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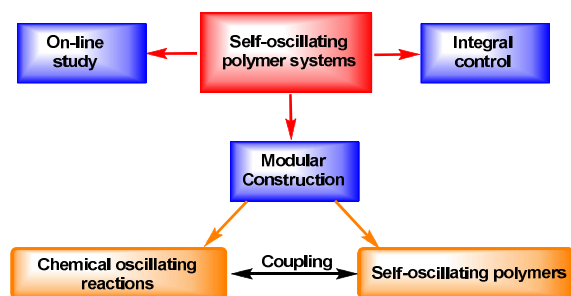
This review explores the principle, modular construction, integral control and engineering aspects of self-oscillating polymer systems driven by the Belousov-Zhabotinsky reaction.

# A modular approach to self-oscillating polymer systems driven by the Belousov-Zhabotinsky reaction

Hongwei Zhou,[*a] Zhaohui Zheng,[b] Qiguan Wang[a], Guohe Xu,[b] Jie Li[b] and Xiaobin Ding[*b]

[a] *School of Materials and Chemical Engineering, Xi'an Technological University, Xi'an 710032, P. R. China. E-mail:xatuzhou@163.com*
[b] *Chengdu Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chengdu 610041, P. R. China. E-mail: xbding@cioc.ac.cn*

**Abstract:** Inspired by the self-oscillating phenomena in nature, such as heartbeat, brain waves, pulsatile secretion of hormones, cell cycles and biorhythms, a new kind of responsive polymers, so-called the self-oscillating polymers (SOPs) are developed. Different from the traditional responsive polymers, SOPs are driven by chemical oscillating reactions and exhibit autonomous response without "ON/OFF" switching of external stimuli. From a perspective of modular design, we explore in this review the principle, construction, integral control of SOPs systems based on the recent developments. Attention is also paid to the emergent techniques for on-line study of self-oscillating behaviors and engineering approaches to novel SOPs systems with unique functions and high oscillating performances.

## 1 Background

Responsive polymers have been extensively studied due to their combined performances of traditional polymer materials and the responsive behaviors to external stimuli.[1] Upon variation of environmental conditions (including temperature, pH, light, electric field, magnetic field, *etc.*), this kind of materials can dynamically and drastically alter their properties by shape or color change, optical properties, surface characteristics and solubility. Due to their responsiveness, responsive polymers have found many potential applications, including molecular devices, controlled drug delivery, diagnostics, sensors, healing, display, information writing and reading, separation, biomimetic catalysis, microfluid valves and others.[2, 3] In the past few decades, great progress has been made and the related research was focused on the responsive behavior, the preparation method, new responsive materials and the responding mechanism. Even many polymer materials responsive to multi-stimuli have been constructed. However, the rapid development of other areas, like nanotechnology, biotechnology, life sciences and information technology, supramolecular assembly, *etc.* brings greater

challenge for responsive polymers, especially the elegant design and precise preparation of responsive polymers, sophisticated construction of intelligent systems by integrated engineering approach.

A breakthrough was made in the 1990s by a new kind of responsive polymers, so-called the self-oscillating polymers (SOPs). SOPs can also be considered as a kind of responsive polymers which bear an embedded chemical oscillating reaction as driving source. When the chemical oscillating reaction starts, some factors in the reaction systems exhibit autonomous, reversible and periodical change and drives the SOPs to show self-oscillating behaviors. One biggest advantage over traditional responsive polymers is that SOPs can exhibit autonomous response without "ON/OFF" switching of external stimuli. The first example is presented by autonomous volume swelling and deswelling of a pH-responsive hydrogel driven by a pH-oscillator in a continuous flow stirred tank reactor (CSTR).[4] This method was further developed to design new SOPs by utilizing the Belousov–Zhabotinsky (BZ) reaction as a driving source.[5, 6] Compared with the SOPs systems driven by pH oscillator, those with the BZ reaction as the driving source can be carried out in a batch system, which makes such systems more self-regulated and popular. In this review, we will mention mainly the SOPs systems driven by the BZ reaction.

In many previous reviews and articles, the mechanism of SOPs has been clearly stated and several kinds of SOPs systems have been designed and constructed.[7-11] SOPs with different chemical structures and physical structures were studied[12-18] and the potential applications of the SOPs systems were explored, for instance, autonomous mass transportation devices,[8, 19-23] self-walking gel,[24-26] *etc.*. So far, however, the design of SOPs greatly depends on the periodical redox variation of the $Ru(bpy)_3$. The options and performances of such systems are restricted.[7, 11, 27] In recent years, many new approaches to SOPs systems have been developed, which may provide new provoking clues for the further research of such intelligent systems. In the present review, we will mainly explore the modular design and integral control of SOPs systems based on the recent progress, also paying attention to the engineering aspects in SOPs systems.

Dr. Hongwei Zhou, born in 1987, received his BS degree in 2009 from Xi'an Jiaotong University and PhD degree in 2014 from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences (CAS) under the guidance of Prof. Xiaobin Ding and Prof. Zhaohui Zheng. During 2013.9-2014.9, he worked with Prof. Hans-Jürgen Butt and Dr. Si Wu at Max Planck Institute for Polymer Research (Mainz, Germany) as a visiting PhD student. He is currently working at School of Materials and Chemical Engineering in Xi'an Technological University. His research interests include responsive polymers, supramolecular polymers and functional polymers.

# 2 Principles of self-oscillating polymer systems

Normally, a SOPs system is composed of a self-oscillating polymer (or gel) as responsive component and a chemical oscillating reaction as the cyclic stimulating source.[7] In such systems, the responsive component can respond timely and reversibly to the periodical variation of the oscillating factors generated in the chemical oscillating reaction. Different from the traditional responsive polymers which approach to an equilibrium state upon an external stimulus, SOPs can show autonomous and periodical change. This means that the response of SOPs should be reversible and the response dynamics should be in an appropriate range to couple with the BZ reaction. In other words, the responsive component should be well synchronized with the rhythmically changing factors in the chemical oscillating reaction. From a perspective of modular design, therefore, not only the chemical oscillating reaction and the responsive components should be well studied, but also the precisely coupling of these two parts should be carefully considered.
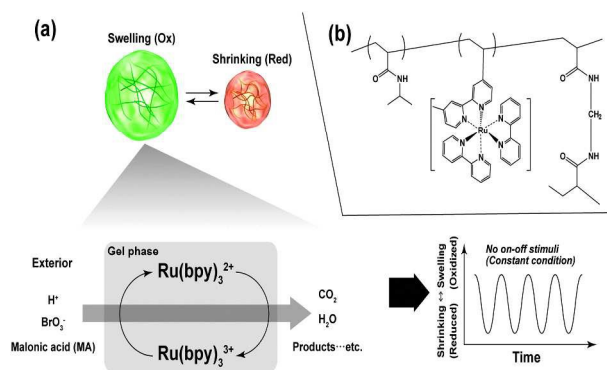


Figure 1 (a) Concept of the periodical volume variation of self-oscillating gels driven by the BZ reaction; (b) the chemical structure of the self-oscillating gel (Poly(NIPAAm-*co*-Ru(bpy)$_3$) gel). Reproduced with permission from ref. [28]

For a typical SOPs system, the BZ reaction is introduced as the driving source and the responsive components are often tailor-made polymers or hydrogels with covalently bonded Ru(bpy)$_3$ groups, as illustrated in Figure 1. The Ru(bpy)$_3$ moieties work as the catalyst of the BZ reaction and show autonomous, reversible and periodical redox variation, "bridging" the BZ reaction and the polymer systems. Due to the redox oscillation of Ru(bpy)$_3$, the polymer chains undergo spontaneous soluble-insoluble transition or swelling-deswelling (for gels). Generally, the polymer chains are relatively hydrophilic when the Ru(bpy)$_3$ moieties are in their oxidized state. The polymer is soluble and gel swells. In contrast, when the Ru(bpy)$_3$ moieties are in their reduced state, the polymer chains become hydrophobic. The polymer is insoluble and gel deswells. Other SOPs with copolymerized components like AMPS, MAPTAC, NAS, and AA and gels with different chemical or physical structures also show self-oscillating behaviors in a similar way. In some SOPs with new chemical structures, however, it is in a completely opposite case, as observed in self-oscillating gels crosslinked by active cross-linkers and Poly(VP-*co*-Ru(bpy)$_3$) systems *etc.*.[29-32] Therefore, for some special SOPs, the mechanism should be considered individually.

# 3 Modular design of self-oscillating polymer systems

SOPs systems are often highly integrated. But various new SOPs systems can be obtained by modularly analyzing the systems. As illustrated in Figure 2, SOPs systems can be designed and constructed by modularly considering two aspects: the chemical oscillating reactions which serve as the driving source and the self-oscillating polymers. The properties of the chemical oscillating reactions can be adjusted by several parameters such as the initial concentration, temperature, light, reaction medium *etc*. The self-oscillating polymers can be designed by considering the introduction of functional components, new BZ catalysts, new topological structures. And the recently developed SOPs systems based on supramolecular interactions also give some provoking clues. As the driving source and self-oscillating polymers are coupled, an on-line study technique should be selected according to the types of SOPs systems. Many techniques, such as UV-Vis spectra, rheology curves, DLS, fluorescence signal, microscopic images and videos, AFM, QCM-D and micro-force sensing *etc*. have been developed. Moreover, an integrated system can also be controlled by external parameters or engineering methods, as typically exampled by light, mechanical force, or microfluidics-controlled SOPs systems. By this way, one can not only construct new SOPs systems on-demand, but also easily adjust the properties of SOPs systems from different aspects.

## 3.1 Driving source: the Belousov-Zhabotinsky reaction

It is conventionally known that the concentration of reactants and products in chemical reactions shows directional decrease or increase until the system reaches an equilibrium state. For chemical oscillating reactions, however, the concentration of some components exhibit periodical spatialtemporal variation, resulting in a self-regulated and self-fed reaction network. Since the early studies which can date back to 1828, many chemical oscillating reaction systems have been discovered and studied. The typical examples include the Belousov-Zhabotinsky (BZ) reaction,[33-40] Bray-Liebhafsky (BL) reaction,[41-43] Briggs-Rauscher (BR) reaction,[44-46] pH oscillators[47, 48] and biological oscillators.[49]

