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PhysChemChemPhys: Perspective article

**Recent aspects of self-oscillating polymeric materials: Designing
self-oscillating polymers coupled with supramolecular chemistry
and ionic liquids science**

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Abstract

Herein, we summarise recent developments of self-oscillating polymeric materials based on the concepts of supramolecular chemistry, where aggregates of molecular building blocks with non-covalent bonds evolve the temporal or spatiotemporal structure. By utilising the rhythmic oscillation of the association/dissociation of molecular aggregates coupled with the redox oscillation by the BZ reaction, novel soft materials that express a similar function as those of living matter will be achieved. Further, from the viewpoint of materials science, our recent approach to prepare self-oscillating materials that operate long-term under mild conditions will be introduced.

1. Introduction

Since the first report in 1996,¹ we have systematically investigated self-oscillating polymer and gel that can exhibit spontaneous changes with temporal or spatiotemporal periodicity (called “temporal structure” or “spatiotemporal structure”, respectively) without applying any on-off switching of external stimuli.²⁻⁵ The self-oscillating polymeric materials involve a cyclic reaction network of the chemical oscillating reaction (the Belousov-Zhabotinsky (BZ) reaction⁶⁻⁸) in themselves, and they can directly convert the chemical energy of the reaction into mechanical energy. The overall process of the BZ reaction consists of the oxidation of an organic substrate (e.g., malonic acid (MA)) by an oxidising agent (e.g., sodium bromate (NaBrO₃)) in the presence of a strong acid (e.g., sulphuric acid) with the aid of a metal catalyst. Over the course of the reaction, the metal catalyst such as ruthenium bipyridine (Ru(bpy)₃) and ferroin undergoes a spontaneous rhythmic change between the reduced and oxidized states. As a result, temporal/spatiotemporal structures are created as one of dissipative structure in the chemical systems. The BZ reaction has many analogies to the tricarboxylic acid (TCA) cycle which is a key metabolic process in a living body, and it is recognised as a chemical model for understanding several autonomous phenomena in biological systems. For designing the self-oscillating polymer gel, we copolymerized the Ru(bpy)₃ catalyst to poly(*N*-isopropylacrylamide) (PNIPAAm) as a functional redox site to cause hydrophilicity/hydrophobicity changes of the polymer chain in response to the redox changes. (**Fig. 1**) This induces the change in LCST-type phase separation temperature of the polymer or

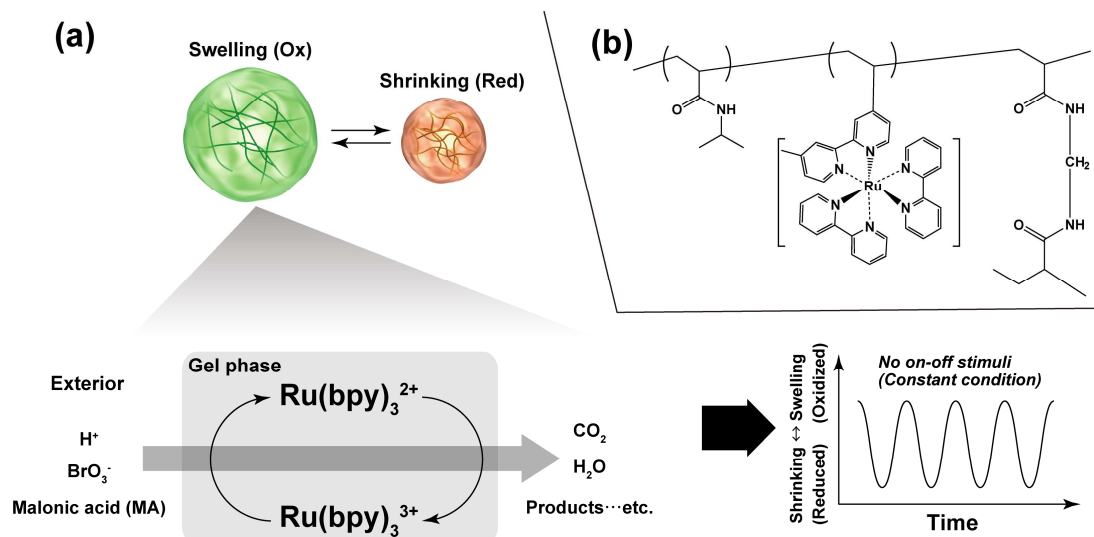


Fig. 1 (a) Basic concept of self-oscillation for poly(NIPAAm-*r*-Ru(bpy)₃) gel and (b) its chemical structure.

swelling ratio of the gel as well as the volume phase transition temperature, responding to the redox states. As a result of the redox oscillation caused by the BZ reaction, the polymer or the gel undergoes spontaneous soluble-insoluble or swelling-deswelling oscillation under constant condition.

The development of self-oscillating polymeric materials did pioneering work in the field of not only nonlinear chemistry and dynamics but also functional or biomimetic materials. The design concept has been expanding into the materials science to create autonomous biomimetic actuators⁹ such as artificial cilia¹⁰ and self-walking gel¹¹ functional self-oscillating surfaces,^{5, 12, 13} autonomous mass transport systems by intestine-like gel tube,¹⁴ functional fluid as the polymer solution or the microgel suspension,¹⁵⁻¹⁸ comb-type grafted self-oscillating gels showing fast and large swelling/shrinking behaviour,¹⁹ and so on (**Fig. 2**). Like living organisms that undergoes spontaneous changes with temporal periodicity, e.g., a

