Ternary Phase Diagram for the Belousov−Zhabotinsky Reaction-Induced Mechanical Oscillation of Intelligent PNIPAM Colloids

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Belousov−Zhabotinsky (BZ) reaction-induced mechanical oscillation of poly(*N*-isopropylacrylamide) (PNIPAM) gel particles was investigated by the systematic variation of BZ substrate concentrations. The correlation between the dynamic behavior and substrate concentrations was presented in a ternary phase diagram. Both oscillatory and steady-state regimes exist on the phase diagram and are separated by a high-frequency oscillation band. Dependence of oscillation frequency and induction time on the substrate concentrations was also studied. To achieve size uniformity, these PNIPAM gel particles with covalently bound tris(bipyridyl)ruthenium(II) were synthesized via the coordination chemistry between a ruthenium complex and the monodispersed PNIPAM gel particles bearing bipyridine ligands.

The Belousov−Zhabotinsky (BZ) reaction is a well-known nonlinear dynamic chemical system that exhibits fascinating phenomena such as periodic and chaotic temporal oscillations, traveling waves, and Turing structures.[1−7] It includes a series of metal-ion-catalyzed oxidative reactions of organic substrates, such as malonic acid, by an acidified bromate solution. The complex nature of this system, as well as its profound significance in understanding the biological oscillators related to some basic aspects of life, have attracted extensive attention from both experimentalists and theoreticians.[7−19] A detailed chemical mechanism, the Field−Körös−Noyes (FKN) mechanism, was established as the framework for understanding and modeling the complicated phenomena of this system.[7−9] Recent studies of BZ reactions in a variety of microheterogeneous media,[14,16,20−23] such as PDMS-separated BZ compartments,[23] water-in-oil microemulsions,[14] and catalyst-loaded resin-exchange beads,[20−22] have brought insights into the communication and self-organization of large quantities of individual relaxation oscillators through the concentration of chemicals in the external media, mimicking living systems such as ventricular cells and neurons.[4]

The BZ reaction has been used to induce mechanical oscillation in polymeric systems to mimic biological materials.[24,25] Yoshida and his co-workers reported the development of a self-oscillating gel composed of stimuli-responsive poly(*N*-isopropylacrylamide) (PNIPAM) polymer with grafted Ru(bipy)$_3$ moiety as the BZ catalyst.[18,26−31] It was found that the chemical oscillation induced a periodic volume oscillation in the PNIPAM gel. This discovery stimulated our interest in the study of colloidal interactions coupled with BZ oscillations, with the long-term goal being to control colloidal self-assembly. Currently, ubiquitous domain defects pose great challenges to the fabrication of large colloidal crystals.[32−34] We envision that these defects can be annealed by the introduction of controlled autonomous mechanical oscillations as in the self-oscillating PNIPAM gel particles via the BZ reaction.

It is well-known that the BZ reaction can exhibit a variety of dynamic regimes, such as steady state, periodic oscillation, and chaos, in both open and closed systems, depending on reagent concentrations and a number of external factors such as temperature, speed of agitation, and flowing rate.[1,215,35−40] As shown by Yoshida and his co-workers, factors such as temperature and substrate concentrations not only turn on or off of the Hopf bifurcation,[27,30,41,42] but also control the frequency and magnitude of the mechanical oscillation of the self-oscillating gel.[28,30,31,41,43] For the practical application of the self-oscillating microgels to colloidal crystal annealing, it is therefore important to identify the main ‘tuning knobs’ for self-assembly and understand the interplay between the polymer system and the BZ reaction. In this study, we focused our attention on controlling the oscillation dynamics of colloids by varying the BZ substrate concentrations.