Among these, the BZ reaction is extensively studied because it can be easily constructed and carried out in a one-batch system. In fact, the BZ reaction refers to a family of related reactions which contain certain concentrations of citric acid (CA) or malonic acid (MA) as the organic compounds, a proper metal catalyst which has standard potential between 0.9-1.6 V[39, 40], an acid ($H_2SO_4$ or $HNO_3$) as proton source, and a bromate salt ($NaBrO_3$) as oxidant.[50] The overall process of the BZ reaction is the metal-catalyzed oxidation of organic acid by bromate salt in a strongly acidic condition. During the reaction, the metal catalyst can change periodically between reduced state and oxidized state *via* a single electron transition redox reaction and the organic acid is oxidized into $CO_2$, $H_2O$ and other products. According to the reported literatures, $Ce^{3+}$, $Ce^{4+}$, $Mn^{2+}$, $Fe(phen)_3^{2+}$, $Fe(bpy)_3^{2+}$, $Ru(bpy)_3^{2+}$, $Ru(tpy)_2^{2+}$ and $Ru(bpy)_2(py)_2^{2+}$ can be utilized as the metal catalyst for the BZ reaction (Figure 3a). The single electron transition redox oscillation can be understood by the FKN model.[39, 51] In this model, intermediate products are regarded as the vital component in the system and Br$^-$ controls the oscillation process. An autocatalytic and the corresponding positive feeback effect are mediated by $HBrO_2$. Taking the $Ce^{3+}$-MA-
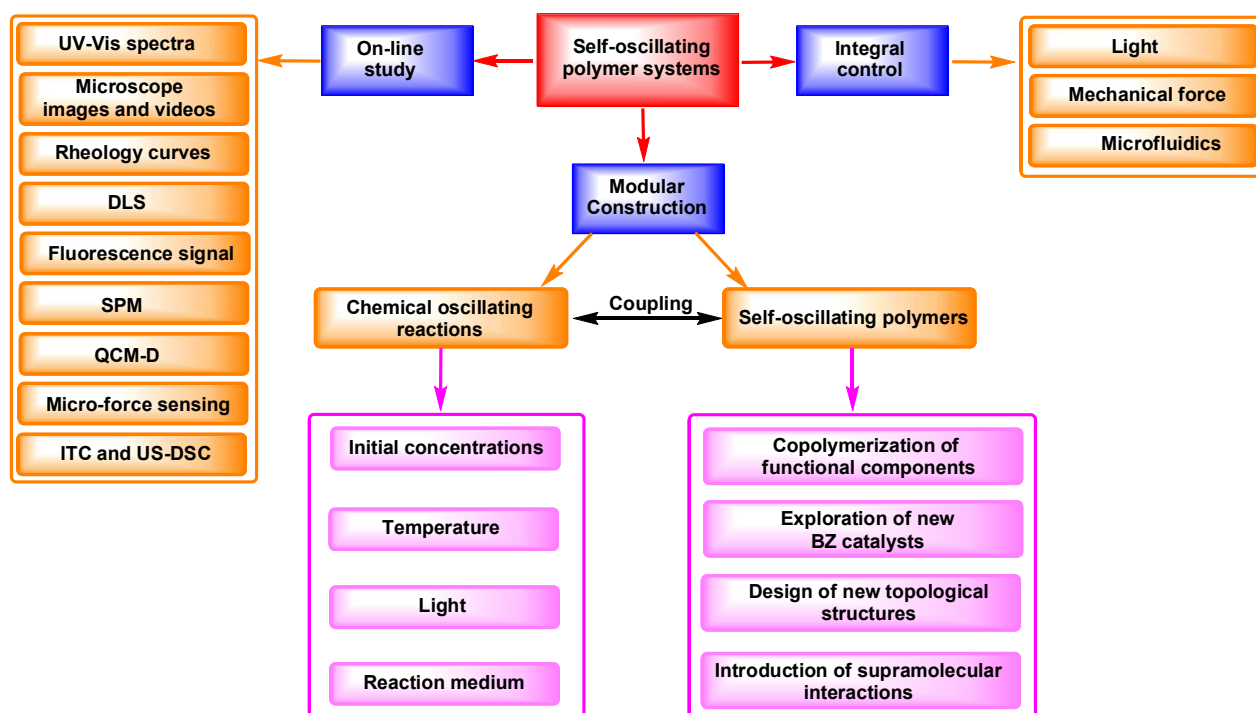
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Figure 2 Framework of modular approach, on-line study methods and integral control for self-oscillating polymer systems.
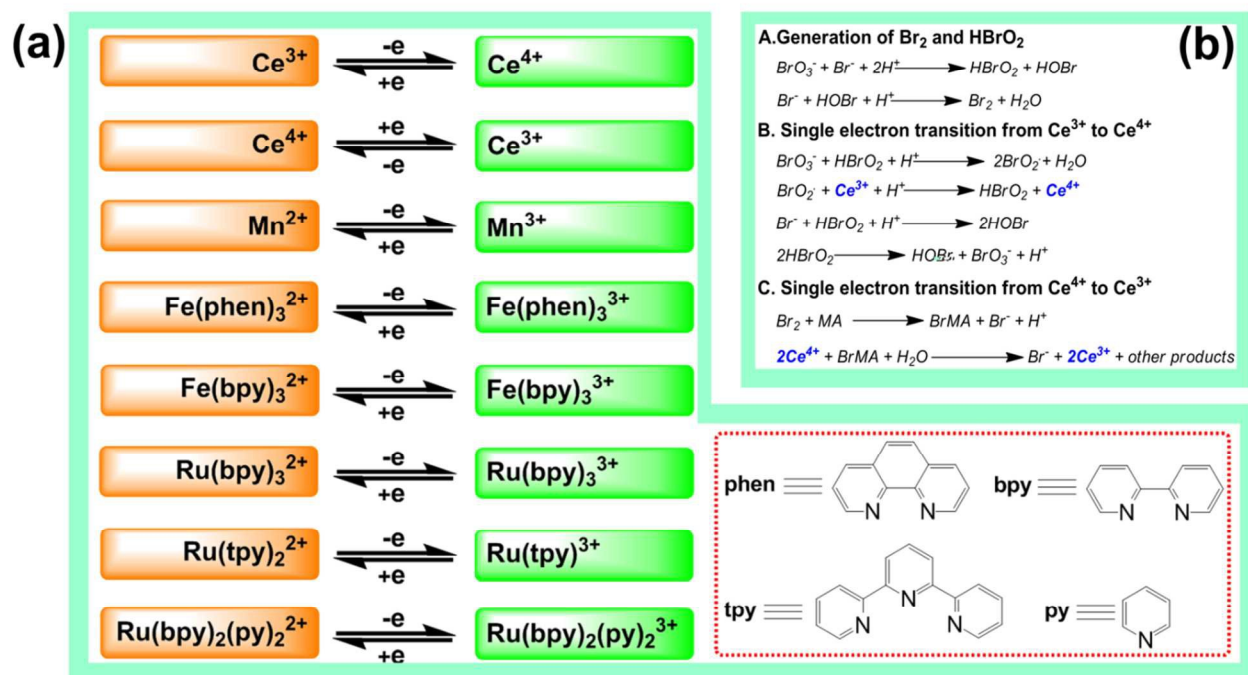
Figure 3 (a) Single electron transition oscillation of various metal catalysts in the BZ reaction and (b) the simplified chemical processes of $Ce^{3+}$-MA-$NaBrO_3$-$H^+$ BZ reaction system according to the FKN model.

$NaBrO_3$-$H^+$ system as an example, the metal catalyst is oxidized in process B and goes back to the reduced state again in process C. That is why the catalyst can exhibit autonomous, reversible and periodical redox oscillation (Figure 3b).

Considering together the mechanism of the SOPs systems, the redox oscilaltion of the BZ-catalysts is an ideal stimulating factor in the chemcial oscillating reaction. However, the harsh conditions (highly acidic and oxidative) of the BZ reaction should be at least

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considered when a new SOPs systems is designed and constructed. Moreover, the free radicals formed during the BZ reaction may have some negtive effect on the polymer chain stability. Especially, if SOPs are applied, some problems have to be solved: the strong acidic conditions and the short duration of the oscillation. In order to establish a stable BZ reaction under mild conditions, Yoshida *et al*[52] recently developed a novel approach to the BZ reactions by utilizing protic ionic liquids (ILs) (ILs containing active protons) as proton source instead of traditional strong acid like $H_2SO_4$ or $HNO_3$. Utilizing ILs as the proton-source provide many advantages: (1) the duration of the BZ reaction is extended and the amplitude is enhanced. For instance, the oscillation with large amplitude can last as long as 7 h by utilizing [dema-H$^+$][HSO$_4^-$] (dema, *N,N*-Diethylmethylamine) as the proton source; (2) the condition is milder than the traditional ones utilizing strong acid like sulfuric acid or nitric acid; (3) the solvent evaporation problem can be to some extent solved by partially utilizing the protic IL. Therefore, the BZ reaction system in protic ionic liquids provides a completely new platform for the design of high performance self-oscillating biomimetic materials.

Other parameters that should be carefully considered are the initial conditions of the BZ reaction, mainly including the initial concentrations of the substrates and the temperature of the system. Generally, these two parameters are important for the coupling of the BZ reaction with responsive components because the redox oscillation dynamics should be well matched with the responding rate of the responsive components. Moreover, in some cases, high concentrations of the substrates and the temperature may leads to a seriously irreversible contraction of the gel or precipitation of polymers. On the other hand, many structured media, like microemulsions containing nanoscale droplets of water and water droplet arrays in oil, flow reactors, gels and other kinds of media, such as membranes, ion exchange beads, phospholipids or glasses, all support fascinating behavior of the BZ reaction and paves a way for constructing novel SOPs systems.[50, 53, 54]

### 3.2 Design of self-oscillating polymers

Except for the properties of the BZ reaction, tailor-made design of SOPs is also an effective way for improving the performances of SOPs systems. According to the principles of SOPs systems, SOPs are often composed of a metal catalyst for the BZ reaction (like Ru(bpy)$_3^{2+}$) and other water soluble components. Most of the traditional SOPs are copolymers of NIPAAm and Ru(bpy)$_3^{2+}$. The option, performances and versatility of SOPs systems are restricted. In the following chapter, we will introduce recently developed approaches to SOPs systems.

### 3.2.1 Copolymerization of functional components

One way to design SOPs with new chemical structures is copolymerization of other components with Ru(bpy)$_3^{2+}$. Several SOPs have been studied by introduction of other functional components, such as AMPS, MAPTAC, NAS, VP, AAm, AA *etc.*. By introduction of AMPS, the solubility of the polymer can be enhanced and the self-oscillation of the polymers can be realized in an acid-free condition.[12] When the AMPS is introduced into hydrogel networks, a phase-separated structure can be obtained and the amplitude of volume oscillation of the hydrogel can be improved.[20] MAPTAC is regarded as a reservoir of BrO$_3^-$ and enables the self-oscillation behavior under oxidant-free conditions.[55] By introducing both AMPS and MAPTAC, self-oscillation of the polymer in only MA solution can be realized, just like a fuel-driven machines.[13]

Introduction of AAm[56] and VP[30, 31] components makes the polymer nonthermosensitive and can break through the limitation of temperature to realize the self-oscillation behavior at relatively high temperature. What is interesting, when AA[17] is introduced, the occurrence and stop of self-oscillating behaviors can be controlled by temperature.

Another clue is the introduction of responsive groups into SOPs. The self-oscillating behavior can be regulated by controlling the properties of the responsive groups. Recently, Yoshida *et al*[57] demonstrated light-controlled self-oscillating behavior by introducing photochromic groups. In their polymer, spirobenzopyran monomer was utilized as photo-responsive group and copolymerized with NIPAAm and Ru(bpy)$_3^{2+}$ (Figure 4). During the BZ reaction process, the polymer undergoes periodical soluble/insoluble variation and the self-oscillating behavior can be controlled by light irradiation through the reversible photochromism of spirobenzopyran groups. When the polymer is irradiated by light (wavelength 400~440 nm) with the intensity of 50 mW/cm$^2$, spirobenzopyran changs into a closed ring state, the LCST of the polymer is consequently lowered and the oscillation behavior can be stopped. When the polymer is kept in dark, on the contrary, spirobenzopyran changes back to the ionized state and the self-oscillating behavior is recovered. This provides an new method for remote control of the self-oscillating systems.
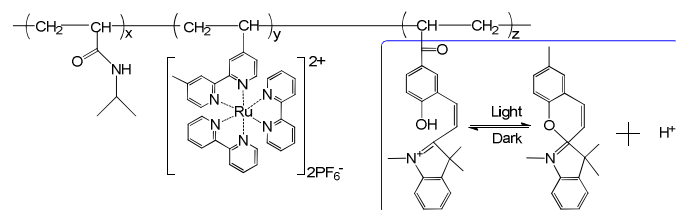


Figure 4 Chemical structure of self-oscillating polymer containing spirobenzopyran groups and the photochromism of spirobenzopyran groups under light illumination and dark condition.[57]

### 3.2.2 Exploration of new BZ catalysts

Introduction of new BZ catalysts also result in new SOPs. Normally, the BZ catalyst is first modified with double-bond and then copolymerized into the polymer systems.[5] A newly developed method also allows introducing the BZ catalysts by a simple one-step coupling reaction, succinimide−amine coupling reaction.[27, 58] Except for Ru(bpy)$_3^{2+}$, many other metal ions or their complex can also serve as the BZ catalysts, for instance the above-mentioned Ce$^{3+}$, Ce$^{4+}$, Mn$^{2+}$, Fe(phen)$_3^{2+}$, Fe(bpy)$_3^{2+}$, Ru(tpy)$_2^{2+}$ and Ru(bpy)$_2$(py)$_2^{2+}$. Some of the BZ catalysts have been recently developed for the design of SOPs and the options of SOPs are expanded. A typical example is presented by the self-oscillating gel actuator driven by ferroin.[59] A ferroin monomer (iron (5-acrylamido-1,10-phenanthroline) bis(1,10-phenanthroline)) is first synthesized and then copolymerized with NIPAAm to get the gel. When the gel is immersed into the BZ reaction solution, a redox oscillation of ferroin can be observed and the gel can exhibit 7% swelling/deswelling variation in the gel length (Figure 5a).