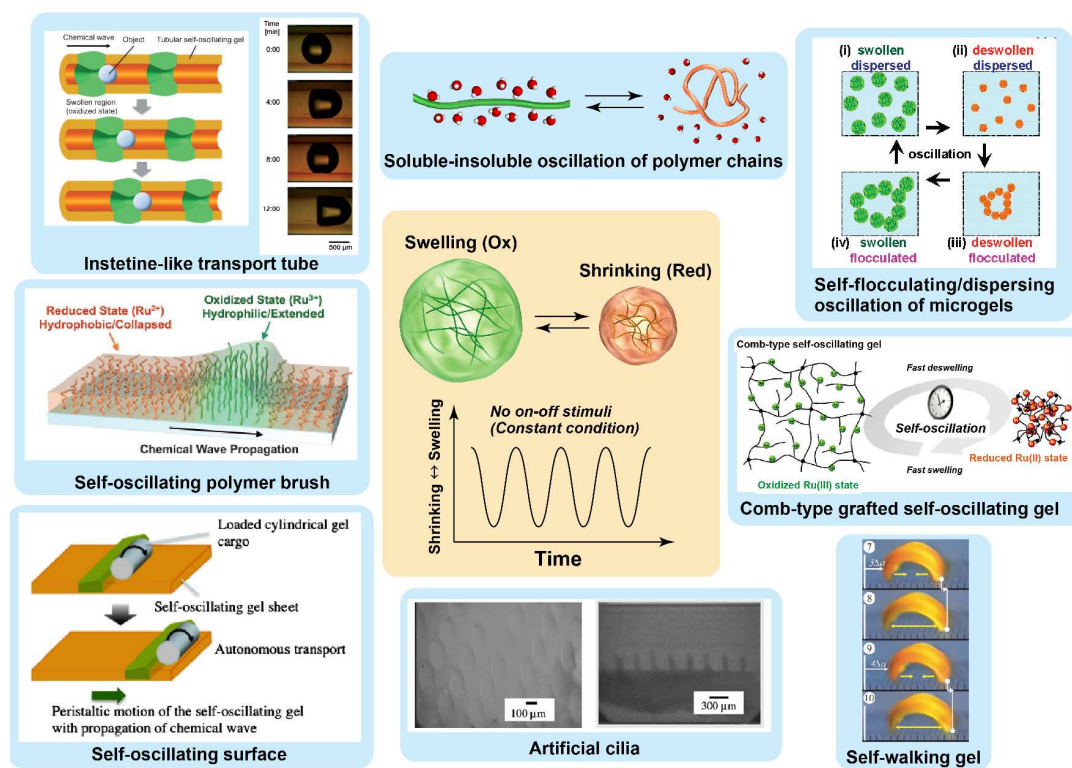


Fig. 2 Typical examples of progress in self-oscillating polymeric materials. Reproduced with permission from ref. 10-12, 14, 15, and 19.

beating heart, the self-oscillating gels express their autonomous functions under constant conditions. Because of their unique characteristics, our researches on the self-oscillating polymers and gels have attracted much attention and inspired various other studies.

Recently, soft materials which have unprecedented and unique physical properties or functions are fabricated based on design concept of supramolecular chemistry.^{20, 21} Supramolecular chemistry, in a narrow sense, is defined as multiple small molecule building blocks spontaneously aggregating through non-covalent bonds to give higher-ordered structures and/or functions. Supramolecules are held together by a variety of non-covalent intermolecular interactions such as electrostatic, hydrophobic, dipole, van der Waals forces, and hydrogen bonding. The resulting structure has unique features as a whole system in

addition to those originating from the individual components. The pioneer of this scientific research field, Lehn, defined supramolecular chemistry as “*Chemistry beyond the molecule,*” bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces.”³¹ The concept can be applied to designing novel functional polymer gels. For example, gels with high mechanical strength²² or self-healing function²³ were obtained using rotaxane formation with poly(ethylene glycol) (PEG) and cyclodextrin. Self-healing gels obtained from autonomous structure formation by metal coordination,²⁴⁻²⁷ hydrogen bonding,²⁸⁻³⁰ and ionic interactions,³¹⁻³³ etc. have also been studied.

Under such background, we recently attempted to construct new self-oscillating polymer systems using supramolecular chemistry. In this perspective, we summarise the recent topics of self-oscillating polymeric materials based on the concepts of supramolecular chemistry, where aggregates of building blocks with non-covalent bonds evolve the temporal or spatiotemporal structure. By utilising the rhythmic oscillation of the association/dissociation of molecular aggregates coupled with the redox oscillation by the BZ reaction, novel soft materials that express a similar function as those of living matter such as amoeba-like motion, higher-ordered structure transition, and autonomous self-healing properties will be achieved. From the viewpoint of materials science, it is also of interest to establish self-oscillating materials without using strong acid or high concentrations of oxidant, as the reaction condition is a serious drawback. In the last part, our recent approach to prepare self-oscillating materials that operate long-term under mild conditions will be introduced.

2. Self-oscillating polymeric materials coupled with metal-ligand coordination supramolecular chemistry

In supramolecular chemistry, Ru coordination compounds with terpyridine (tpy) ligands have attracted significant attention for their applications in reversible cross-linking, which depends on the redox states of the Ru.³⁴ As is the case in many metal-tpy compounds, the reduced (Ru^{2+}) state is more stable within the bis-tpy structure, in which two tpy ligands are coordinated to the Ru centre, than in the mono-tpy coordination state, which has just one tpy ligand. On the other hand, the oxidised (Ru^{3+}) state is more stable within the mono-tpy state than the bis. Schubert and co-workers reported that the Ru-tpy coordinate linkage could be used for preparation of many supramolecular polymer systems such as reversible cross-linking for block copolymer preparation^{35, 36} and polymerisation/depolymerisation of macromonomers³⁷ by the addition of reductants/oxidants. Preparation of unique triangular architecture formed by DNA hybrids³⁸ involving Ru-tpy coordination is also of great interest in the field of biohybrid supramolecular science. Other than Ru-tpy coordination, control of the viscoelastic properties has also been reported for various metal-ligand supramolecules.³⁹ These pioneering works are based on static formation/deformation of metal-tpy ligand complexes in equilibrium or meta-stable state.

