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Influence of Initial Substrate Concentration of the Belouzov-Zhabotinsky Reaction on Transmittance Self-Oscillation for a Nonthermoresponsive Polymer Chain

Yusuke Hara * and Rumana A. Jahan

Nanosystem Research Institute (NRI), National Institute of Advanced Science and Technology (AIST), Central 5-2, 1-1-1 Higashi, Tsukuba 305-8565, Japan

* Author to whom correspondence should be addressed; E-Mail: y-hara@aist.go.jp; Tel.: +81-29-861-9318; Fax: +81-29-861-6236.

Abstract: We succeeded in causing transmittance self-oscillations of a novel self-oscillating polymer chain induced by the Belouzov-Zhabotinsky (BZ) reaction under constant conditions. The novel polymer chain was composed of a biocompatible and non-thermoresponsive poly-vinylpyrrolidone (PVP) main-chain, covalently-bonded to the ruthenium catalyst (Ru(bpy)$_3$) of the BZ reaction. We investigated the influence of initial substrate concentrations of the three BZ substrates on the transmittance self-oscillation of the novel polymer solution. As a result, we demonstrated that the width of the transmittance self-oscillation is significantly affected by these initial concentrations. However, the amplitude of the transmittance self-oscillation is hardly affected by the BZ substrate conditions. Furthermore, the period of the self-oscillation has a good linear relationship to the concentration of the BZ substrates. Therefore, the period of the self-oscillation can be controlled by the selection of the initial concentrations of the BZ substrates.

Keywords: self-oscillation; BZ reaction; polymer chain; biomimetic; biocompatible

1. Introduction

Intelligent materials with changing properties and functions have been much investigated in various fields. In particular, stimuli-responsive polymer systems have been considerably studied for the purpose of the many types of possible applications, such as soft actuators, microfluidics and medical devices, *etc.* due to their light weight, flexibility and low noise, *etc.* [1-10]. However, in order to drive stimuli responsive polymer system, external devices are needed. On the other hand, living organisms can generate the autonomous motion without external stimuli. In recent years, in order to construct an autonomous polymer system like a living organism, self-oscillating polymer systems were developed [11-13]. The driving energy for these polymer systems is produced by the dissipating chemical energy of the Belouzov-Zhabotinsky (BZ) reaction [14-18]. The BZ reaction is well known as an oscillating reaction accompanying spontaneous redox oscillations to generate a wide variety of nonlinear phenomena, e.g., a target or spiral pattern in an unstirred solution, and periodicity, multi-periodicity, or chaos in a stirred solution. The overall process of the BZ reaction is the oxidation of an organic substrate by an oxidizing agent in the presence of the catalyst under strong acidic conditions. In the BZ reaction, the metal catalyst undergoes spontaneous redox self-oscillation. In this cyclic reaction, the Ru catalyst has different solubility in the reduced and oxidized state. In order to cause the self-oscillation, the different solubility of the Ru catalyst in the reduced and oxidized state was utilized. In our previous studies, we synthesized self-oscillating polymer chains composed of poly(Nisopropylacrylamide) (poly(NIPAAm)) covalently bonded to (ruthenium (4-vinyl-4'-methyl-2,2-bipyridine) bis(2,2'-bipyridine)bis(hexafluorophosphate)) (Ru(bpy)$_3$) and a negatively charged acrylamide-2-methylpropanesulfonic acid (AMPS) as a pH and solubility control site [19-26]. The AMPS-containing polymer solution caused transmittance self-oscillations originating from the different solubility of the Ru(bpy)$_3$ moiety in the oxidized and reduced state. In our previous investigations, we clarified the detail self-oscillating behaviors for the AMPS-containing self-oscillating polymer solutions.

In this study, in order to expand the application field, we selected a biocompatible and non-thermoresponsive poly-vinylpyrrolidone (PVP) as a polymer main-chain of a novel self-oscillating polymer (see Figure 1). As a result, we first succeeded in causing the transmittance self-oscillation of the novel polymer solution under the constant condition induced by the BZ reaction. We studied the influence of the concentration of the three BZ substrates (sodium bromate, malonic acid and nitric acid) other than the metal catalyst on the waveform and period of the self-oscillation. As a result, we showed that the transmittance self-oscillation caused damping, originating from the change in the ionic strength of the polymer solution when the BZ reaction started. Moreover, we demonstrated that the amplitude of the self-oscillation is hardly affected by the initial concentration of the BZ substrates. In addition, the period of the transmittance self-oscillation has a good linear-relationship to the initial concentration of the BZ substrates. Therefore, the period of the self-oscillation for the novel polymer chain can be controlled by the selection of the initial concentration of the BZ substrates. We believe that the development of a novel self-oscillating polymer system and the discovery of its self-oscillating behavior leads to a wide variety of nonlinear phenomena which may inspire new experimental and theoretical considerations.