Fe(bpy)$_3^{2+}$, similar to Ru(bpy)$_3^{2+}$, can also work as an efficient catalyst for the BZ reaction and SOPs. This has been experimentally demonstrated utilizing a new polymer Poly(NIPAAm-*co*-Fe(bpy)$_3$). The chemical structure is shown in Figure 5b. The Fe(bpy)$_3$ moieties are covalently bonded to the polymer chain with the same method to Poly(NIPAAm-*co*-Ru(bpy)$_3$) systems. By controlling the redox states of the Fe(bpy)$_3$ moieties, a LCST difference can also be observed and the copolymer undergoes a soluble−insoluble self-oscillation driven

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by the BZ reaction.[60, 61] In gel, Fe(bpy)$_3$ also efficiently catalyze the BZ reaction, as demonstrated by Hara *et al.*[62] Their gel is obtained by copolymerization of acryloylmorpholine (ACMO) and bis(2,2'-bipyridine)(4-vinyl-4'-methyl-2,2'-bipyridine) iron bis(hexafluorophosphate) ([Fe(bpy)$_3$].2PF$_6$) in the presence of BIS (Figure 5c). Further study of the oscillation period at different temperatures gives the activation energy (*Ea*) which is 78 kJ mol$^{-1}$. Compared with the *Ea* of Ru(bpy)$_3$-based systems which is *ca.* 60 kJ mol$^{-1}$, it can be concluded that the catalytic activity of Fe(bpy)$_3$ is lower than that of Ru(bpy)$_3$. However, the utilization of iron greatly lowered the cost for preparing the BZ reaction catalyst.
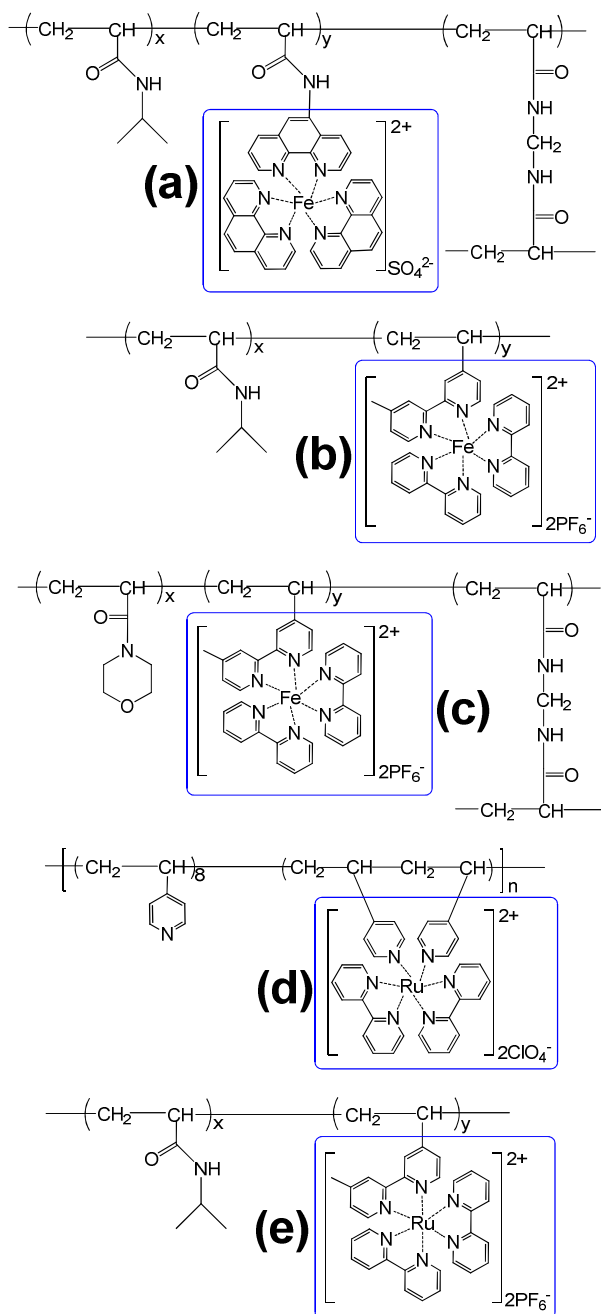


Figure 5 Chemical structures of self-oscillating polymers containing different BZ catalysts: (a) Fe(phen)$_3^{2+}$ (ferroin); (b) and (c) Fe(bpy)$_3^{2+}$; (d) Ru(bpy)$_2$(py)$_2^{2+}$; (e) Ru(bpy)$_3^{2+}$ for comparison.[59, 61-63]

Another alternative ruthenium complex is also developed for designing SOPs according to Ru(bpy)$_3$.[63] The new ruthenium complex is synthesized by coordination of Ru(II) with two bipyridyl molecules and two pyridine molecules in the polymer chain of PVP (denoted as Ru(bpy)$_2$(py)$_2^{2+}$) (Figure 5d). By carefully tuning the molar ratio between Ru(II) and PVP, the solvent, LiClO$_4$, a soluble polymer containing Ru(bpy)$_2$(py)$_2^{2+}$ can be obtained (denoted as RuPVP). It has been demonstrated that The BZ reaction can be successfully catalyzed RuPVP. RuPVP may provide another facile and relatively inexpensive approach to new self-oscillating polymer systems.

### 3.2.3 Design of new topological structures

A key approach to new self-oscillating polymer gels is focused on the design of various topological structures. Introduction of new topological structures into self-oscillating gels has two advantages. One is to improve the performances of self-oscillating gels. As has reviewed in many previous articles, the performances can be enhanced by introduction of porous structures,[18] ordered structures,[64] phase-separated structures,[20, 65] hierarchical structures,[14, 66] *etc*. The other one is to obtain new functionalities, such as molecular devices.[67]

Integral design of topological self-oscillating gels is an efficient way to improve the mechanical oscillation. In comb-like hydrogels, the side polymer chains can freely move and interact with the water molecules, which enable such hydrogels to have faster and larger swelling/deswelling upon external stimuli compared with the conventional hydrogels. Based on this principle, Yoshida and coworkers designed a comb-like self-oscillating gel in which the Ru(bpy)$_3$ groups exit in both the main chains and the side chains (Figure 6). Due to the unique structure, the comb-like self-oscillating gel can exhibit faster and larger swelling/deswelling oscillation in the BZ reaction systems.[15]
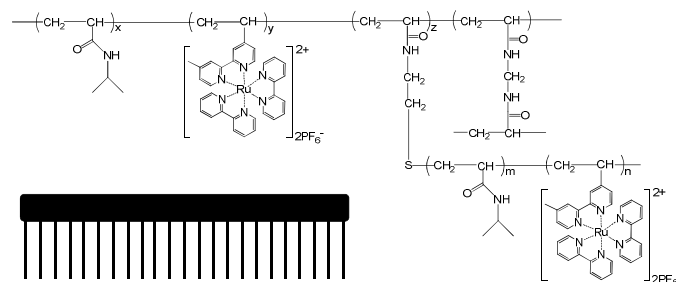


Figure 6 Self-oscillating gel with comb-like topological structure.[15]

In order to improve the mechanical oscillation performances of self-oscillating gel, we also designed a self-oscillating hydrogel with topologically "polyrotaxane-interlocked" structure.[68] In our hydrogel, double-bond modified PEG/α-CD polyrotaxane was utilized as the cross-linking agent (Figure 7) instead of the traditionally used BIS. In such polymer networks, the mobility of polymer chains is strongly enhanced, because the ring-like molecules trapped in the polyrotaxane can freely rotate and slide along the axles, even in the cases of gels.[69-71] Therefore, the "polyrotaxane-interlocked" hydrogel can respond very quickly to external stimuli and undergoes a large deformation. When immersed into the BZ reaction solution, the topological hydrogel can exhibit large mechanical oscillation compared with the traditional BIS-crosslinked hydrogel. This approach not only provides an alternative method to improve the performances of self-oscillating gels, but also offers some clues for

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constructing new autonomic soft actuators and molecular devices.

In addition to the above mentioned topological self-oscillating gels, some other attempts by utilizing unique crosslinker also provide provoking clues for developing new self-oscillating gels. In Epstein and Xu's work,[29] they designed a octahedral ruthenium bipyridine complex (active crosslinker) and utilized it as both the crosslinker and the catalyst for bridging the BZ reaction and the hydrogels (Figure 8). A periodical volume oscillation of this hydrogel can also be observed in the BZ reaction. However, the volume swelling/deswelling behavior behaves in an inverted way compared with the traditional self-oscillating gels cross-linked by BIS.[5] Namely, the gel shrinks when the octahedral ruthenium complex is in the oxidized state while expands when the octahedral ruthenium complex is in the reduced state.
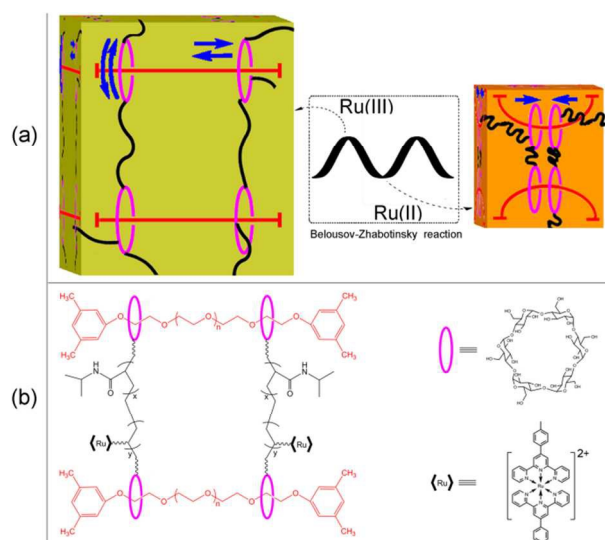


Figure 7 (a) Conceptual illustration of the self-oscillatory network variation in the BZ reaction and (b) the chemical structure of the topologically "polyrotane-interlocked" auto-active gel. Reproduced with permission from ref.[68]
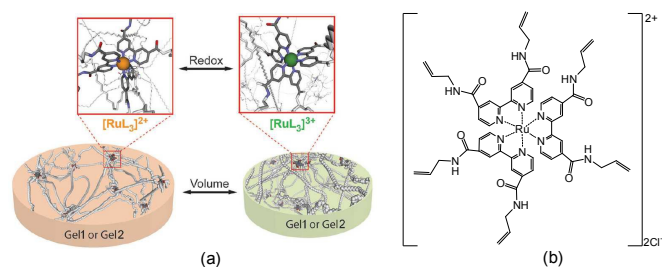


