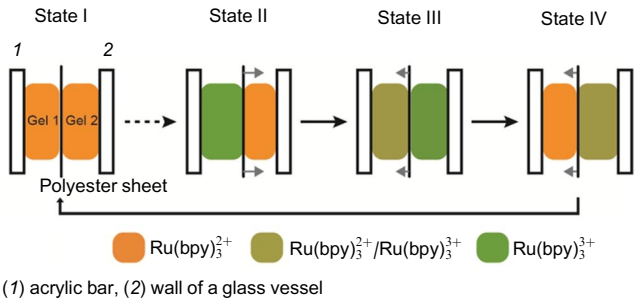


Figure 22. Chemical diode constructed from pentagons of gel **7** immobilized on a glass surface.[218] (*a*) Periodic BZ waves propagate from the plane face of one pentagon to the corner of another pentagon, but (*b*) do not propagate in the opposite direction. The drawing is published with the permission of Wiley – VCH.



(*1*) acrylic bar, (*2*) wall of a glass vessel

Figure 23. Two pieces of gel **4** (Gel 1 and Gel 2) are sandwiched between an acrylic bar and the wall of a glass vessel that contains the BZC solution. The pieces of gel **4** are pressed with an acrylic rod so that the pressure on them is always constant and does not depend on the degree of swelling of the gel (the pressure is controlled by a stepper motor by moving the rod to the required distance). A sheet of polyester is placed between the gel pieces to separate them from each other. In State I, both pieces are in the reduced state. In State II, Gel 1 is in the oxidized state (green), swells and squeezes Gel 2. In State III, Gel 1 has already reached its maximum swelling and begins to shrink, while Gel 2 is oxidized and begins to swell. However, the volume of Gel 2 cannot increase significantly, since Gel 1 presses on it. In State IV, Gel 2 continues to expand and contract Gel 1. Then Gel 2 shrinks and the system returns to State I.[229] The Figure is reproduced with permission from the American Chemical Society.

A system of two pieces of gel **4** is shown in Fig. 23, in which these two pieces are separated by a plastic spacer, squeezed from the outside and placed in the BZC solution. Without contraction and spacer, the gel pieces were synchronized in phase. Adding a spacer caused synchronization to disappear. However, upon subsequent application of a constant external pressure to the separated pieces of gel, synchronization with a phase shift occurred, the magnitude of which depended on the contraction strength. A similar phenomenon was observed with gel pieces of different size. The oscillation period of the gel did not influence the effect of the chemical-mechanical interaction either. Experimental results have shown that a physical change (contraction) in one piece of gel can lead to chemical changes in another piece and *vice versa*.

Theoretically, pieces of self-oscillating polymer gel can also be connected using piezoelectric plates,[31, 217, 230, 231] which act as a special connection between the pieces of gel. In a sense, these plates play the same role as the external constant pressure used experimentally in the previous case, namely, they are necessary for the connection between the pieces of gel. In the given theoretical schemes, sensitivity of the pieces of self-oscillating gel to pressure is utilized.

The method of connecting the pieces of gel is illustrated in Fig. 24. A pair consisting of one piece of self-oscillating gel and a piezoelectric connected to it (in the form of a thin elastic plate) was called by the authors[230] a micro-electro-mechanical system (MEMS). Two such pairs are electrically connected, which gives the highest rate for information transfer between MEMS pairs. This entire system does not require any external energy for its operation. The expansion of the oscillating BZ gel to the left deflects the piezoelectric plate (console), which creates an electric voltage U. The generated voltage U, in turn, causes the console to deflect to the right. This deviation generates a force (pressure) acting on the underlying BZ gel, which changes the phase of its

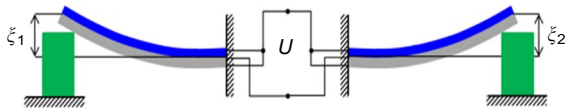


Figure 24. Theoretical diagram of two electrically coupled piezoelectric MEMS (micro-electro-mechanical systems), which are driven by self-oscillating polymer gels (green rectangles).[230] The deviation of the piezoelectric console (grey-blue) ξ due to the swelling of the gel generates the difference *U* in electric potentials. The piezoelectric console consists of two layers (blue and grey). The inner and outer surface electrodes of the console are connected in parallel. The Figure is reproduced with permission from Springer Nature.

oscillations. This interaction of two MEMS leads theoretically to synchronization of two pieces of gel.