Figure 1. Chemical structure of poly(VP-*co*-Ru(bpy)$_3$).
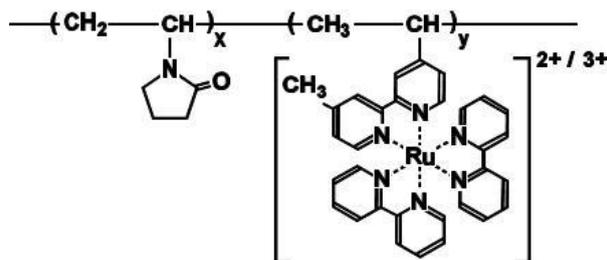
2. Experimental Section

2.1. Synthesis of the Poly(VP-co-Ru(bpy)₃)

The polymer chain was prepared as follows. 0.5g of ruthenium(4-vinyl-4'-methyl-2,2'-bipylridine)bis(2,2'-bipyridine)bis(hexafluorophosphate) (Ru(bpy)$_3$) as a metal catalyst for the BZ reaction, 9.5 g of vinylpyrrolidone (VP) and 0.35 g of 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator were dissolved in the methanol solution (31 g) under total monomer concentration of 20 wt%. These polymerizations were carried out at 60 °C for 24 h *in vacuo*. These resulting reaction mixtures were dialyzed against graded series of water/methanol mixtures, for 1 day each in 0, 25, 50, 75, and 100 wt% of water, and then freeze-dried.

2.2. Measurement of Lower Critical Solution Temperature (LCST)

The lower critical solution temperature (LCST) of the polymer solution was measured under the reduced and oxidized states, by using $Ce(SO_4)_2$ as an oxidizing agent and $Ce_2(SO_4)_3$ as a reducing agent, respectively. The polymer solutions (0.5 wt%) of poly(VP-*co*-Ru(bpy)$_3$) were prepared by dissolving the polymer in a 0.3 M HNO_3 aqueous solution and adding 5 mM $Ce(SO_4)_2$ or 5 mM $Ce_2(SO_4)_3$, respectively. The LCST measurements were carried out with a spectrophotometer (JASCO, Model V-630) equipped with magnetic stirrers and a thermostatic controller. In this measurement, the 570 nm wavelength was used because it is the isosbestic point for the reduced and oxidized states of Ru(bpy)$_3$. The transmittance (%) of the polymer solution at 570 nm was then recorded by raising the temperature at a rate of 0.5 ℃/min.

2.3. Measurement of Optical Oscillations

The poly(VP-*co*-Ru(bpy)$_3$) solutions were prepared by dissolving the polymer (0.5 wt%) into an aqueous solution containing the three BZ substrates (malonic acid (MA) and sodium bromate (NaBrO$_3$), nitric acid (HNO$_3$)). The transmittance self-oscillations of the polymer solutions were measured under constant temperature and stirring. In order to detect the transmittance change which is based on the autonomous transmittance change, 570-nm wavelength was used. The time course of the transmittance at 570 nm was monitored by a spectrophotometer.

3. Results and Discussion

The measurement of the solubility for the poly(VP-*co*-Ru(bpy)$_3$) solution in the reduced and oxidized state was conducted by changing the temperature from 10 to 50 ℃. As shown in Figure 2, there are no LCST for the polymer solutions in the reduced and oxidized state. The polymer solutions in the reduced and oxidized state have different transmittance values. That is, this result indicates that the polymer solution has different solubility in the reduced and oxidized state, respectively. The solubility of the polymer solution in the reduced state is higher than that in the oxidized state. This solubility tendency of the VP-based polymer solution is contrary to the conventional-type poly(NIPAAm-*co*-Ru(bpy)$_3$) [13] and AMPS-containing (poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS)) polymer solution [19-23]. In the case of the NIPAAm-based self-oscillating polymer systems, the reduced Ru(bpy)$_3^{2+}$ moiety in the polymer chain works the strongly hydrophobic part in the polymer chain due to the interaction among bipyridine ligands surrounding the Ru ion. On the other hand, in the oxidized state, the orientation of the bipyridine ligands surrounding the Ru ion disturbs the interaction among the Ru(bpy)$_3$ moieties in the polymer chain. Therefore, the hydrophilicity of the polymer chain in the oxidized state is higher than that in the reduced state. In contrast, in the case of this study, the interaction among the bipyridine ligands surrounding the Ru ion is obstructed by the VP based main-chain. This is because the five membered rings of the VP-based main-chain interacted with the bipyridine ligands surrounding the Ru ion. The solubility of the polymer chain is determined by the strength of the interaction with the bipyridine ligands [19-23]. That is, the stronger the interaction with the bipyridine ligands, the lower the solubility of the polymer solution.