Figure 8 (a) Conceptual illustration of the autonomous volume swelling/deswelling of self-oscillating gels crosslinked by active hyper cross-linker and (b) the chemical structure of the active hyper cross-linker. Reproduced with permission from ref.[29]

Topological structure also leads to some fascinating functionalities. An interesting example was presented by the autonomous shuttling of the pseudorotaxane system driven by a pH-oscillator (Figure 9).[67] The pseudorotaxane system is composed of cucurbit[7]uril as the host molecule and bodipy as the guest molecule. When the pH value is lower than 5, bodipy is protonated and cucurbit[7]uril moves to the alkyl chain part, while a pH value higher

than 7 leads to a deprotonation of bodipy and cucurbit[7]uril shuttles to the bodipy part. When the pseudorotaxane system is properly coupled with the pH oscillator in which the pH value changes periodically, an autonomous shuttling behavior of the host molecule can be observed. This work gives the first example of autonomic molecular devices and may inspire further study on intelligent molecular machines. Besides, many other functionalities can be realized by designing new topological structures, like self-oscillating micelles, concentration oscillation, spiral waves and concentric waves etc..[72, 73]
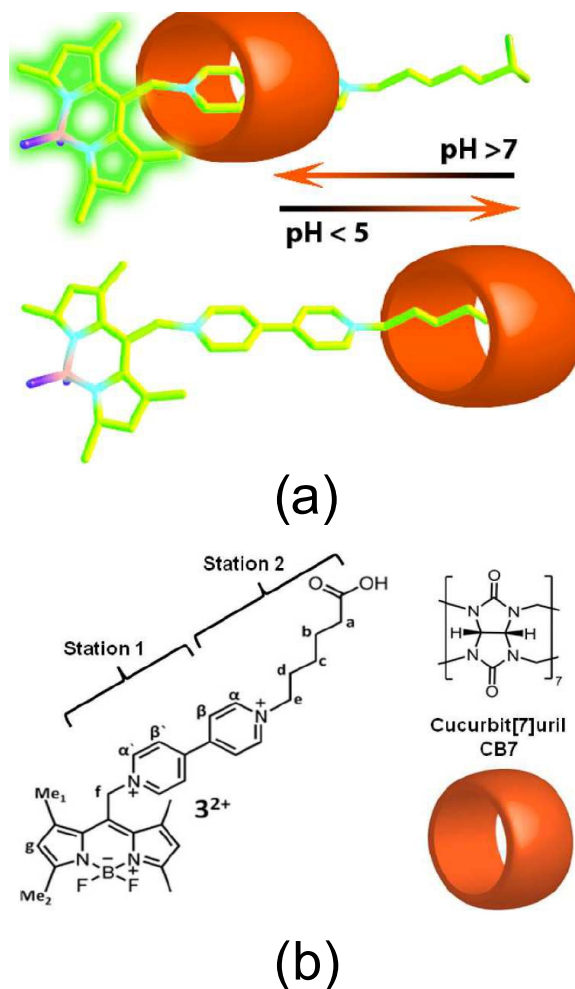


Figure 9 (a) Illustration of the autonomous shuttling motion of the pseudorotaxane system driven by a pH-oscillator and (b) the chemical structure of cucurbit[7]uril (CB7) and the fluorogenic "axle unit" with two potential stations for CB7. Reproduced with permission from ref.[67]

### 3.2.4 Introduction of supramolecular interactions

With the rapid development of supramolecular chemistry, some work in the field of SOPs also introduces supramolecular interactions and pays attention to the interface of supramolecular chemistry and nonlinear chemistry. For example, a recently developed Ruthenium complex $Ru(tpy)_2$ can also be an efficient catalyst for the BZ reaction[74] and utilized to design SOPs systems. The combination of the BZ reaction and $Ru(tpy)_2$ has been theoretically demonstrated and

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has inspired many interesting SOPs systems.[75-78] Expect for the redox oscillation during the BZ reaction which is similar to the redox oscillation of Ru(bpy)$_3$, Ru(tpy)$_2$ also exhibits unique adaptive property upon redox stimuli, as shown in Figure 10. When Ru ion is in an oxidized Ru(III) state, one terpyridine ligand coordinates with Ru(III) to form mono-complex (Ru(III)(Tpy)), while reduced Ru(II) forms a biscomplex (Ru(II)(Tpy)$_2$) with terpyridine ligand. In this way, Ru(II)(Tpy)$_2$ works as a dynamic conjunction point from a perspective of supramolecular chemistry. For more details, one can refer to a recent review by T. Ueki and R. Yoshida.[28]
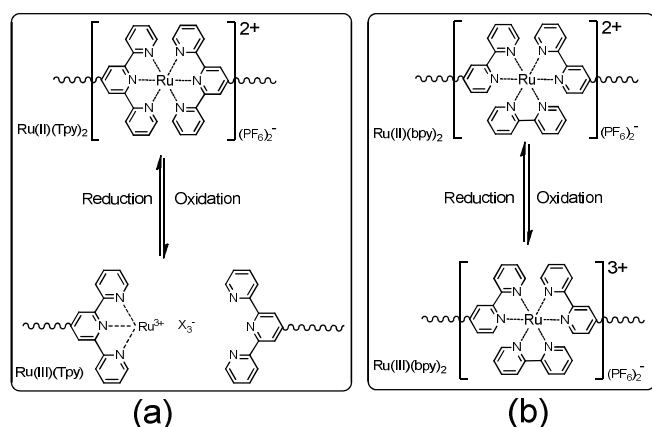


**(a)**          **(b)**

Figure 10 Reversible complex formation of terpyridine-ruthenium complex Ru(II)(Tpy)$_2$ and redox variation of bipyridine-ruthenium complex Ru(II)(bpy)$_3$ driven by the BZ reaction. Reproduced with permission from ref.[77]

### 3.3 Engineering in self oscillating polymer systems

After modular analyzing and stepwise design of SOPs systems, the engineering aspects should be considered in the next step. By utilizing the engineering techniques, one can construct new SOPs systems, realize novel functionalities, and integrally control the self-oscillating behavior at a higher level. The following three aspects will be considered: (1) The techniques for on-line study of self-oscillating behaviors; (2) Engineering for biomimetic construction of self-oscillating gels; (3) Integral control of the SOPs systems by external parameters.

### 3.3.1 On-line techniques for study of self-oscillating behaviors

To demonstrate the self-oscillating behaviors, an on-line technique should be at least established according to the types of SOPs systems. For polymer solutions and microgel dispersions, the self-oscillating behavior of the systems can be monitored by detection of UV-Vis spectra, rheology curves, DLS, fluorescence signal *etc*. The oscillating behavior of hydrogels, normally the volume changes and the colorful chemical wave propagation, can be on-line observed by a CCD-equipped microscopic. Besides, some newly developed techniques also provide powerful demonstration of the self-oscillating behaviors, for instance, AFM, QCM-D and micro-force sensing.

**UV-Vis**

UV-Vis spectrum is a common method for on-line detection of self-oscillating behaviors in solution systems or suspension systems. UV-Vis spectra curves are often recorded as time-dependent profiles at a certain wavelength. For the SOPs systems driven by the BZ reaction, the metal catalysts exhibit periodical redox oscillation and the color change can be meanwhile observed. Therefore, the occurrence of the BZ oscillation can be revealed by the periodical variation of the transmittance or absorbance in the system, even in a gel form.[79] Besides, the redox oscillation-induced soluble-insoluble change of polymer chains[13, 55, 57, 61, 80, 81] or aggregation-disaggregation of microgels[51, 82-85] can also be revealed by the transmittance variation of the system. This is based on the fact that the insoluble change of polymer chains or microgel aggregation can induce the turbidity increase and soluble change of polymer chains or a disaggregation process will lead to a transparent system. In order to obtain the signal from conformational change of polymer chains, the wavelength at an isobestic point (a wavelength where the reduced state and the oxidized state of the polymer have the same absorbance) is often utilized to avoid the effect from the redox oscillation. For example, Yoshida and coworkers[80] firstly demonstrated a rhythmical soluble/insoluble changes of polymer chains by spectrophotometer. The soluble/insoluble oscillation of the polymer chains are revealed by the periodical optical transmittance change at an isosbestic point of 570 nm. As illustrated in Figure 11, the reduction of Ru(bpy)$_3$ induces an turbidity increase and the oxidation of Ru(bpy)$_3$ leads to a decrease of the turbidity. Therefore, the periodical optical transmittance change indicates the soluble/insoluble oscillation of the polymer chains driven by the BZ reaction.
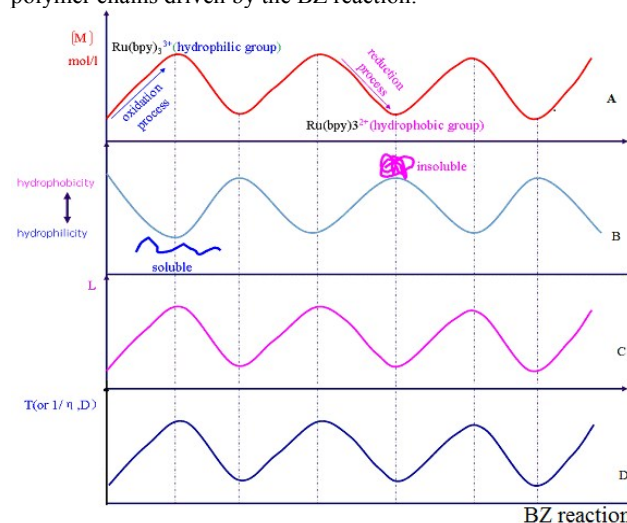


Figure 11 In-phase variations of Ru(bpy)$_3$ and the self-oscillating behaviors against time. A: [M]-Content variation of oxidized Ru(bpy)$_3$; B: Hydrophilicity variation of polymer chains; C:L-Length of self-oscillating gels; (D) T-Transmittance of self-oscillating polymer solution or microgel suspension，1/η-Reciprocal of apparent viscosity of self-oscillating polymer solution or microgel suspension，D-Diameter of self-oscillating microgel. Dotted lines represent the phase relation among these changes. Reprinted with permission from ref.[9]

**Microscope images and videos**

Taking live videos from microscope equipped with a CCD and

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connected to a computer is a direct way to observe the volume swelling/deswelling and the chemical wave propagation in self-oscillating gel systems.[5, 68] However, this method requires a high contrast between the gel system and the environmental solutions. If the color of the hydrogel is not strong enough, the volume change of the gel may not be clearly observed. Many self-oscillating behaviors are directly studied by on-line observation utilizing microscope. For instance, Shiraki and Yoshida studied the autonomous intestine-like motion of tubular self-oscillating gel by microscope. The chemical wave, mechanical motion, and autonomous transport of gas bubble can be clearly seen from the time-course images of the tubular gel (Figure 12). By analyzing the videos and images, one can also get other parameters, such as the velocity of chemical wave propagation, the amplitude and frequency of mechanical oscillation, *etc.*.
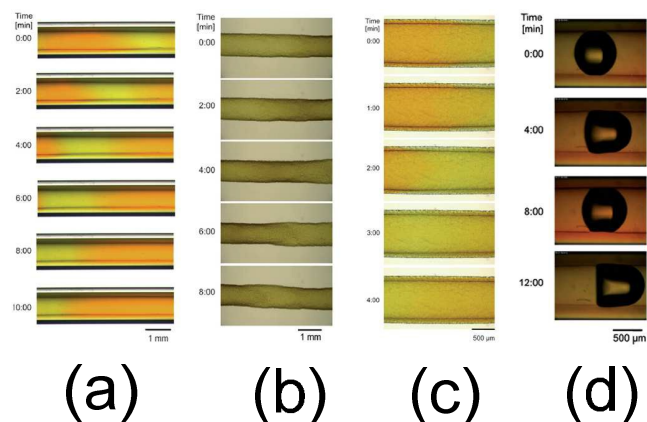