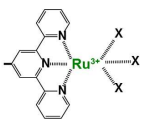

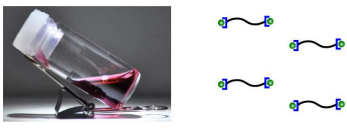
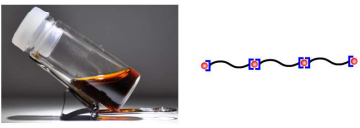

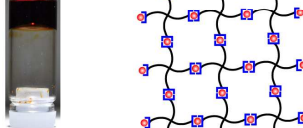

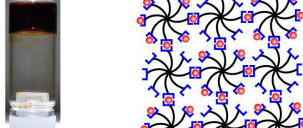
	Oxidized 	Reduced 
(a) linear-PEG (2 branches)		
(b) tetra-PEG (4 branches)		
(c) octa-PEG (8 branches)		

Fig. 3 Difference in appearance of 2-, 4-, and 8-branched PEGs in equilibrium depending on the redox state of the modified Ru metal ligand at the terminal. Illustrations of expected structures are also shown. Reproduced with a permission from ref. 42.

Recently, by computational simulation, Balzs *et al.* demonstrated a novel type of self-reinforcing behaviour of autonomously oscillating materials using $\text{Ru}(\text{tpy})_2$ as dynamic cross-linkages.⁴⁰ Inspired by the study, we experimentally confirmed that the BZ reaction was caused by $\text{Ru}(\text{tpy})_2$ with a proper amount of substrate,⁴¹ and realized autonomous viscosity oscillation accompanied by a rhythmic association/dissociation of a PEG backbone with a different number of branches coordinating to $\text{Ru}(\text{tpy})_2$ as a dynamic cross-linking point. In fact, telechelic PEGs with a different number of branches (2, 4, and 8) containing the tpy ligand at their termini were prepared.⁴² The autonomous viscosity oscillation derived from the association/dissociation of the PEG coupled with the BZ reaction was investigated in terms of the number of PEG branches as a main variable parameter. **Fig. 3** shows the

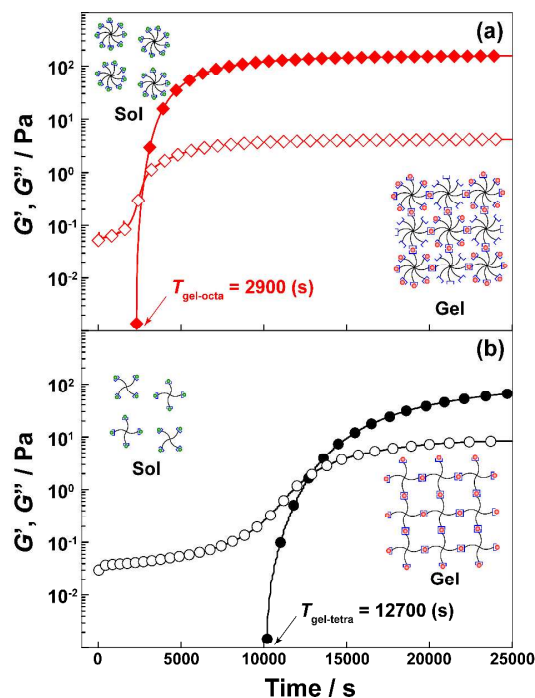


Fig. 4 Viscoelastic measurements for (a) octa- and (b) tetra-PEGs in the course of reduction of the terminal $\text{Ru}(\text{tpy})^{3+}$, along with the illustration of expected structure of branched PEGs. KI was added as a reductant for the oxidised solution at time zero. Reproduced with a permission from ref. 42.

appearance of the Ru-tpy-modified linear-, tetra-, and octa-PEG solutions in the equilibrated oxidised $\text{Ru}(\text{tpy})^{3+}$ and reduced $\text{Ru}(\text{tpy})_2^{2+}$ states. When the Ru was oxidised, the solution was light purple, and it changed to orange when the Ru was reduced. When tetra- and octa-PEGs were used as the polymer backbone, gelation occurred in the reduced state. Considering that it is known that mono-tpy and bis-tpy coordination are the most stable forms for Ru in its oxidised and reduced states, respectively, the Ru metal centre could act as a cross-linking point for the branched PEG, resulting in gelation. No gelation was observed with linear PEG, indicating that no network structure was formed. Reversibility of the sol-gel transitions accompanying colour changes were also confirmed.