Since the size uniformity of the colloid particles is essential for crystallization,[44−46] we prepared the PNIPAM particles with covalently bound Ru(bipy)$_3$ catalyst using an approach different from that of Yoshida and his co-workers’[29] (Figure 1). First, uniform gel particles of poly(NIPAM-*co*-vmbipy) were prepared by emulsion polymerization. The bipyridyl groups were then converted into Ru(bipy)$_3$ by a subsequent reaction with *cis*-Ru(bipy)$_2$Cl$_2$. Both confocal scanning laser microscopy (CSLM) and UV−vis spectroscopy convincingly supported the conversion of bipyridyl moiety into Ru(bipy)$_3$ via coordination chemistry. The fluorescence confocal microscopy showed discrete poly(NIPAM-*co*-Ru(vmbipy)(bipy)$_2$) particles with relatively uniform fluorescent emission from the Ru(bipy)$_3$ centers. On the basis of a UV−vis absorbance analysis, we estimated a 50 ± 5% conversion of the bipyridyl groups. The

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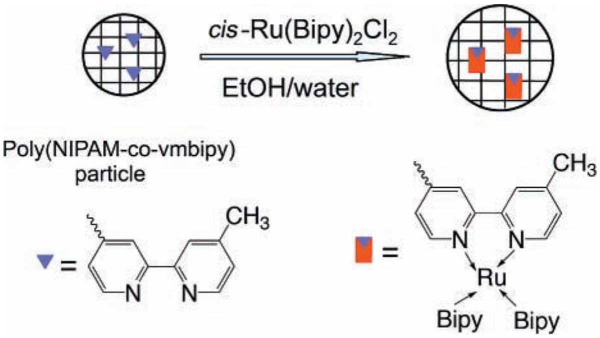

Figure 1. Scheme for the preparation of uniform PNIPAM particles with covalently bound Ru(bipy)$_3$ catalyst via coordination chemistry. The uniform poly(NIPAM-*co*-vmbipy) gel particles, as represented by the checked spheres, are prepared by emulsion polymerization. Subsequent coordination with *cis*-Ru(bipy)$_2$Cl$_2$ converts the bipy ligand group into Ru(bipy)$_3$ moiety.

size uniformity of the colloidal particles was confirmed by dynamic light scattering (DLS) measurement and reflectance confocal microscopy. The DLS measured polydispersity (PDI) are below 14% for the PNIPAM particles with and without loaded catalyst, demonstrating good monodispersity for both particles.[47] We foresee that this approach can be utilized for preparation of uniform polymer gel particles with different sizes and various catalytic metal centers.

The BZ reactions conducted using these catalytic PNIPAM gel particles, together with BZ substrates malonic acid (MA) and sodium bromate, were monitored by use of UV−vis spectroscopy. The transmittance of the mixed solutions in the 190−856 nm wavelength range was measured continuously in an episodic data capture mode. Figure 2a corresponds to a BZ reaction in which periodic oscillations were observed. The oscillations in transmittance at 460 and 685 nms reflect the chemical oscillation of the Ru(bipy)$_3$ catalyst between the Ru(II) and Ru(III) states, whereas the oscillations at the isosbestic wavelength 570 nm are attributable to the conformation change of the PNIPAM polymers.[18] For the control experiment using a free Ru(bipy)$_3^{2+}$ complex and PNIPAM polymers with no grafted catalyst, we observed no oscillations at 570 nm in spite of the regular oscillations at 460 and 685 nms (Figure 2b). This observation confirms that the oscillations at 570 nm for the PNIPAM polymer gels truly arise from the mechanical oscillation of the gel particles induced by the BZ reaction.

We found that such chemical and mechanical oscillations critically depend on the substrate compositions, as also noted by Biosa and Yoshida.[41,48] We were therefore motivated to analyze the concentration dependence of the BZ oscillation in these catalytic PNIPAM particles. Our subject is a five-component system composed of water, nitric acid, bromate, malonic acid, and the gel-supported Ru catalyst. In such a system, the concentration of four components can be given independently. To circumvent the difficulty of exploring a four-dimensional parameter space, we studied the oscillation dynamics in a three-dimensional subspace by keeping the nitric acid concentration constant at 0.3 M. We further simplified our system by applying the following restrictions on the remaining three independent concentrations,

$$[\mathrm{MA}]/[\mathrm{MA}]_0 + [\mathrm{NaBrO_3}]/[\mathrm{NaBrO_3}]_0 + [\mathrm{Ru\text{-}gel}]/[\mathrm{Ru\text{-}gel}]_0 = 1$$