(a)        (b)        (c)        (d)

Figure 12 (a) Time-course images of the tubular self-oscillating gel attached to the inner wall of a glass capillary, (b) peristaltic motion of free standing tubular self-oscillating gel,  (c) peristaltic motion of the tubular gel with interpenetrating polymer network structure and (d) autonomous transport of a $CO_2$ bubble in the tubular gel. Reproduced with permission from ref.[23]

### Rheology curves

Viscosity oscillation is often detected by on-line measurement on a viscometer with a cylindrical spindle under constant shear rate. Generally, the viscosity self-oscillation is originated from the solubility difference of the polymer chain between the reduced state and oxidized state. In the reduced state, the polymer chain is in the globule state, which induces a relatively higher viscosity of the polymer solution. In contrast, an oxidation process of the polymer leads to a decrease of the viscosity. The viscosity difference between the reduced state and oxidized state of the polymer is at a scale of several mPa s (Figure 13a).[12, 86] In colloidal gel dispersion systems, the rheological properties behave in a different way. Both the swelling/deswelling of individual microgels and the dispersion/flocculation oscillation of the microgels can be revealed. From the time-dependent viscosity curve of the microgel dispersion, the dispersion/flocculation oscillation is followed by the swelling/deswelling oscillation. When the microgel is swollen or flocculated, the viscosity is higher while the viscosity is lowered when the microgel deswells or disperses (Figure 13b).[87] The recently developed SOPs systems based on the supramolecular chemistry can also be studied by viscometer. For example, Yoshida *et al*[76, 78] successfully realized viscosity oscillation in several SOPs systems based on the dynamic complex formation of $Ru(tpy)_2$ in the BZ

reaction. This kind of viscosity oscillation can be explained by the autonomous molecular weight change. When the $Ru(tpy)_2$ froms, the molecular weight is higher and the viscosity is also higher. In contrast, dissociation of $Ru(tpy)_2$ induces a decrease of the viscosity (Figure 13c).
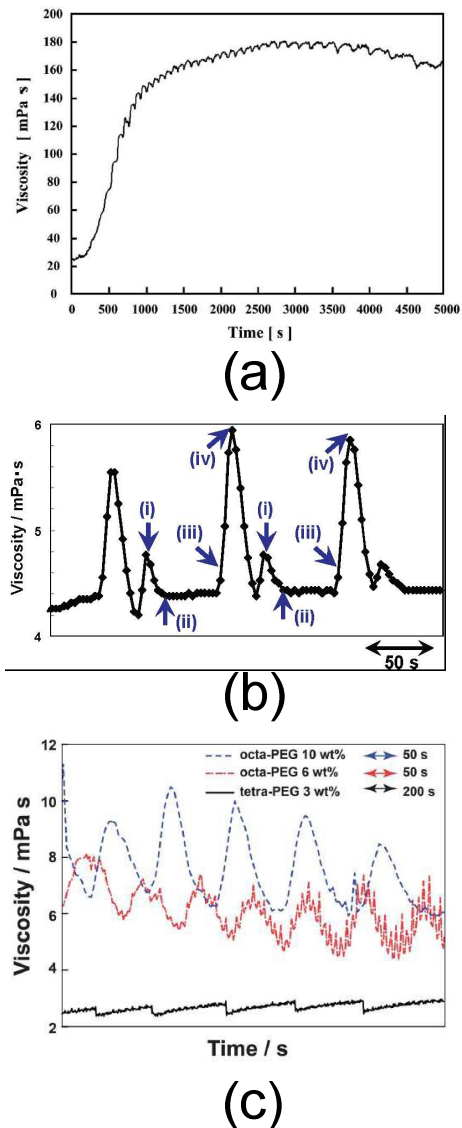


(a)



(b)



(c)

Figure 13 (a) Viscosity oscillation of Poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) solution, (b) viscosity oscillation profiles of self-oscillating microgel dispersions and (c) autonomous viscosity oscillation of terpyridine-terminated multi-armed PEG mediated by reversible Ruthenium-terpyridine interaction. Reproduced with permission from refs.[12, 78, 87]

### DLS

When light hits small particles on a scale less than the wavelength of the light, Rayleigh scattering occurs and scattering intensity fluctuates over time because of the Brownian motion of the particles. Therefore, the size of micelles, polymers, and nanoparticles can be confirmed by dynamic light scattering (DLS). For example, the transition between unimer and micellar structures can be studied

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by obtaining the hydrodynamic radius (Rh) as a function of time with the aid of time-resolved DLS (Figure 14).[72] By introducing traditional SOPs block Poly(NIPAAm-*co*-Ru(bpy)$_3$) into PEG chain, a block copolymer can be obtained (PEO-*b*- Poly(NIPAAm-*co*-Ru(bpy)$_3$)). In the reduced state of Ru(bpy)$_3$, Poly(NIPAAm-*co*-Ru(bpy)$_3$) block is hydrophobic and the polymer assembles into micellar structures, while the micellar disaggregates when the Ru(bpy)$_3$ is oxidized and the Poly(NIPAAm-*co*-Ru(bpy)$_3$) block changes into hydrophilic state. When Ru(bpy)$_3$ oscillates autonomously in the BZ reaction, the polymer system can undergoes a periodical unimer/micellar transition. Due to the size variation between unimer state and micellar state, the unimer/micellar transition can be studied by DLS.
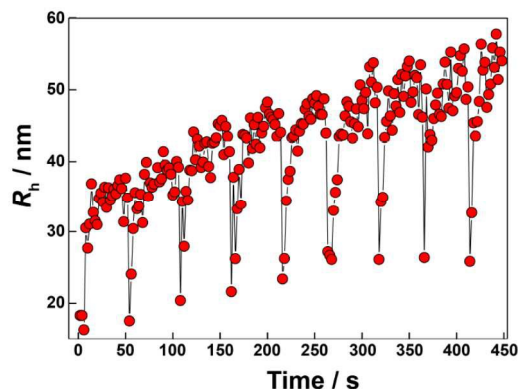


Figure 14 Rh oscillation profiles of PEO-*b*-Poly(NIPAAm-*co*-Ru(bpy)$_3$) in the BZ reaction solution determined by time-resolved DLS measurements. Reproduced with permission from ref.[72]
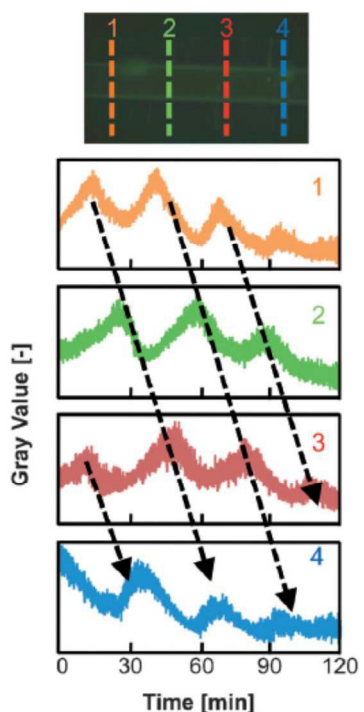


Figure 15 Fluorescent images of self-oscillating polymer brushes grafted on the inner surface of a glass capillary observed by a fluorescence microscope (top) and the fluorescence intensity variation at each position over time. Reproduced with permission from ref.[88]

**Fluorescence signal**

Fluorescence signal is a very sensitive method to study various systems, such as films, chemosensors, unimolecular layers *etc.* For SOPs systems, fluorescence signal mainly comes from the fluorescent molecules Ru(bpy)$_3$. When Ru(bpy)$_3$ is in the reduced state, it emit green light under the excitation at a wavelength of 425 nm. While in the oxidized state, Ru(bpy)$_3$ is not fluorescent. Therefore, the self-oscillating behaviors can be studied by recording and analyzing the fluorescence signal from the Ru(bpy)$_3$ moieties in a fluorescence microscope systems. For example, Yoshida *et al*[88] successfully observed periodical change of the fluorescence intensity in a brush system grafted onto a glass substrate or the inner surface of a glass capillary (Figure 15). Besides, one can also get information of the 3D distribution of the Ru(bpy)$_3$ and the microstructure in gel network by utilizing confocal microscopy.[29]

**SPM**

Scanning probe microscope (SPM) gives direct information of the self-oscillating behavior of the polymer chains. The Z-axis movement of the cantilever in SPM system reveals the autonomous conformation change of SOPs chains.[89] To observe the self-oscillating behavior of SOPs, polymer chains should be first immobilized onto a substrate. Generally, an *N*-succinimidyl group (NAS) is copolymerized into SOPs for the linkage of the polymer to the substrate. After immobilization, the nanomechanical motion induced by conformational change of the SOPs chains can be studied by in-situ SPM in the BZ reaction solution (Figure 16).
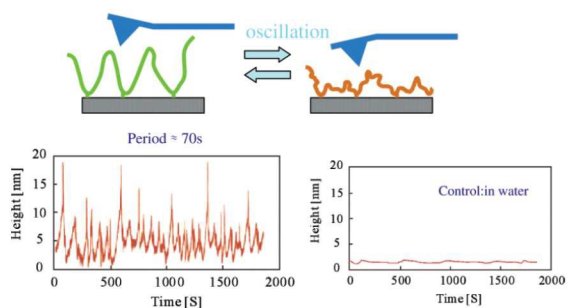


Figure 16 AFM observation of self-oscillating behaviors of polymer chains immobilized on a aminosilane-modified glass surface. Illustration of the interaction between the AFM cantilever and the polymer chain (top), the height imformation variation over time (lower left) and the control experiment (lower right). Reproduced with permission from ref.[89]

**QCM-D**

Quartz crystal microbalance with dissipation (QCM-D) is an ultra-sensitive (up to a scale of ng) method for mass analysis and is extensively applied in various fields. During the oscillation of SOPs, the polymer chains exhibit periodical soluble/insoluble change, which is accompanied by the adsorption/desorption of water molecules. Therefore, the autonomous change in the mass and structure can be detected by QCM-D. The self-oscillatory behavior of the resonance frequency ($\Delta f$) and dissipation ($\Delta D$) reveals the periodical change of the polymer chains in the BZ reaction. For example, this technique has been utilized to detect the periodic change of viscosity and

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density in an chemical oscillating reaction[90] and to directly observe the periodic swelling and collapse of SOPs chains in the BZ reaction.[91] As can be seen in Figure 17, Δf self-oscillation indicates the solubility change of the self-oscillating polymer chains and the stable oscillation period suggests the synchronization between periodic change in Δf and cyclic solubility change of the polymer chains driven by the BZ reaction. This demonstrates that QCM-D is an effective and reliable method for studying self-oscillating behavior in SOPs systems.
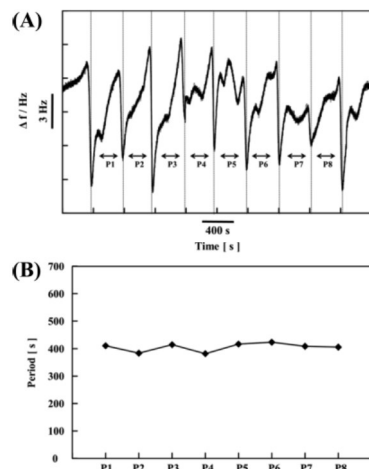