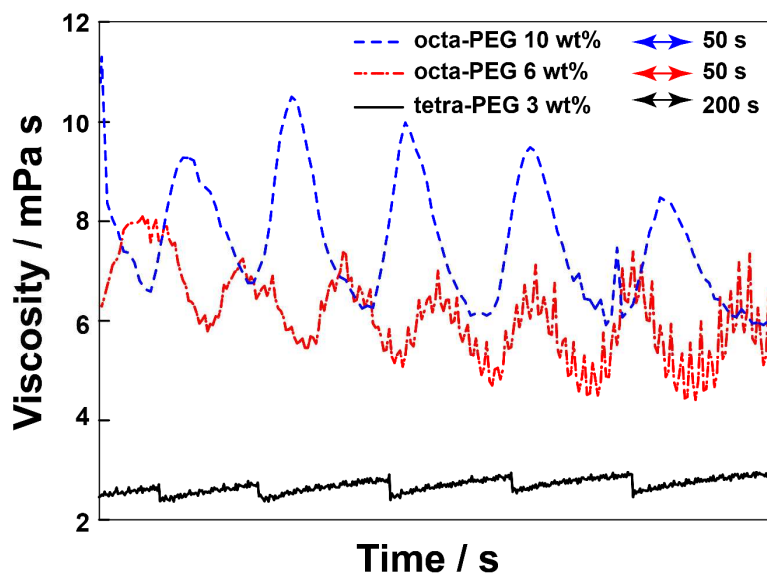


Fig. 5 Comparison of viscosity oscillation between tetra- and octa-PEG systems. The BZ substrates in the feed are $[\text{HNO}_3] = 0.2 \text{ M}$, $[\text{NaBrO}_3] = 0.4 \text{ M}$, and $[\text{MA}] = 0.1 \text{ M}$ for octa-PEG, and $[\text{HNO}_3] = 0.3 \text{ M}$, $[\text{NaBrO}_3] = 0.4 \text{ M}$, and $[\text{MA}] = 0.1 \text{ M}$ for tetra-PEG. Reproduced with a permission from ref. 42.

These observations were quantitatively supported by viscoelastic measurements for the supramolecular gels prepared from the tetra- and octa-PEG backbones. **Fig. 4** shows the rheological behaviour (storage elastic modulus G' and loss elastic modulus G'') after the addition of 0.1 M KI as a reductant to the equimolar mixture of Ru^{3+} -tpy-tetra-PEG and tpy-tetra-PEG as well as the mixture of Ru^{3+} -tpy-octa-PEG with tpy-octa-PEG. Both sets of results clearly indicate that the initial polymer solutions ($G' < G''$) became gels ($G' > G''$) over time. Here, the time for the sol-gel transition (T_{gel}) was defined as the time at which the value of G' exceeded that of G'' . The octa-PEG system yielded a gel more quickly, with a gelation time of 2,900 s, compared to 12,700 s for the tetra-PEG. It was thus revealed that an increase in the branching number of the polymer caused gelation with a lower rate of cross-linking

points. **Fig. 4** also shows that the G' value at saturation does not depend strongly on the backbone structure. This indicates that the number of efficient cross-linking points participating in the gel network is almost the same irrespective of the branching number of the backbone.

Fig. 5 shows the viscosity oscillation profiles of the tetra- and octa-PEGs solutions under the optimised conditions of polymer and BZ substrate concentrations. All the polymer solutions exhibited a viscosity oscillation along with a periodic colour change owing to the reversible and dynamic association/dissociation of the tpy-modified PEGs with the Ru metal centre, which acted as a catalyst for the BZ reaction. It was clear that the viscosity baseline increases as the concentration of the polymer and the branching number of the PEG backbone increases. We are now aiming to adjust the viscosity oscillation so that we may observe macroscopic sol-gel oscillations coupled with the microscopic association/dissociation of the polymer. Further optimisation of the branching number, the concentration of the polymers, and the concentration of the BZ substrate will also be required to achieve this goal. There are several reports on applying Ru-tpy supramolecular chemistry to the dynamic oscillation of polymers. Ding and Zheng *et al.* also recently studied the dynamic association/dissociation of a random copolymer consisting of *N*-isopropylacrylamide (NIPAAm) and a vinyl monomer having a tpy ligand with a Ru centre to demonstrate the rhythmic conjugation of Ru-tpy metal-ligand coordination under BZ conditions.^{43,44} A transmittance oscillation was observed in the solution of the random copolymer with appropriate concentrations of the BZ substrates below the LCST-type phase transition temperature of PNIPAAm. Meanwhile, in order to

apply the rhythmic changes of the polymer to an actuator, sensor, or other practical materials, oscillation stability is a critical issue. Epstein *et al.* reported on the factors affecting the oscillation mechanism by using certain bpy or tpy ligands with slight chemical modifications in terms of the oscillation stability.⁴⁵ They pointed out that Ru(tpy)₂ was not as suitable as Ru(bpy)₃ for catalysing the BZ reaction because the oxidised Ru(tpy)₁³⁺ can easily react with the intermediate of the BZ reaction, resulting in a short-lived oscillation.

3. Self-oscillating micelles: Block copolymers with temporal structure

Block copolymers are composed of two or more chemically distinct polymers connected together. They can undergo microphase segregation leading to a well-ordered spatial structure under thermodynamic equilibrium or metastable state, either in the melt or in the selective solvent for one block segment. In block copolymer systems, intramolecular repulsive/attractive forces among the constituent blocks result in regular and thermodynamically stable structure formation (i.e., self-assembly) on the scale of nano to submicron meter.⁴⁶⁻⁴⁸ Micro-patterning and micellisation utilising block copolymers in specific solvents are now recognised as promising technologies for manipulation of a variety of objects on the nano or mesoscale. Not only linear block copolymers, but also non-linear copolymers such as cyclic⁴⁹ or radial block copolymers⁵⁰ are now being exploited, accompanied by recent significant developments in polymerisation methodologies. For example, thermally stable micellisation using cyclic block copolymers, unique morphologies using block copolymers with a radial arrangement, and porous functional materials using

unique block copolymers are now available. Thus, there have been numerous efforts in the area of controlled self-assembly using block copolymers, focused mainly on the formation of static and stable structures under thermodynamic equilibrium or a kinetically relaxed metastable state.⁵¹

Most recently, on the other hand, we demonstrated a novel class of block copolymer that could undergo spontaneous unimer-micelle oscillation driven by the BZ reaction.⁵² Although there have been many reports on the chemical oscillation derived from the BZ reaction with low molecular weight ionic or neutral surfactants as modifiers for the formation of a chemical pattern,⁵³⁻⁵⁸ our amphiphilic block copolymer was developed to convert the chemical energy of the BZ reaction into the dynamic association/dissociation of block copolymers. A peptide block copolymer as a polymerisable hydrogelator was also recently reported as a platform for chemical patterning.^{59, 60}