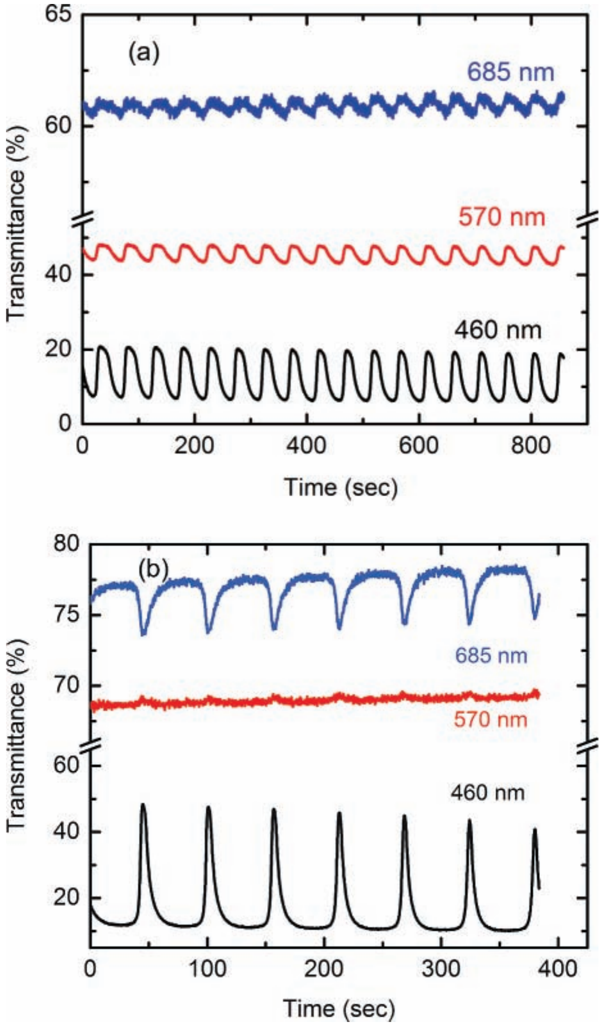

Figure 2. Temporal oscillations in UV−vis transmittance for the Ru(bipy)$_3$ catalyzed BZ reactions. (a) Experiment in which the poly(NIPAM-*co*- Ru(vmbipy)(bipy)$_2$) gel particles were used. The transmittance oscillations at 570 nm are solely due to the mechanical oscillation of the polymers. (b) Control experiment in which discrete Ru(bipy)$_3$ complex and PNIPAM gel with no covalently bound catalyst replaced the poly(NIPAM-*co*-Ru(vmbipy)(bipy)$_2$) gel particles. Although chemical oscillations were observed at 460 and 685 nms, no mechanical oscillations were observed at 570 nm.

Here, MA denotes malonic acid, Ru-gel stands for the gel-supported Ru catalyst, and the subscript 0 denotes the original bulk concentration. The original substrate concentrations are as follows: malonic acid 0.30 M, sodium bromate 0.75 M, and net Ru(bipy)$_3^{2+}$ 1×10^{-4} M. Concentrations of the BZ substrates were systematically changed by dilution of the original bulk solutions, as detailed in the Supporting Information section. The temperature was controlled at 22 °C. The dynamic behavior of the samples was monitored by UV−vis spectroscopy. For the oscillating samples, the frequency and induction time were also analyzed.