Figure 17 (A) Δf self-oscillation induced by the self-oscillatory water adsorption/desorption on the polymer chain in the BZ reaction and (B) the period of resonance frequency self-oscillation. Reproduced with permission from ref.[91]
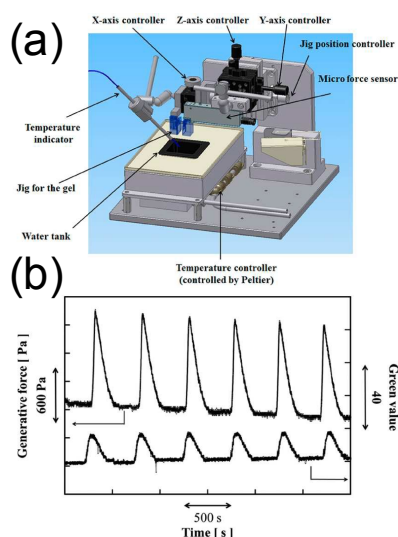


Figure 18 (a) Overall view illustration of the apparatus for measuring the generative force of self-oscillating gel driven by the BZ reaction and (b) time-dependent variation of generative force and the green value of the Poly(NIPAAm-*co*-Ru(bpy)₃-*co*-AMPS) gel. Reproduced with permission from ref.[92]

**Micro-force sensing**

Force generated simultaneously with the periodical volume

oscillation of self-oscillating gels is a very important parameter for autonomous gel actuators. However, it is often difficult to determine the exact force value because the gels are small and oscillates on a very small scale. There is also no commercially available apparatus for measuring the generative force. Recently, Yusuke Hara *et al.*[92] developed a self-designed apparatus with a microforce sensor for measuring the generative force of small-sized (1 mm³) self-oscillating gels (Figure 18a). The self-oscillating gel is sandwiched between the jigs and immersed into an aqueous solution containing certain concentration of the BZ reaction reactants. The microforce sensor transduces the generative force into readable signal. As the self-oscillating polymer gel converts the chemical oscillation into mechanical swelling/deswelling, a *ca.* 972 Pa generative force can be observed, which is about a hundredth the generative force of the muscle in the body. The oscillation of generative force is well synchronized with the redox oscillation of the BZ catalyst as revealed by the oscillatory green value (Figure 18b).

**ITC and US-DSC**

Calorimetry is another effective method for studying the self-oscillating systems because there always exits energy change during chemical or physical processes. For example, calorimetry has been demonstrated to be an effective method to study the BZ reactions.[93-95] Compared with the conventional calorimetry method, isothermal titration calorimetry (ITC) and ultrasensitive differential scanning calorimetry (US-DSC) can detect small energy variation. For example, Zhang *et al*[96] systematically studied the effects of temperature and stirring on the self-oscillating behaviors in the periodic swelling/deswelling of Poly(NIPAAm-*co*-Ru(bpy)₃) microgels, utilizing ITC and US-DSC techniques (Figure 19).
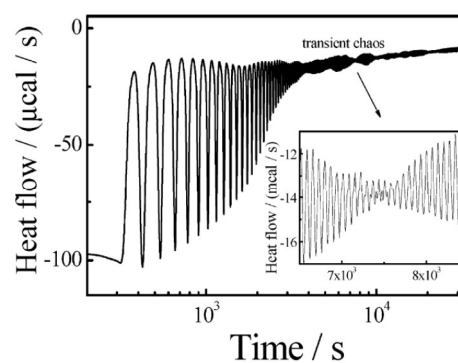


Figure 19 Time-dependent heat flow of Poly(NIPAAm-*co*-Ru(bpy)₃) microgel dispersion in the BZ reaction solution. Reproduced with permission from ref.[96]

**3.3.2 Gel engineering in self oscillating polymer systems**

Various functional gel actuators activated by temperature, pH, magnetic field *etc.* have been developed, such as the artificial muscles, robot hands, artificial fish, artificial loopers *et al.*[1, 97, 98] Similarly, biomimetic actuators can also be constructed based on the self-oscillatory volume change of self-oscillating gels, utilizing tailor-made gel engineering[8] method. Many examples have been reported, such as self-beating motion which imitates heartbeat,[5, 6, 99, 100] intestine-like actuators,[23] autonomous transportation surface,[19, 21, 22, 101] self-walking gel robot,[24, 25] ciliary motion actuator[26] and autonomous rotation actuator[102].

A heterogenous gel can exhibit anisotropic motion, which promotes the displacement of the gel like insects.[103] Based on this strategy, many interesting self-propelled gel systems have been constructed. A recent example by Hara *et al*[104] observed that the self-oscillating gel containing gradient concentration of Ru(bpy)$_3$ can climb up a meniscus wall in the BZ reaction, just like the climbing motion of the insects. When the BZ reaction starts in the gel network, a periodical bending/stretching motion occurs and changes the balance of the surface tension. Consequently, the gel climbs up along the wall. When the gel is in the rectangular shape, it advances along the length and moved up the wall. When the gel is in the square shape, it moves randomly. Surprisingly, the maximum speed of the gel robot can go as fast as 1.5 mm/s, which is much higher than the swelling/deswelling speed of the gel.

Recently developed tailor-made printing method provides an effective and efficient approach to self-oscillating gels. The introduction of Ru(bpy)$_3$ moieties into polymer systems is based on a succinimide–amine coupling reaction between amine-containing polymers and bis(2, 2′ -bipyridine) 4′ -methyl 4-carboxybipyridine ruthenium *N*-succinimidyl ester bis(hexafluorophosphate).[27, 105, 106] The immobilized BZ catalysts are located along the gelatin chain on a molecular scale and various patterns can be obtained by a simple printing procedure. The fabrication is completed by two steps: one polymerization step to create a cross-linked film and a second printing step to create the reactive patterns. For the printing procedure, the BZ catalyst is delivered in an ink solution of DMF supplied by a micro-dispenser or inkjet printer (Figure 20).
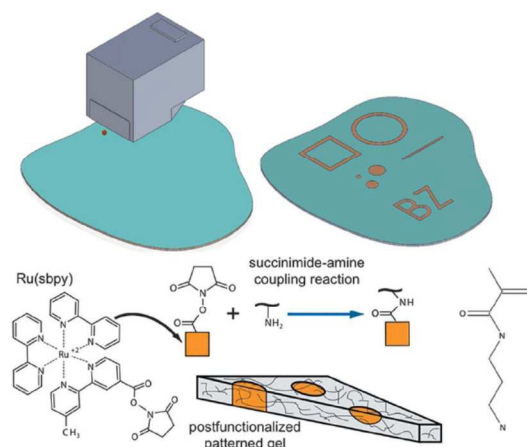


Figure 20 Schematic illustration of the reactive printing procedure to produce complex patterns such as spots, lines, shape outlines, and letters (upper) and the chemical process of succinimide–amine coupling reaction (lower). Reproduced with permission from ref.[106]

### 3.3.3 Integral control of the self-oscillating polymer systems by external parameters

From the modular analysis of SOPs systems, it can be seen that the self-oscillating behaviors can be tuned by both tailor-made design and construction of SOPs and precisely adjusting the properties of the BZ reaction. To obtain a SOPs system, SOPs and the BZ reaction should be properly coupled. For coupled SOPs systems, the self-oscillating behaviors can also be integrally controlled by external parameters, such as light, mechanical force, *etc*.

The BZ reaction catalyst Ru(bpy)$_3$ has a metal to ligand charge transfer (MLCT) absorption at 453 nm in the reduced state and 421

nm in the oxidized state.[80] A proper illumination may promote producing some important intermediates, such as Br$^-$ (inhibitor) or HBrO$_2$ (activator).[11] Therefore, the self-oscillating behavior can be regulated by light irradiation.[107, 108] The light-controlled self-oscillating behaviors have been demonstrated by both the theoretical simulation and experimental results. In Balazs's model, they not only considered the BZ reaction and the mechanical aspects of the gel, but also argued that their model can be utilized to investigate the effect of light on BZ gels and demonstrated that the gels can exhibit spontaneous movement away from an illuminated region.[109, 110] In an experimental study, Gao and Epstein[111] observed that self-oscillating gel (Poly(NIPAAm-*co*-Ru(bpy)$_3$-AMPS) inside a capillary can exhibit photophobic and phototropic movement, just like phototropic behavior of sunflowers (Figure 21). Patterned illumination was utilized in the BZ gels to study the photophobic and phototropic movement behaviors. They found that when higher intensity illumination by LED light with a wavelength of 460 nm is used, the oscillation frequency of the BZ gel in the dark region (I = 205.0 μW cm$^{-2}$) is higher than that in the bright region (I = 904.0 μW cm$^{-2}$) and the gel moves toward the dark region (photophobic behavior). In contrast, when lower intensity illumination is used, light promotes the local oscillatory frequency. Therefore, the oscillation frequency of the gel in the brighter region (I = 106.0 μW cm$^{-2}$) is higher than that in the darker region (I = 32.9 μW cm$^{-2}$) and the gel moves toward the bright region (phototropic behavior).
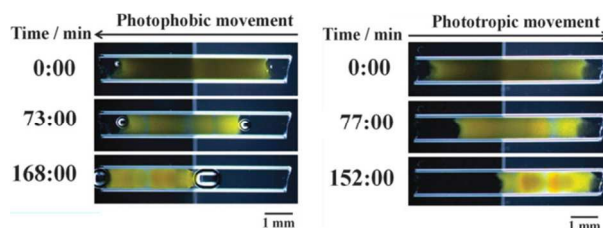


Figure 21 Photophobic and phototropic movement of BZ photosensitive gel within a capillary. Left: Photophobic movement under illumination with intensity of 205.0 μW cm$^{-2}$ (darker region) and 904.0 μW cm$^{-2}$ (bright region). Right: Phototropic movement under illumination with intensity of 32.9 μW cm$^{-2}$ (darker region) and 106.0 μW cm$^{-2}$ (bright region). Reproduced with permission from ref.[111]
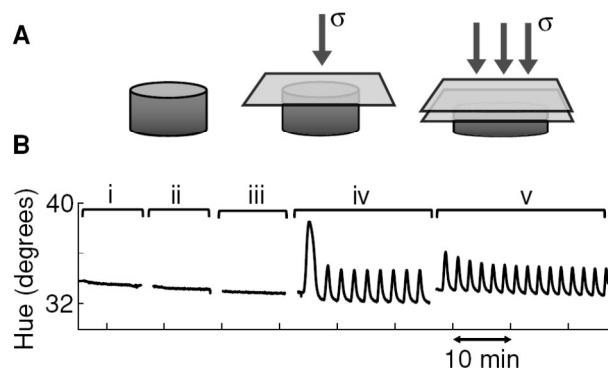


Figure 22 Mechanically triggered resuscitation of the the BZ reaction in Poly(NIPAAm-*co*-Ru(bpy)$_3$) gels. (A) Schematic of a gel being macroscopically compressed. (B) The resuscitation of the BZ reaction by exerting increasing amounts of stress to the gel: i) 0.1 kPa, ii) 0.3 kPa, iii) 0.4 kPa, iv) 1.2 kPa, and v) 5.6 kPa. Reproduced with permission from ref.[112]

Another important parameter during the mechanical oscillation of gels is the generative force. In chapter 3.3.1, it has been analyzed that the generative force can be measured by unique sensing devices. In an opposite point of view, the self-oscillating behaviors can also be adjusted by mechanical force.[112, 113] A typical example is given by Vliet and coworkers.[112] They demonstrated that in self-oscillating gel systems, the BZ reaction in a steady state upon depletion of reagents can be resuscitated by stimuli of compressive stress (Figure 22). This is because that such macroscopic compression increases the volume fraction of polymer chains containing the BZ catalysts and the oscillation starts again utilizing the unreacted reagents. This mechanical resuscitation behavior may be utilized to design novel gel-based pressure sensors.