The target diblock copolymer consisted of hydrophilic PEG as the first block segment with a random copolymer of NIPAAm and a vinyl monomer with a Ru(bpy)₃ side chain as the second block segment. The well-defined diblock copolymer, PEG-*b*-P(NIPAAm-*r*-Ru(bpy)₃) (**Fig. 6(a)**), was prepared by reversible addition fragmentation chain transfer (RAFT) polymerisation from a PEG-based macro-chain-transfer agent (macro-CTA).⁶¹ The aggregation behaviour of the PEG-*b*-P(NIPAAm-*r*-Ru(bpy)₃) in the equilibrium state was first investigated. **Fig. 6(b)** shows the average R_h values for the polymer as a function of the temperature by dynamic light scattering (DLS) measurements. The measurements were carried out in both the reduced

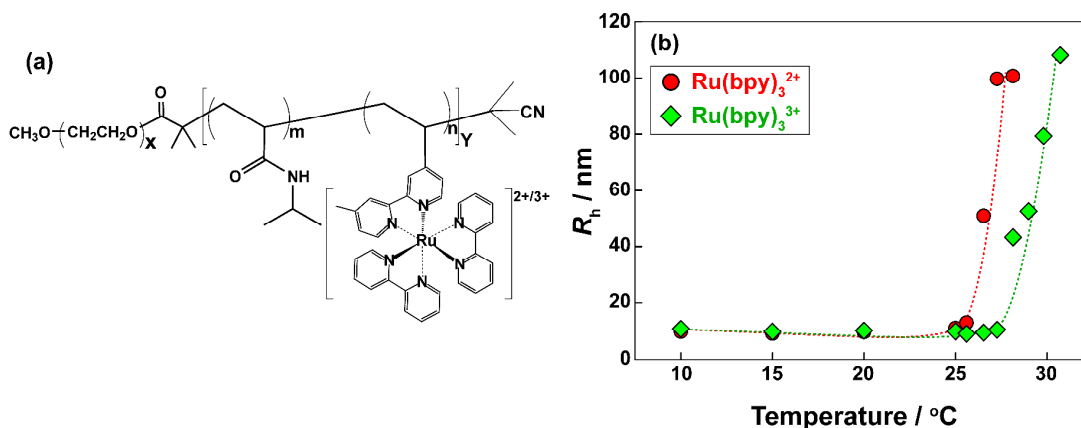


Fig. 6 (a) Chemical structure of PEG-*b*-P(NIPAAm-*r*-Ru(bpy)₃) diblock copolymer and (b) relationship between R_h of the diblock copolymers and the temperature for the reduced state (red circle) and oxidised state (green diamond). Reproduced with a permission from ref. 52.

(PEG-*b*-P(NIPAAm-*r*-Ru(bpy)₃²⁺)) and oxidised (PEG-*b*-P(NIPAAm-*r*-Ru(bpy)₃³⁺)) states at the same ionic strength. The average R_h values were confirmed to increase sharply above a certain temperature, indicating that self-assembly from unimers to micelles occurs with heating, irrespective of the redox states of Ru(bpy)₃. The R_h values at lower temperatures were around 7–10 nm, suggesting the dissolution of single chains, while those at higher temperatures ranged between several tens of nm and over 100 nm. The reversibility of the unimer-micelle transition with the change in temperature was also confirmed. More importantly, there was an approximately 2.5 °C difference in the aggregation temperature between the oxidised and reduced states. The reduced block copolymer aggregated at 25.6 °C, whereas the oxidised block copolymer aggregated at 28.1 °C. This is because the second block is more hydrophilic in the oxidised state than the reduced state because of the increase in charge.

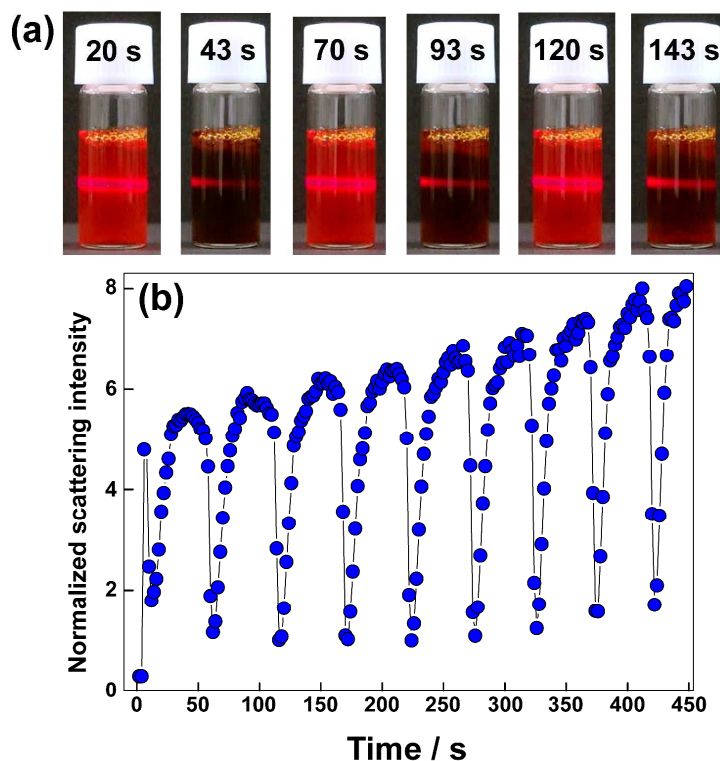


Fig. 7 (a) Photographs of the block copolymer solution (1 wt%) showing periodic changes in the Tyndall effect derived from the self-oscillating micelle synchronised with the BZ reaction at 25 °C. In order to observe the Tyndall effect more clearly, the sample was irradiated with a red laser (690 nm, <1 mW) from the left hand side. (b) Normalised scattering intensity of the block copolymer solution (0.5 wt%) as a function of time at 26 °C. Scattering intensities were collected every 2 s at a scattering angle of 90°. The BZ substrates for the measurements in the feed are as follows: (a) $[\text{NaBrO}_3] = 0.3 \text{ M}$, $[\text{HNO}_3] = 0.3 \text{ M}$, and $[\text{MA}] = 0.2 \text{ M}$; (b) $[\text{NaBrO}_3] = 0.2 \text{ M}$, $[\text{HNO}_3] = 0.3 \text{ M}$, and $[\text{MA}] = 0.3 \text{ M}$. Reproduced with a permission from ref. 52.