A ternary phase diagram (Figure 3a) summarizes the concentration dependence of the oscillating behavior in this MA−NaBrO$_3$−Ru(bipy)$_3$ (grafted) system. Each of the three axes on the diagram corresponds to a dilution ratio of a BZ reactant with respect to its original solution. It is clearly shown that the phase diagram can be separated into oscillating and non-oscillating regions, with the oscillating region mostly located in the area where the dilution ratio of NaBrO$_3$ is below 50%. Moreover, there exists a minimum concentration of the Ru(bipy)$_3$ catalyst below which no oscillation was observed. A series of control experiments were conducted in which the grafted PNIPAM polymer suspension was replaced by a Ru(bipy)$_3$SO$_4$ solution with a similar catalyst concentration. The

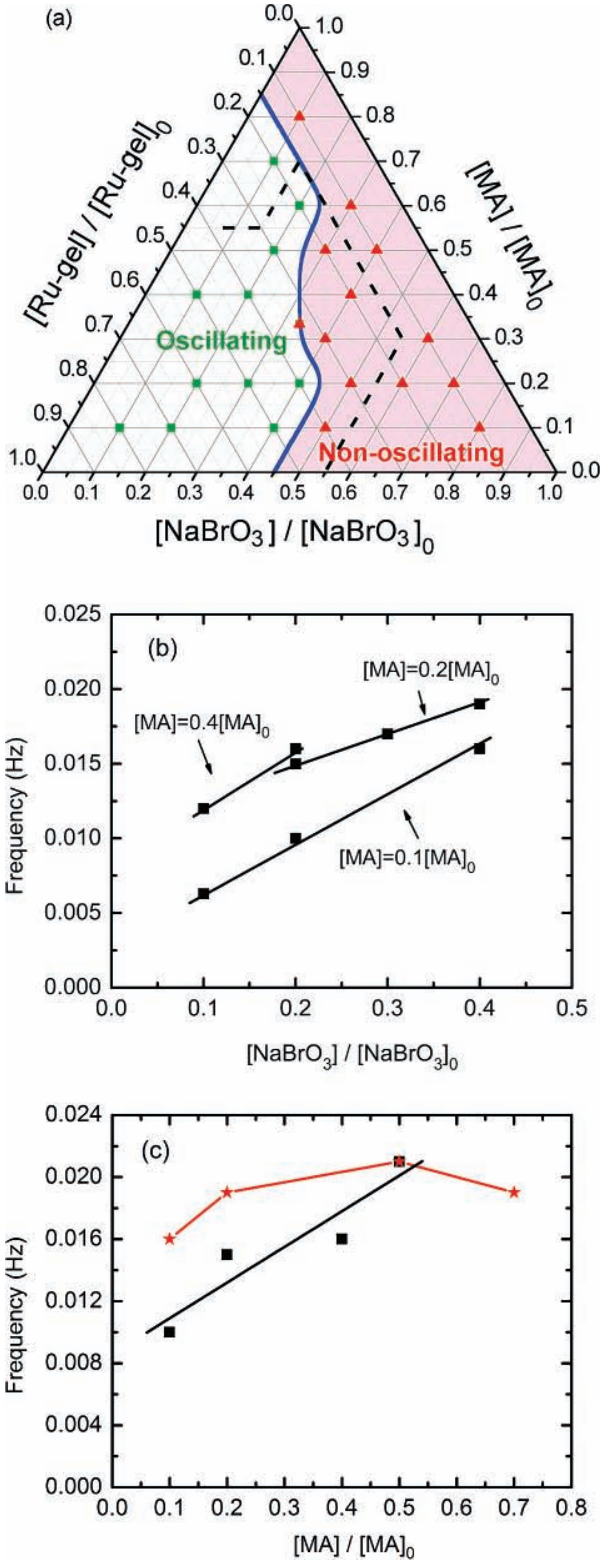

Figure 3. Dynamic behavior of BZ reactions in PNIPAM gel particles with covalently bound Ru(bipy)$_3$. (a) A ternary phase diagram for the BZ-reaction-induced mechanical oscillation of poly(NIPAM-*co*-Ru-(vmbipy)(bipy)$_2$) gel particles with variation of substrate concentrations. The solid line inside the triangle was added for the guidance of the eye to separate the oscillating and non-oscillating regions. The dashed line shows the borderline of the oscillatory-steady-state regimes for a control study using non-polymerized Ru(bipy)$_3$SO$_4$. (b) Dependence of oscillating frequency on the sodium bromate concentration. (c) Dependence of oscillating frequency on the malonic acid concentration. Squares denote samples with [NaBrO$_3$] = 0.2 [NaBrO$_3$]$_0$ and stars denote samples near the oscillation, non-oscillation boundary.