8. Note added in proof

During the preparation of this review for publication, its authors published an original work,[232] which solves many problems with feeding micro-oscillators with fresh BZ reactants. Moreover, the new system makes it possible to control the type of coupling between neighbouring MOs, changing the excitatory type of coupling to inhibitory one and *vice versa*.

The problem of feeding the BZ MOs is solved in this work by immersing the polymer microspheres with the immobilized catalyst, $Ru(bpy)_3$, in a water-in-oil AOT microemulsion, which is loaded with all the initial reactants of the BZ reaction except for the catalyst. Dowex 50WX2 beads with a diameter of about 100 μm or/and SiO_2 microspheres were used as microspheres. The feeding of microspheres with fresh reactants occurs due to mass transfer between immobile microspheres and diffusing microemulsion nanodroplets with a diameter of about 10 nm. Such continuous feeding of MOs allows them to maintain a stable oscillatory regime for days.

In the AOT microemulsion, the water-soluble activator of the BZ reaction, $HBrO_2$, diffuses together with a nanodroplet and, therefore, has a low diffusion coefficient of the order of 10^{-7} cm^2 s^{-1}. The hydrophobic inhibitor, Br_2, can diffuse freely in the continuous oil phase and therefore has a diffusion coefficient of the order of 10^{-5} cm^2 s^{-1}. A rapidly diffusing inhibitor and a slowly diffusing activator are necessary conditions for the formation of Turing structures in a homogeneous medium. In our case of a heterogeneous medium, the Turing conditions lead to a new effect. At small distances between two neighbouring microspheres (less than 20 μm), the oscillations of these MOs are synchronized in-phase due to the diffusion of the activator. At large distances (say, from 20 to 50 μm), the oscillations are synchronized in antiphase due to the diffusion of the inhibitor. At very large distances (100 μm and more), there is no synchronization. Thus, in a new medium, in the AOT microemulsion, it is possible to change not only the strength, but also the type of coupling between MOs by varying the distance between them.

9. Conclusion

In the presented review, the main approaches to the microlocalization of the BZ reaction and the creation of the BZ MOs are considered and discussed. From the analysis of the methods presented in the review, it can be concluded that at present there is no universal method for creating BZ MOs that would satisfy all the requirements for the functioning of MO networks, and especially networks capable of intelligent behaviour. All methods have advantages and at least one disadvantage.

Microdroplets with the BZ reaction dispersed in an organic medium or fluorinated oil cannot be in an oscillatory state for a sufficiently long period of time, since they are not fed with fresh BZ reactants. Without feeding, the period and amplitude of oscillations of the BZ droplets change significantly over time (due to the consumption of the BZ reactants), which makes working with both single droplets and ensembles of BZ droplets rather inconvenient and inaccurate.

Another disadvantage of BZ droplets dispersed in an organic medium is the predominance of a diffusive inhibitory coupling between them, which limits the diffusion interaction between the BZ MOs to the region of antiphase synchronization.

The use of BZ droplets enclosed in organic phospholipid membranes (BZ liposomes) can theoretically solve the problem of feeding BZ MOs in the organic phase, although this problem has not yet been solved in practice. In addition, BZ liposomes are also interesting because they allow us to control the type of interaction between MOs, inhibitory or excitatory.