Then we demonstrated a dynamic unimer-micelle transition with appropriate concentrations of the BZ substrates at the bistable temperature. Accompanying the periodic colour change between orange and light green due to the redox oscillation of $\text{Ru}(\text{bpy})_3$, a rhythmic oscillation of the Tyndall effect was observed. When the colour of the solution was orange, indicating the reduced state, intense light scattering of the incident laser could be clearly seen. In contrast, the Tyndall effect was weakened in the oxidised state because the

aggregation temperature of the oxidised polymer was higher than the experimental temperature. This result implies that the block copolymer periodically undergoes a transition between two different states of unimer (oxidised form) and self-assembled micelle (reduced form) with a size large enough to scatter the incident light. We further quantified this periodic oscillation with the aid of time-resolved DLS measurements.

Fig. 7 shows the oscillating profiles of the scattering intensity for the 0.5 wt% block copolymer solution with appropriate concentrations of the BZ substrates at the bistable temperature (26 °C); the obtained scattering angle was 90°. The average scattering intensity was measured every 2 s, and a periodic scattering intensity oscillation was clearly observed. The baseline of the scattering intensity increased with time, indicating that the size of micelles essentially increased during the oscillation process. From the oscillating waveform, it can be seen that the decrease in the scattering intensity accompanying the demicellisation occurred much faster than the increase in intensity accompanying the micellisation. This is explained by the characteristics of the BZ reaction, where the autocatalytic reaction from $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Ru}(\text{bpy})_3^{3+}$ occurs more quickly than the opposite reduction step. The waveform also suggests that the scattering intensity oscillation was completely coupled with the periodic redox changes induced by the BZ reaction. Another possible explanation for the waveform may be the difference in the mechanisms of micelle formation and dissociation. Breaking of the micelle proceeds more quickly, as there is no polymer diffusion.

Further analysis of the autocorrelation function obtained from the time-resolved DLS measurements provides detailed information of the rhythmic micellisation/demicellisation.

Fig. 8 shows the oscillating profiles of the average R_h estimated from theoretical analysis of the autocorrelation function; fitting the curve to exponential function to obtain diffusion coefficient and applying the Stokes-Einstein relation at each time. Even in the oxidised state, the smallest R_h was estimated to be 17 nm. This value seems too large to suggest that the micelles were completely broken into individual polymer chains. However, the scattering intensity is theoretically proportional to the sixth power of the particle size and to the number of particles. In the presence of large aggregates, the DLS signal is heavily influenced by the aggregates, even if it is the minor component. Such an influence might be considered.

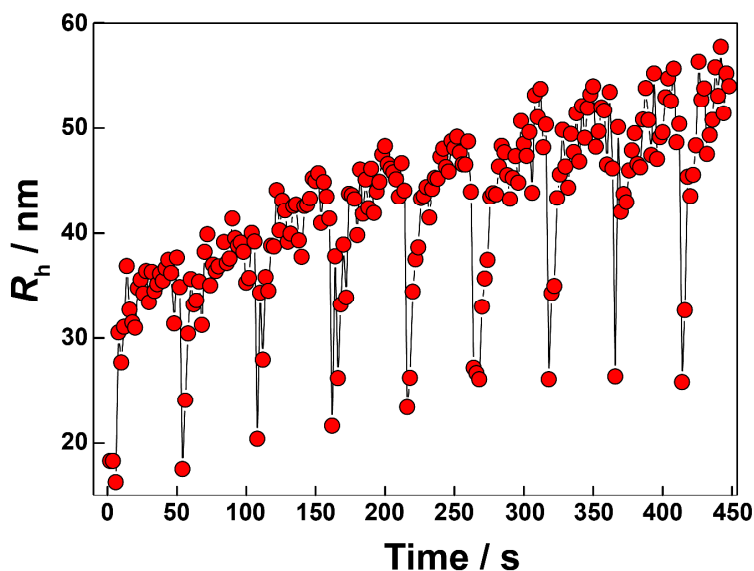


Fig. 8 Oscillation profiles of R_h of the diblock copolymer determined by time-resolved DLS measurements under BZ reaction conditions at 26 °C. All correlation functions were collected every 2s. Reproduced with a permission from ref. 42.