phase diagram of the latter system was overlaid with that of the polymer system (Figure 3a). The dashed line separates the oscillating and non-oscillating regions for the Ru(bipy)$_3$SO$_4$ catalyzed system. Judging from the similarity between the two phase diagrams, we may conclude that the separation between the oscillatory and steady-state regimes for the gel-supported system has the same origin as in the MA−NaBrO$_3$−Ru-(bipy)$_3$SO$_4$ system. We also found that the oscillation frequency is discontinuous at the oscillatory−stationary phase boundary, while the oscillation amplitude is continuous, confirming the Hopf bifurcation scenario (except for at the high NaBrO$_3$ concentration). Details of the oscillation amplitude analysis are included in the Supporting Information. The shrinkage of the oscillatory region for the PNIPAM system at high NaBrO$_3$ concentration conditions, relative to the Ru(bipy)$_3$SO$_4$ system, can be accounted for by colloidal aggregation of the polymer gels due to enhanced screening of Coulombic interactions and subsequent increase in the van der Waals attraction.

The dependence of oscillation frequency on the malonic acid (MA) and NaBrO$_3$ concentrations is plotted in Figures 3, parts b and c. At constant MA concentrations, it was found that the oscillation frequency increases linearly with the NaBrO$_3$ concentration (Figure 3b). However, at fixed NaBrO$_3$ concentrations, the oscillation frequency increases monotonically with the MA concentration (Figure 3c). This trend was fit linearly in consistence with a simplified two-variable Oregonator model.[2] The correlation between frequency and substrate concentration reported here bears a similar trend with the findings of Yoshida and co-workers on the poly(NIPAM-*co*-Ru(bipy)$_3$) gel beads,[28] with the difference being that a power law relationship was found in the latter case. We did not use the power law fitting due to the limited data range. Moreover, it is interesting to note that the oscillation frequency keeps increasing toward the oscillatory−stationary phase boundary and abruptly drops to zero across the borderline. The oscillation frequency does not vary much for the samples near the boundary (Figure 3c). Hence, a high-frequency band separates the two dynamic regimes.

More interestingly, we observed that the preoscillatory time, i.e., the induction time, is dramatically longer for the gel-supported system when compared to the conventional non-polymerized Ru(bipy)$_3$ system. It is usually 1−2 min at 22 °C for the Ru(bipy)$_3$SO$_4$ system, whereas it is 20−50 times longer for the gel-supported system depending on the substrate concentrations. We hypothesize that the polymeric matrix affects the steric accessibility of the catalytic centers, hence the induction time.

The dependence of induction time on the MA and NaBrO$_3$ concentrations for the gel-supported system is shown in Figure 4. Figure 4a shows that the NaBrO$_3$ concentration is the predominant factor for determining the induction time at low MA concentration (the MA dilution ratio is no greater than 40%). The induction time increases monotonically with the increase in NaBrO$_3$ concentration, and an approximate exponential correlation can be found. At a fixed NaBrO$_3$ concentration, the induction time remains almost constant when the malonic acid concentration is below 40% of the original, whereas it increases abruptly with the change in malonic acid concentration beyond that critical point (Figure 4b). A similar dependence of induction time on the NaBrO$_3$ and malonic acid concentrations was observed for the cerium catalyzed BZ reactions in bulk system.[9,19] Here, we offer a rather qualitative explanation by pointing out the important inhibition effects to the HBrO$_2$ autocatalysis process. It is known that bromide competes with HBrO$_2$ for bromate and the autocatalysis process