Figure 2. Temperature dependence of transmittance for poly(VP-*co*-Ru(bpy)$_3$) solutions under the different conditions of reduced Ru(Ⅱ) (in Ce(Ⅲ) solution) and Ru(Ⅲ) (in Ce(Ⅳ) solution) states.
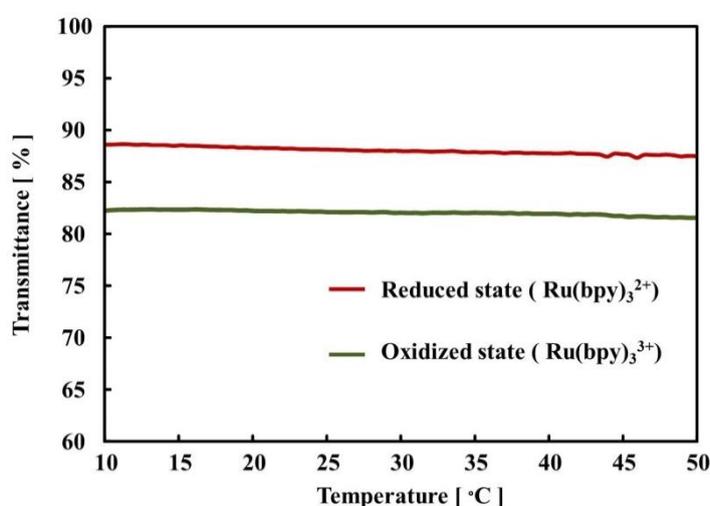
Therefore, in the case of the VP-based polymer chain, the strength of the interaction with the bipyridine ligands in the oxidized state is higher than that in the reduced state. This is because the orientation of the bipyridine ligands in the reduced state is suitable for the interaction with the

VP-based main-chain. The driving force of the transmittance self-oscillation for the VP-based polymer solution is attributed to the different solubility of the polymer chain in the reduced and oxidized state.

Figure 3. Oscillating profiles of transmittance at 14 ℃ for 0.5 wt% poly(VP-*co*-Ru(bpy)$_3$) solution in the fixed nitric acid and sodium bromate conditions ([HNO$_3$] = 0.3 M and [NaBrO$_3$] = 0.3 M): (**A**) [MA] = 0.04 M, (**B**) [MA] = 0.05 M, (**C**) [MA] = 0.06 M, (**D**) [MA] = 0.07 M, (**E**) [MA] = 0.08 M, (**F**) [MA] = 0.09 M.
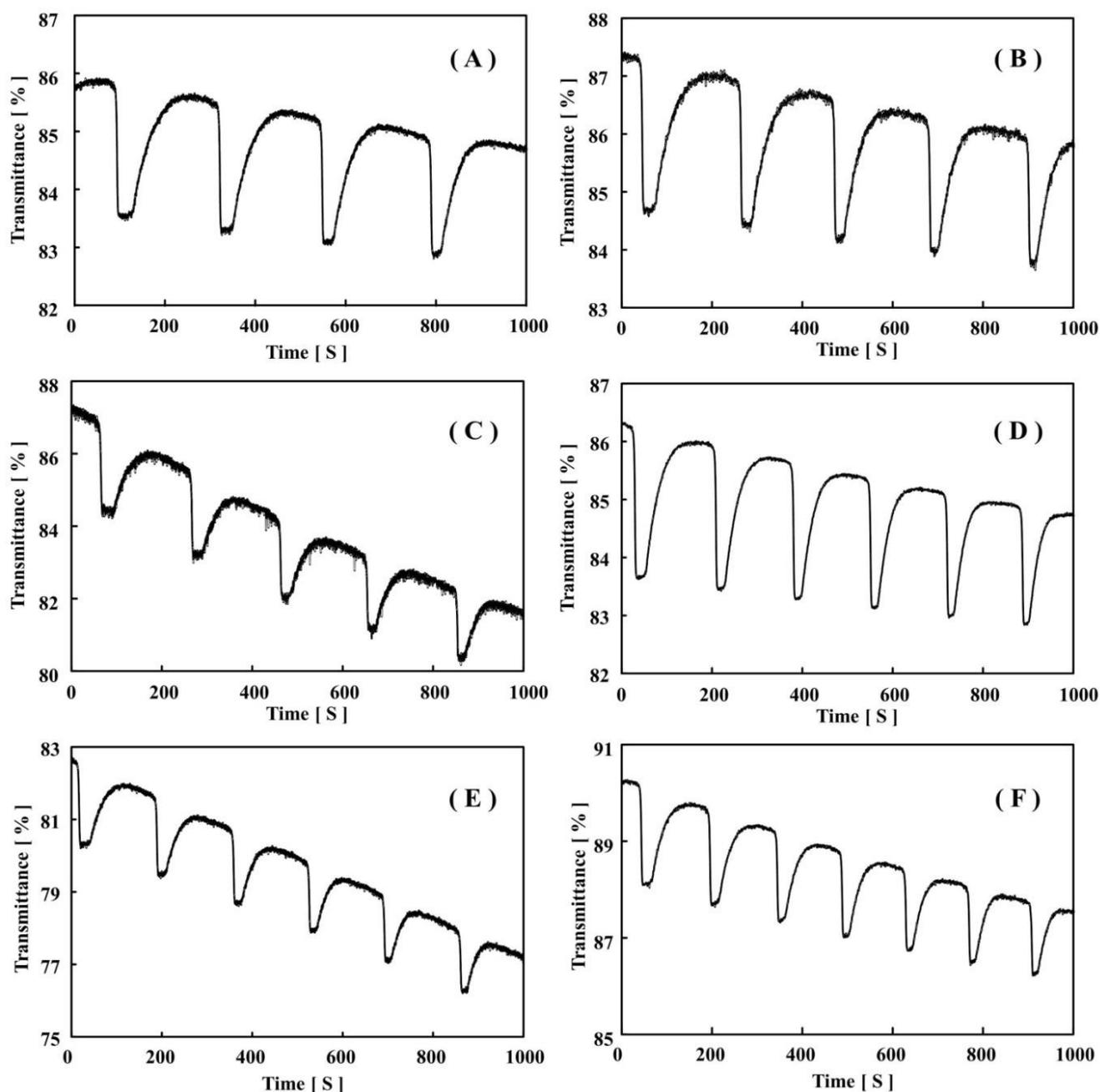