As a critical technique for biochips, microfluidics is now attracting more and more attention, not only in the field of biotechnology, but also in the fields of chemistry and materials.[114] This new technique is recently introduced into SOPs systems and has been demonstrated to be an effective way to enhance the performances of SOPs systems. Epstein and Xu[115] demonstrated that a continuous flow of reactant solution in microfluidic channels leads to larger volume changes of self-oscillating gels than that without flow (Figure 23). In such system, they also observed so far the largest volume change of self-oscillating gels driven by the BZ reaction. These results not only offers a facile approach to optimizing the performances of self-oscillating gels, but also represents for an insightful method for designing high performance chemomechanical actuators by engineering approach.
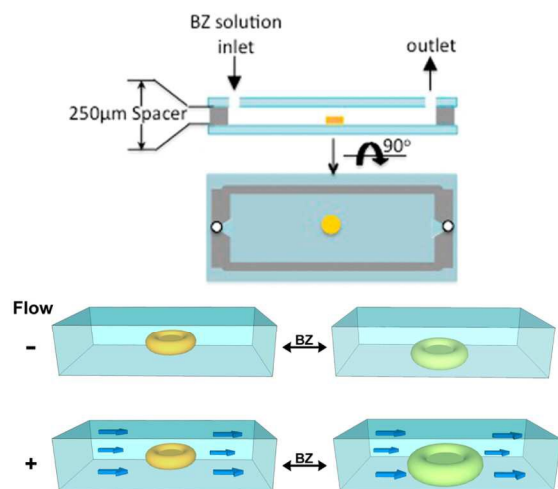


Figure 23 Self-oscillating behaviors in a microfluidic channel. Microfluidic setup fabricated for monitoring the volume change of the microgel (upper) and chemomechanical oscillation illustration of the active gels with and without flow of the BZ reaction solution (lower). Reproduced with permission from ref.[115]

# 4 Conclusion and outlook

As a creative example of high-level polymer-based intelligent systems, SOPs systems are attracting more and more attention. It is worth considering such kind of systems from two aspects: (1) It's a good platform for simulating and understanding self-oscillating phenomena in nature, such as heartbeat, brain waves, pulsatile secretion of hormones, cell cycles and biorhythms; (2) The coupling of driving source and the responsive components also provides some clues for constructing other embedded intelligent systems.

Using QCM-D, AFM and other techniques, it has been directly demonstrated that the polymer exhibit conformational change in SOPs systems and gels can show periodical volume swelling/deswelling. However, there is still no definite model for explaining the autonomous oscillating behaviors, though several possible mechanisms have been proposed, hydrophilicity change of the polymer chains, phase transition temperature shift, *etc.*. In some specific examples, the oscillation process even behaves in a completely opposite way. For instance, in Epstein and Xu's work, they observed an inverted volume swelling/deswelling behavior[29] and Konotop also obtained the same phenomenon when they introduced the BZ catalyst into polymer networks by physical interaction.[32] No matter what the molecular mechanism behind is, the autonomous soluble/insoluble behavior of polymer chains and periodical volume change of gels driven by the chemical oscillating reactions have given some provoking clues for constructing soft actuators and other intelligent systems.

For the design and construction of SOPs systems, one can consider modularly from both aspects of the chemical oscillating reaction and the responsive components. In this way, the properties of SOPs systems can be easily adjusted and improved. Moreover, when every part has been well designed and precisely organized, the performances can also be controlled by some external parameters. To achieve new functionalities and applications of SOPs systems, engineering aspects plays an increasingly important role. Except for the on-line techniques for studying the self-oscillating behavior, gel engineering and other newly developed engineering techniques also help a lot in design of new SOPs systems, for instance the self-oscillating behavior in microfluidic channels. It is also worth mentioning that theoretical simulation, which is not included in the present review, is an effective tool for the construction of SOPs systems, especially for those that are unexplored and difficult to construct experimentally.[110, 116-124]

In conclusion, SOPs systems are still in the primary stage from a perspective of engineering and it is better to treat it as an integrated systems. Because the construction of such systems has gone beyond the design and preparation of SOPs themselves. Therefore, it may be more effective and easier to design such kind of systems in a modular and then an engineering way. Not only learning form nature gives endless inspiration and innovation for the construction of SOPs systems,[21, 23, 29, 103, 104, 115] but also exploration at the interfaces of other fields, such as supramolecular chemistry, system chemistry, biotechnology, nanoscience, photoelectricity also creates some new ideas.[15, 68, 72, 88, 125]

# Acknowledgements

# References

1.      L. D. Zarzar and J. Aizenberg, *Acc. Chem. Res.*, 2014, **47**, 530-539.

2.      M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Muller, C. Ober, M. Stamm, G. B. Sukhorukov, I.

Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov and S. Minko, *Nat. Mater.*, 2010, **9**, 101-113.

3.  D. Roy, J. N. Cambre and B. S. Sumerlin, *Prog. Polym. Sci.*, 2010, **35**, 278-301.

4.  R. Yoshida, H. Ichijo, T. Hakuta and T. Yamaguchi, *Macrom. Rapid Comm.*, 1995, **16**, 305-310.

5.  R. Yoshida, T. Takahashi, T. Yamaguchi and H. Ichijo, *J. Am. Chem. Soc.*, 1996, **118**, 5134-5135.

6.  R. Yoshida, T. Takahashi, T. Yamaguchi and H. Ichijo, *Adv. Mater.*, 1997, **9**, 175-178.

7.  H. Zhou, X. Ding, Z. Zheng and Y. Peng, *Soft Matter*, 2013, **9**, 4956-4968.

8.  R. Yoshida, *Adv. Mater.*, 2010, **22**, 3463-3483.

9.  H. W. Zhou, E. X. Liang, Z. H. Zheng, X. B. Ding and Y. X. Peng, *Prog. Chem.*, 2011, **23**, 2368-2376.

10. R. Yoshida, *Curr. Org. Chem.*, 2005, **9**, 1617-1641.

11. R. Yoshida and T. Ueki, *Npg Asia Mater*, 2014, **6**, e107, doi: 10.1038/am.2014.32.

12. Y. Hara and R. Yoshida, *J. Chem. Phys.*, 2008, **128**, doi: 22490410.1063/1.2931543

13. Y. Hara and R. Yoshida, *J. Phys. Chem. B*, 2008, **112**, 8427-8429.

14. D. Suzuki, T. Kobayashi, R. Yoshida and T. Hirai, *Soft Matter*, 2012, **8**, 11447-11449.

15. R. Mitsunaga, K. Okeyoshi and R. Yoshida, *Chem. Commun.*, 2013, **49**, 4935-4937.

16. Y. Hara and R. Yoshida, *J. Phys. Chem. B*, 2005, **109**, 9451-9454.

17. Y. Ito, M. Nogawa and R. Yoshida, *Langmuir*, 2003, **19**, 9577-9579.

18. S. Shinohara, T. Seki, T. Sakai, R. Yoshida and Y. Takeoka, *Chem. Commun.*, 2008, 4735-4737.

19. R. Yoshida and Y. Murase, *Colloid Surface B*, 2012, **99**, 60-66.

20. Y. Murase, S. Maeda, S. Hashimoto and R. Yoshida, *Langmuir*, 2009, **25**, 483-489.

21. Y. Murase, M. Hidaka and R. Yoshida, *Sensor Actuat B-Chem*, 2010, **149**, 272-283.

22. Y. Murase, R. Takeshima and R. Yoshida, *Macromol. Biosci*, 2011, **11**, 1713-1721.

23. Y. Shiraki and R. Yoshida, *Angew. Chem. Int. Ed.*, 2012, **51**, 6112-6116.

24. S. Maeda, Y. Hara, R. Yoshida and S. Hashimoto, *Adv. Robot.*, 2008, **22**, 1329-1342.

25. R. Yoshida, *Bull. Chem. Soc. Japan*, 2008, **81**, 676-688.

26. O. Tabata, H. Hirasawa, S. Aoki, R. Yoshida and E. Kokufuta, *Sens. Actuator A-Phys.*, 2002, **95**, 234-238.

27. M. L. Smith, K. Heitfeld, C. Slone and R. A. Vaia, *Chem. Mater.*, 2012, **24**, 3074-3080.

28. T. Ueki and R. Yoshida, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10388-10397.

29. Y. Zhang, N. Zhou, S. Akella, Y. Kuang, D. Kim, A. Schwartz, M. Bezpalko, B. M. Foxman, S. Fraden, I. R. Epstein and D. B. Xu, *Angew. Chem. Int. Ed.*, 2013, **52**, 11494–11498.

30. Y. Hara and R. A. Jahan, *Polymers*, 2011, **3**, 330-339.

31. Y. Hara and R. A. Jahan, *Manufacturing Systems Engineering*, 2012, **429**, 42-45.

32. I. Y. Konotop, I. R. Nasimova, N. G. Rambidi and A. R. Khokhlov, *Polym. Sci. Ser. B*, 2011, **53**, 26-30.

33. P. A. Nogueira, H. Varela and R. B. Faria, *Chem. Phys. Lett.*, 2012, **530**, 137-139.

34. T. Bansagi, V. K. Vanag and I. R. Epstein, *Science* , 2011, **331**, 1309-1312.

35. V. Petrov, Q. Ouyang and H. L. Swinney, *Nature*, 1997, **388**, 655-657.

36. V. Petrov, V. Gaspar, J. Masere and K. Showalter, *Nature*, 1993, **361**, 240-243.

37. E. J. Reusser and R. J. Field, *J. Am. Chem. Soc.*, 1979, **101**, 1063-1071.

38. R. M. Noyes, R. J. Field and E. Koros, *J. Am. Chem. Soc.*, 1972, **94**, 1394-1395.

39. R. J. Field, R. M. Noyes and E. Koros, *J. Am. Chem. Soc.*, 1972, **94**, 8649-8664.

40. A. N. ZAIKIN and A. M. ZHABOTINSKY, *Nature*, 1970, **225**, 535-537.

41. G. Schmitz, *Phys. Chem. Chem. Phys.*, 2011, **13**, 7071-7080.

42. K. R. Sharma and R. M. Noyes, *J. Am. Chem. Soc.*, 1976, **98**, 4345-4361.

43. K. R. Sharma and R. M. Noyes, *J. Am. Chem. Soc.*, 1975, **97**, 202-204.

44. P. D. Kepper and I. R. Epstein, *J. Am. Chem. Soc.*, 1982, **104**, 49-55.

45. S. D. Furrow and R. M. Noyes, *J. Am. Chem. Soc.*, 1982, **104**, 38-42.

46. S. D. Furrow and R. M. Noyes, *J. Am. Chem. Soc.*, 1982, **104**, 45-48.

47. E. Poros, V. Horvath, K. Kurin-Csorgei, I. R. Epstein and M. Orban, *J. Am. Chem. Soc.*, 2011, **133**, 7174-7179.

48. O. Pesek, L. Schreiberova and I. Schreiber, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9849-9856.

49. C. C. Jolley, K. L. Ode and H. R. Ueda, *Cell reports*, 2012, **2**, 938-950.

50. I. R. Epstein, *Chem. Commun.*, 2014, **50**, 10758-10767.

51. D. Suzuki and R. Yoshida, *Macromolecules*, 2008, **41**, 5830-5838.

52. T. Ueki, M. Watanabe and R. Yoshida, *Angew. Chem. Int. Ed.*, 2012, **51**, 11991-11994.

53. J. Delgado, N. Li, M. Leda, H. O. Gonzalez-Ochoa, S. Fraden and I. R. Epstein, *Soft Matter*, 2011, **7**, 3155–3167.