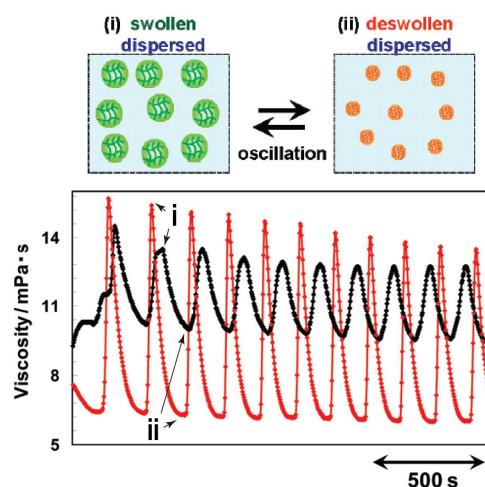


Fig. 9 Autonomously oscillating profiles of the viscosity in the microgel dispersions measured at 15 °C. The numbers in each oscillating profile refer to the corresponding cartoons. The chemical composition of the microgels in the feed is as follows: (black line): [NIPAAm]:[Ru(bpy)₃]:[BIS] = 95:1:4; (red line): [NIPAAm]:[Ru(bpy)₃]:[BIS] = 96:2:2. Methylene bisacrylamide (BIS) was used as a cross-linker. The BZ substrates for the measurements in the feed are as follows: (a) [NaBrO₃] = 0.15 M, [HNO₃] = 0.5 M, and [MA] = 0.1 M. The microgel concentration was 5.0 wt% in both measurements. The data were collected at a constant shear rate of 132 s⁻¹. Reproduced with a permission from ref. 15 and 17.

So far, studies on block copolymers have mainly focused on control of static

structure belonging to the category of self-assembly. However, introduction of dissipative structures into block copolymer systems would result in novel concept of polymer self-organisation with the ability to undergo rhythmic structural change, where self-assembly and dissipative structures assist each other. Rhythmic oscillation of macroscopic solution properties (viscosity, etc.) synchronised with microscopic rhythmic aggregation of the building blocks will be realised if the block copolymer architecture is properly designed. Other than block copolymer, we have also prepared self-oscillating microgel particles and reported that the suspension could exhibit rhythmic oscillation of the viscosity derived from swelling/shrinking or flocculating/dispersing behaviour of the microgels driven by the BZ reaction (**Fig. 9**).^{15, 17} The suspension has a potential to be developed as a smart viscoelastic fluid. This system is also designed under the concept of self-organisation based on combining self-assembly with a dissipative structure. In particular, it is of interest that the system can construct hierarchical structure by assembling the microgels which causes macroscopic changes in higher order.

4. Development of a stable chemical oscillation reaction under mild conditions with ionic liquids

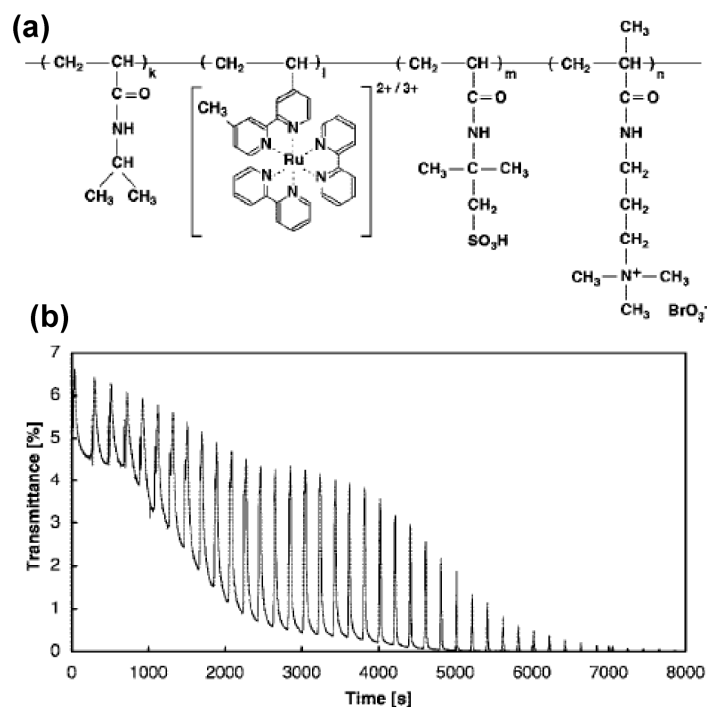


Fig 10 (a) Chemical structure of the built-in self-oscillating polymer P(NIPAAm-*r*-Ru(bpy)₃-*r*-AMPS-*r*-MAPTAC) where all of the BZ substrates other than MA were incorporated into its structure. (b) Oscillating profiles of the optical transmittance for the random copolymer solutions at 12 °C with [MA] = 0.3 M. Reproduced with a permission from ref. 62.

The conditions of the BZ reaction will be an obstacle for practical applications. The BZ reaction typically requires both strongly acidic conditions, as low as pH <1, and concentrated oxidant conditions. From this viewpoint, we have developed quaternary self-oscillating polymers that incorporate not only a Ru(bpy)₃ monomer, but also acrylamidomethylpropane sulphonate (AMPS) as a proton reservoir site and methacrylamidopropyltrimethylammonium chloride (MAPTAC) as an oxidising species in the polymer structure (**Fig. 10**).^{62, 63} The linear polymer exhibits a favourable transmittance oscillation simply by adding an appropriate amount of MA. By preparing the gels composed

of these component at an appropriate ratio, self-oscillation of gels will be realised under mild outer conditions.

In order to achieve self-oscillating polymeric materials under mild conditions, different approaches have been recently proposed by causing the BZ reaction in hydrated ionic liquids (ILs).⁶⁴ ILs are room temperature molten salts and have attracted much attention because of their unique properties. The typical properties of ILs are high ion conductivity, non-flammability, negligible volatility, and thermal and chemical stability.⁶⁵⁻⁶⁹ ILs are versatile liquids that have recently been utilised in many scientific research fields, including polymer science.⁷⁰⁻⁷³ Because ILs offer great flexibility in designing cationic and anionic structures and their combinations, one can theoretically manipulate their properties on demand; therefore, ILs have been termed “designer solvent.” As ILs are regarded as the “third solvent” following water and organic solvent, they have been expected to be used in many applications such as reaction solvents for organic synthesis,^{67, 68} and polymerisation,^{74, 75} solvents for materials that are difficult to solubilise,⁷⁶⁻⁸¹ and ion conductive materials for energy conversion/preservation purposes.^{72, 73}