If, instead of BZ droplets, microspheres made of ion-exchange resins containing an immobilized BZ reaction catalyst are used, then it becomes possible to feed the MOs with fresh BZ reactants, provided that interaction between them occurs in an aqueous BZC solution. Moreover, these microspheres have satisfactory mechanical properties. But their disadvantage is the washing of the catalyst out into the surrounding strongly acidic solutions, like the BZC solution. In an aqueous solution, a dominant excitatory diffusive coupling arises between these BZ MOs. Under harsh conditions of the BZ reaction, ion-exchange resins are destroyed over time. In non-aqueous media, it is difficult to organize the feeding of these BZ MOs. We believe that ion-exchange resins based on polystyrene are not an ideal material for sorption of the catalyst of the BZ reaction and for use in BZ MO networks which take a long time for functioning. Perhaps, perfluorinated analogues of polystyrene microspheres, which, first, are chemically inert in harsh media, and, second, have a high charge on sulfo groups, would show better properties and, therefore, can better retain BZ reaction catalysts.

Inorganic polymer materials, such as silica gel and clay, are resistant to degradation in a BZ environment; however, the catalyst adsorbed in silica gel is washed out into acidic BZ medium, albeit at a lower rate than in the case of cation exchange resins.[94]

The problem of washing catalyst out from microspheres is solved by covalently bonding catalyst molecules to polymer chains, as in the case with self-oscillating gels. Studies of such gels have led to the possibility of creating materials that can periodically change not only colour and transparency, but also their viscosity and size, as well as carry out periodic self-assembly of complex associates under conditions of the BZ reaction. The assemblies of particles of self-oscillating gels are capable of exhibiting complex behaviour under conditions of the BZ reaction. The ability of gel pieces to change their sizes can be used to

modulate the strength of the coupling between neighbouring MOs. In addition, self-oscillating gels open up the possibility of creating MOs moving along the surface.

However, the polymers themselves based on acrylamide derivatives are hardly sufficiently stable in an acidic BZC solution and are not able to oscillate steadily for a long time. At present, self-oscillating gels (and BZ MOs based on them) are the subject of intensive research.[233 – 238]

The creation of single MOs and their further integration into networks is probably the first step on the path from chemical macro-oscillators to neural-like networks. But a more powerful, in our opinion, 'matrix' method of creating MO networks has already appeared. This method combines lithography and microfluidic technique. Lithography allows us, first, to obtain the desired geometry (architecture) of networks with microreactors and microchannels that provide interaction between MOs, their separate feeding with fresh reactants and removal of reaction products, and secondly, it also allows us to regulate the strength of the coupling between MOs (which is actually plasticity).[28, 239] Separate feeding of MOs (using the microfluidic technique) makes it possible for MOs to be in different dynamic modes and have a different chemical composition. But lithography is an expensive method, which is being replaced by three-dimensional printing with micrometre resolution in combination with the same microfluidics.[240 – 243] Work along this line is still at the initial stage.

The variety of techniques for creating MOs convinces us that MOs acceptable for a 'chemical computer' will soon be created. In this regard, we would like to conclude the review with our vision of further ways for the development of ChC. As a starting point, we take the HC block diagram of the ChC shown in Fig. 1. All pulse couplings that are realized in this block diagram through light pulses must be replaced by chemical waves propagating along narrow channels, which are built from polymers with a covalently bonded catalyst. In this case, chemical diode technologies will be used to ensure unidirectional wave propagation. Some oscillators, such as the ones that make up the CPG block, can be made of self-oscillating gel to give mobility to the block. Gels that change their size can also be used to control the strength of the coupling between MOs. And finally, the scheme of the ChC should be supplemented with a new block that will allow ChC to 'think', that is, to choose from several possible solutions of the problem only the most optimal one.

For readers wishing to learn more about nonlinear chemistry, systems chemistry, new smart materials, as well as networks of coupled oscillators and their use for unconventional computing, we recommend a number of reviews.[6, 7, 22, 23, 29, 73, 74, 111 – 116, 187, 212, 216, 244 – 250]

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10. List of acronyms

BZ reaction — Belousov – Zhabotinsky reaction,
BZC solution — an aqueous solution with all the components of the BZ reaction, but without a catalyst,
BrMA — bromomalonic acid,
ChC — chemical computer,
MA — malonic acid,
MO — micro-oscillator
SS — stationary state.

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