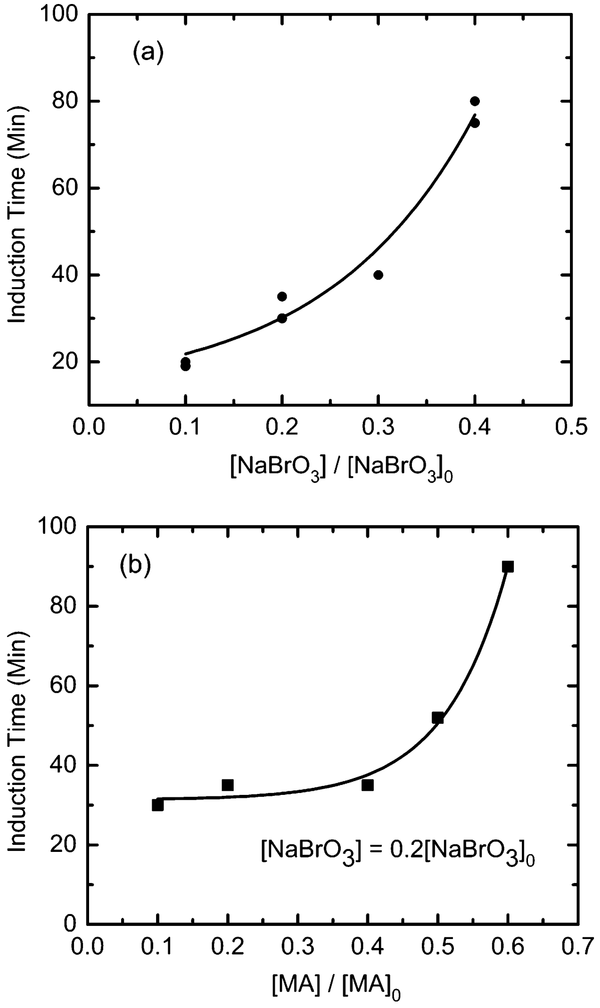

Figure 4. Dependence of induction time on the BZ substrate concentrations. (a) Samples with low [MA] ([MA] ≤ 0.4[MA]$_0$). Note that samples at the same [NaBrO$_3$] have different [MA]. (b) Samples with fixed [NaBrO$_3$] ([NaBrO$_3$] = 0.2 [NaBrO$_3$]$_0$).

would not start until the [Br$^-$] drops to a certain critical value. We assume that an increase in bromate concentration demands longer time for the reduction of [Br$^-$] to the threshold value. Accordingly, an increase in bromate concentration would lead to an increase of induction time. At high [MA]$_0$/[BrO$_3{}^-$]$_0$, the effect of another inhibitor, i.e., the organic radicals, MA•, generated by the catalyst, becomes increasingly important, as noted by Field et al.[9] This explains the dramatic increase of induction time with malonic acid concentrations beyond the critical [MA] at a fixed bromate concentration.

Overall, BZ reactions catalyzed by the Ru(bipy)$_3$ catalyst immobilized in the intelligent gel can be considered as being conducted in nanosized open reactors. Both mass diffusion and the local chemical and mechanical environment of the supporting gel might play very important roles in the chemical kinetics of the reaction. Quantitative studies are necessary to bring more insights to this system.

In summary, we present here a systematic study on the BZ-reaction-induced mechanical oscillation of PNIPAM gel particles by varying the malonic acid, sodium bromate, and the imbedded Ru(bipy)$_3$ catalyst concentrations. A ternary diagram was created to show the correlation between the dynamic behavior of the system and the substrate concentrations. It was found that both oscillating and steady-state regimes exist on the ternary diagram and they are separated by a high-frequency oscillation band. The dependencies of the oscillation frequency and induction time on the substrate concentrations were analyzed and tentatively explained by the inhibition effects. This study provides guidance for tuning induction time and frequency, the two important parameters in mechanical-oscillation-facilitated colloidal assembly.

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Supporting Information Available: Detailed experimental procedure for the preparation and characterization of the poly(NIPAM-*co*-vmbipy) and poly(NIPAM-*co*-Ru(vmbipy)(bipy)$_2$) gel particles, the measurements of mechanical oscillations, the oscillation amplitude analysis, and a control experiment for testing one hypothesis of the lengthened induction time. This material is available free of charge via the Internet at http://pubs.acs.org.

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