ILs can generally be divided into two categories: ILs with an ionic structure that includes active protons (protic ILs: PILs)⁸² and those that do not include active protons (aprotic ILs: APILs). Recently, many research groups have pointed out the affinity between living matter and (P)ILs. (P)ILs or a mixture of water and (P)ILs, otherwise known as “hydrated (P)ILs” are now assumed to be a promising class of preservation media for biopolymers such as DNA⁸³ and proteins.⁸⁴⁻⁸⁶ Studies on the preparation of ILs from

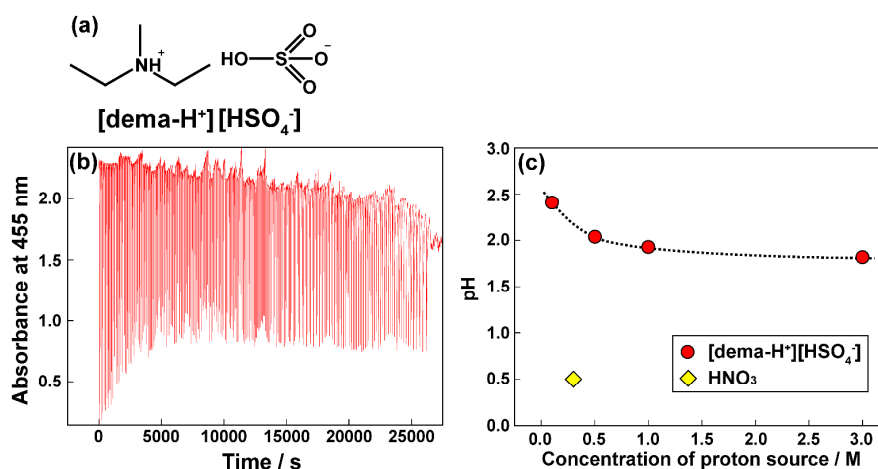


Fig. 11 (a) Chemical structure of [dema-H⁺][HSO₄⁻]. (b) Self-oscillation profile of the BZ reaction in hydrated [dema-H⁺][HSO₄⁻] (1.3 M). Concentration of the other BZ substrates are as follows: [NaBrO₃] = 84 mM and [MA] = 62.5 mM. (c) pH of hydrated [dema-H⁺][HSO₄⁻] as a function of the concentration of [dema-H⁺][HSO₄⁻], along with the pH of a 0.3 M HNO₃ aqueous solution. Reproduced with a permission from ref. 64.

bio-derivatives have also gotten attention.^{87, 88} Excellent review articles are now available on (P)ILs for biopolymers.⁸⁹

Further, PILs are widely used as promising novel proton-conducting media for fuel cell applications,^{90, 91} as opposed to traditional acidic aqueous solutions. Low-frequency vibrational FT-IR studies supported by DFT calculations for certain PILs confirmed that the ammonium hydrogen atoms could interact through hydrogen bonding with the oxygen atoms of the nitrate ion, thus leading to a three-dimensional network structure closely resembling that of water.^{92, 93} These facts strongly imply that certain kinds of PILs have a high proton activity, comparable to acidic water, which encourages us to apply PILs as BZ reaction media. As a result, we found for the first time that certain hydrated PILs, such as diethylmethyl ammonium hydrogen sulphate ([dema-H⁺][HSO₄⁻]) (**Fig. 11(a)**), allowed stable, long-lasting chemical oscillation⁶² without the addition of any inorganic strong acid such as nitric or

sulphuric acid-which is traditionally regarded to be necessary as a proton source to induce the BZ reaction. Although there have been some pioneering works on PILs as acidic catalysts for organic synthesis, this is the first report on using a hydrated PIL as an alternative reaction medium for the BZ reaction. Through our screening studies on the effect of the chemical structure of a PIL, the structure requirements of PILs for the BZ reaction are as follows: 1) water-miscible, 2) the anion is not a conjugate base from a strong acid, and 3) the cation structure does not possess an allyl group. In the case of hydrated [dema-H⁺][HSO₄⁻], the stable self-oscillation continued as long as 7 h while maintaining a large amplitude under optimised conditions (**Fig.11 (b)**). The pK_a of [dema-H⁺][HSO₄⁻] was estimated to be 0.31, which suggests that [dema-H⁺][HSO₄⁻] is a weaker acid than nitric acid (pK_a = -1.8) and sulphuric acid (pK_a = -3). Through the oscillation, the pH of the [dema-H⁺][HSO₄⁻] aqueous solution was kept between 1.82 to 2.41, within a concentration range between 0.3 and 3.0 M (**Fig. 11(c)**). These pH values are much higher than the pH of 0.3 M HNO₃ (pH = 0.52), which means that the BZ reaction can take place at a higher pH using PILs. Optimisation of the ionic structure and incorporation of the PILs into the polymer to realise a stable and long-lasting BZ reaction under mild conditions is now in progress for the evolution of self-oscillating polymeric materials.

5. Concluding remarks

In living organisms, high-order structures are formed through non-covalent molecular interactions to recombine chemical bonds, which leads to unique function as a

whole system. This corresponds to the concept of supramolecular chemistry. In this perspective, we summarised recent aspects of the studies on self-oscillating polymeric materials coupled with supramolecular chemistry, that is, construction of dissipative structures utilizing dynamic metal-ligand coordination and micelle formation of block copolymer. Further, we introduced our recent approach using hydrated PILs for practical application of the self-oscillating polymers. Since the first report of “self-oscillating gel” in 1996, we have developed many kinds of biomimetic or smart material systems. Further evolution of the self-oscillating polymer materials as novel biomimetic materials will be expected through the combination with supramolecular chemistry.

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