54. R. Tomasi, J.-M. Noël, A. Zenati, S. Ristori, F. Rossi, V. Cabuil, F. Kanoufib and A. Abou-Hassan, *Chem. Sci.*, 2014, **5**, 1854-1859.

55. Y. Hara, T. Sakai, S. Maeda, S. Hashimoto and R. Yoshida, *Journal of Physical Chemistry B*, 2005, **109**, 23316-23319.

56. Y. Hara and R. A. Jahan, *Advanced Materials Research:Manufacturing Systems Engineering*, 2012, **429**, 46-49.

57. T. Yamamoto and R. Yoshida, *React. Funct. Polym.*, 2013, **73**, 945-950.

58. M. L. Smith, C. Slone, K. Heitfeld and R. A. Vaia, *Adv. Funct. Mater.*, 2013, **23**, 2835-2842.

59. T. Arimura and M. Mukai, *Chem. Commun.*, 2014, **50**, 5861-5863.

60. Y. Hara, H. Mayama and K. Fujimoto, *J. Phys. Chem. B*, 2014, **118**, 6931-6936.

61. Y. Hara, K. Fujimoto and H. Mayama, *J. Phys. Chem. B*, 2014, **118**, 608-612.

62. Y. Hara, H. Mayama, Y. Yamaguchi and K. Fujimoto, *Chem. Lett.*, 2014, **43**, 673-675.

63. M. Kim, *13th Annual Celebration for Undergraduate Research and Creative Performance (2014)*, 2014, **Paper 62**.

64. S. Tateyama, Y. Shibuta and R. Yoshida, *J. Phys. Chem.B*, 2008, **112**, 1777-1782.

65. S. Maeda, Y. Hara, R. Yoshida and S. Hashimoto, *Macrom. Rapid Comm.*, 2008, **29**, 401-405.

66. S. R. Pullela, Q. Wang and Z. Cheng, *Advances in Nanoparticles*, 2013, **2**, 94-98.

67. O. Buyukcakir, F. T. Yasar, O. A. Bozdemir, B. Icli and E. U. Akkaya, *Org. Lett.*, 2013, **15**, 1012-1015.

68. H. W. Zhou, Y. R. Wang, Z. H. Zheng, X. B. Ding and Y. X. Peng, *Chem. Commun.*, 2014, **50**, 6372-6374.

69. J. Araki and K. Ito, *Soft Matter*, 2007, **3**, 1456-1473.

70. A. Bin Imran, T. Seki, T. Kataoka, M. Kidowaki, K. Ito and Y. Takeoka, *Chem. Commun.*, 2008, 5227-5229.

71. C. M. Zhao, Y. Domon, Y. Okumura, S. Okabe, M. Shibayama and K. Ito, *J. Phys. Condens. Mat.*, 2005, **17**, S2841-S2846.

72. T. Ueki, M. Shibayama and R. Yoshida, *Chem. Commun.*, 2013, **49**, 6947-6949.

73. Y. Zhang, N. Li, J. Delgado, Y. Gao, Y. Kuang, S. Fraden, I. R. Epstein and B. Xu, *Langmuir*, 2012, **28**, 3063-3066.

74. J. Delgado, Y. Zhang, B. Xu and I. R. Epstein, *J. Phys. Chem. A*, 2011, **115**, 2208-2215.

75. H. W. Zhou, E. X. Liang, X. B. Ding, Z. H. Zheng and Y. X. Peng, *Chem. Commun.*, 2012, **48**, 10553-10555.

76. T. Ueno, K. Bundo, Y. Akagi, T. Sakai and R. Yoshida, *Soft Matter*, 2010, **6**, 6072-6074.

77. H. W. Zhou, E. X. Liang, Y. Pan, X. B. Ding, Z. H. Zheng and Y. X. Peng, *Rsc Adv.*, 2013, **3**, 2182-2185.

78. T. Ueki, Y. Takasaki, K. Bundo, T. Ueno, T. Sakai, Y. Akagi and R. Yoshida, *Soft Matter*, 2014, **10**, 1349-1355.

79. Y. Zhang, N. Li, J. Delgado, N. Zhou, R. Yoshida, S. Fraden, I. R. Epstein and B. Xu, *Soft Matter*, 2012, **8**, 3056-3061.

80. R. Yoshida, T. Sakai, S. Ito and T. Yamaguchi, *J. Am. Chem. Soc.*, 2002, **124**, 8095-8098.

81. Y. Hara and R. Yoshida, *Macrom. Rapid Comm.*, 2009, **30**, 1656-1662.

82. J. Shen, S. Pullela, M. Marquez and Z. D. Cheng, *J. Phys. Chem. A*, 2007, **111**, 12081-12085.

83. D. Suzuki, T. Sakai and R. Yoshida, *Angew. Chem. Int. Ed.*, 2008, **47**, 917-920.

84. D. Suzuki and R. Yoshida, *J. Phys. Chem. B*, 2008, **112**, 12618-12624.

85. D. Suzuki and R. Yoshida, *Polymer Journal*, 2010, **42**, 501-508.

86. M. Ueda, Y. Hara, T. Sakai, R. Yoshida, M. Takai and Y. Ito, *J. Polym. Sci. Pt. B-Polym. Phys.*, 2007, **45**, 1578-1588.

87. D. Suzuki, H. Taniguchi and R. Yoshida, *J. Am. Chem. Soc.*, 2009, **131**, 12058-12059.

88. T. Masuda, M. Hidaka, Y. Murase, A. M. Akimoto, K. Nagase, T. Okano and R. Yoshida, *Angew. Chem. Int. Ed.*, 2013, **52**, 7468-7471.

89. Y. Ito, Y. Hara, H. Uetsuka, H. Hasuda, H. Onishi, H. Arakawa, A. Ikai and R. Yoshida, *J. Phys. Chem. B*, 2006, **110**, 5170-5173.

90. M. Yoshimoto, H. Shirahama, S. Kurosawa and M. Naito, *J. chem. phys.*, 2004, **120**, 7067-7070.

91. Y. Hara, H. Mayama, Y. Yamaguchi, Y. Takenaka and R. Fukuda, *J. Phys. Chem. B*, 2013, **117**, 14351-14357.

92. Y. Hara, H. Mayama and K. Morishima, *J. Phys. Chem.B*, 2014, **118**, 2576-2581.

93. J. Ágreda, D. Barragán and A. Gómez, *J. Therm. Anal. Calorim.*, 2003, **74**, 875-881.

94. G. Nagy, E. Körös and I. Lamprecht, *J. Therm. Anal. Calorim.*, 1999, **57**, 209-223.

95. H. Sun, X. Wang, Y. Liu, Z. Nan and H. Zhang, *J. Therm. Anal. Calorim.*, 1999, **58**, 117-120.

96. F. Zhao, Y. W. Ding, Y. J. Lu, X. X. Liu and G. Z. Zhang, *J. Phys. Chem. B*, 2009, **113**, 6661-6665.

97. D. Morales, E. Palleau, M. D. Dickey and O. D. Velev, *Soft Matter*, 2014, **10**, 1337-1348.

98. L. Ionov, *Adv. Funct. Mater.*, 2013, **23**, 4555-4570.

99. R. Yoshida, H. Ichijo, T. Hakuta and T. Yamaguchi, *Macrom. Rapid Comm.*, 1995, **16**, 305-310.

100. R. Yoshida, T. Yamaguchi and E. Kokufuta, *J. Art. Org.*, 1999, **2**, 135-140.

101. Y. Murase, R. Takeshima and R. Yoshida, *Transactions of the Materials Research Society of Japan*, 2009, **34**, 171-174.

102. S. Maeda, Y. Hara, R. Yoshida, S. Hashimoto and Ieee, *A chemo-mechanical rotational actuator driven by BZ reaction*, Ieee, New York, 2006.

103. S. Maeda, Y. Hara, T. Sakai, R. Yoshida and S. Hashimoto, *Adv. Mater.*, 2007, **19**, 3480-3484.

104. Y. Hara, M. Saiki, T. Suzuki and K. Kikuchi, *Chem. Lett.*, 2014, **43**, 938-940.

105. M. L. Smith, C. Slone, K. Heitfeld and R. A. Vaia, *Adv. Funct. Mater.*, 2013, **23**, 2835-2842.

106. R. C. Kramb, P. R. Buskohl, C. Slone, M. L. Smith and R. A. Vaia, *Soft Matter*, 2014, **10**, 1329-1336.

107. S.-i. Shinohara, T. Seki, T. Sakai, R. Yoshida and Y. Takeoka, *Chem. Commun. ,* 2008, **39**, 4735-4737.

108. S. Shinohara, T. Seki, T. Sakai, R. Yoshida and Y. Takeoka, *Angew. Chem. Int. Ed.*, 2008, **47**, 9039-9043.

109. O. K. a. A. C. B. Pratyush Dayal *Langmuir*, 2009, **25** 4298–4301.

110. P. Dayal, O. Kuksenok and A. C. Balazs, *Macromolecules*, 2014, **47**, 3231-3242.

111. X. J. Lu, L. Ren, Q. Y. Gao, Y. M. Zhao, S. R. Wang, J. P. Yang and I. R. Epstein, *Chem. Commun.*, 2013, **49**, 7690-7692.

112. I. C. Chen, O. Kuksenok, V. V. Yashin, A. C. Balazs and K. J. Van Vliet, *Adv. Funct. Mater.,* 2012, **22**, 2535-2541.

113. T. Shiota, Y. S. Ikura and S. Nakata, *J. Phys. Chem. B*, 2013, **117**, 2215-2220.

114. S. Argentiere, G. Gigli, M. Mortato, I. Gerges and L. Blasi, *Italy Advances in microfluidics*, 2012, DOI: 10.5772/38072.

115. Y. Zhang, N. Zhou, N. Li, M. G. Sun, D. Kim, S. Fraden, I. R. Epstein and B. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 7341-7347.

116. P. Dayal, O. Kuksenok and A. C. Balazs, *PNAS*, 2013, **110**, 431-436.

117. V. V. Yashin, O. Kuksenok, P. Dayal and A. C. Balazs, *Rep. Prog. Phys.*, 2012, **75**, Artn 066601, Doi: 10.1088/0034-4885/75/6/066601.

118. P. Dayal, O. Kuksenok, A. Bhattacharya and A. C. Balazs, *J. Mater. Chem.*, 2012, **22**, 241-250.

119. D. Das, M. Das and D. S. Ray, *J. Chem. Phys.*, 2012, **137**, Artn 064103, Doi: 10.1063/1.4742726.

120. V. V. Yashin, O. Kuksenok and A. C. Balazs, *J. Phys. Chem. B*, 2010, **114**, 6316-6322.

121. V. V. Yashin, O. Kuksenok and A. C. Balazs, *Prog. Polym. Sci.*, 2010, **35**, 155-173.

122. V. V. Yashin and A. C. Balazs, *Macromolecules*, 2006, **39**, 2024-2026.

123. V. Yashin Victor and C. Balazs Anna, *Science,* 2006, **314**, 798-801.

124. O. Kuksenok, P. Dayal, A. Bhattacharya, V. V. Yashin, D. Deb, I. C. Chen, K. J. V. Vliete and A. C. Balazs, *Chem. Soc. Rev.*, 2013, **42**, 7257-7277.

125. I. Lagzi, B. Kowalczyk, D. W. Wang and B. A. Grzybowski, *Angew. Chem. Int. Ed.*, 2010, **49**, 8616-8619.