Figure 3 shows self-oscillating behaviors of the poly(VP-*co*-Ru(bpy)$_3$) solution in the different concentrations of malonic acid ([MA] = 0.04, 0.05, 0.06, 0.07, 0.08 and 0.09 M) under the fixed concentration of sodium bromate and nitric acid ([NaBrO$_3$] = 0.3 M and [HNO$_3$] = 0.3 M). As shown in Figure 3, the base line of the transmittance self-oscillation gradually decreased with time in all

malonic acid concentrations. The damping behavior originates from the change in the ionic strength of the polymer solution when the transmittance measurement starts [24-26]. In order to cause the BZ reaction in the polymer solution, the self-oscillating polymer solution and the other solution of the BZ substrates are mixed just before the transmittance measurements. In general, the solubility of the polymer chain is significantly affected by the ionic strength of the solution. Therefore, when the ionic strength increased at the start point of the self-oscillation, the solubility of the polymer chain decreased. In the solution condition of this study, the ionic strength of the polymer solution was very high because the BZ reaction required a significant high concentration of the BZ substrates. Therefore, the damping behaviors occurred from the start point of the self-oscillation. In addition, as shown in Figure 3, the width of the waveform increased with decreasing the concentration of malonic acid. Basically, the width of the waveform of the transmittance self-oscillation depends on the rate of the BZ reaction because the self-oscillation was induced by the BZ reaction. As the concentration of the BZ substrates decreased, the rate of the BZ reaction decreased due to decrease in the collision rate among the BZ substrates. Therefore, the width of the waveform increased with decreasing the concentration of the BZ substrates. This tendency was observed in the transmittance self-oscillation of the AMPS-containing polymer solutions [20].

Figure 4 shows the transmittance self-oscillations of the novel polymer solution in the different concentration of sodium bromate ($[NaBrO_3]$ = 0.1, 0.2, 0.3 and 0.4 M) at 14 °C under the fixed concentration of malonic acid and nitric acid ($[MA]$ = 0.1M and $[HNO_3]$ = 0.3 M). As shown in Figure 4, the amplitude of the self-oscillation gradually decreased with time in the same manner as in Figure 3. Moreover, the width of the waveform decreased with the increase in the concentration of sodium bromate due to the increase in the reaction rate of the BZ reaction. In addition, as shown in Figure 4, the amplitudes of the transmittance self-oscillations were hardly affected by the initial concentration of sodium bromate.

Figure 5 showed the amplitude of the transmittance self-oscillation for the polymer solution under the different concentrations of the BZ substrates. As shown in Figure 5, all the BZ substrate concentrations hardly influence the amplitude of the transmittance self-oscillation. That is, the amplitude values were almost the same in all BZ substrate conditions. In our previous investigations, we studied the effect of the concentration of the BZ substrates on the waveform of the transmittance self-oscillation for the AMPS-containing polymer solution. As a result, we clarified that the amplitude of the self-oscillation is significantly affected by the initial concentration of the BZ substrates [20,21]. This is because the AMPS-containing polymer chain caused damping, that is, the amplitude of the self-oscillation gradually decreased with time. The damping behavior of the polymer solution originates from the change in the size of the polymer aggregation with time. In the case of the NIPAAm-based polymer chains, the reduced Ru moiety in the polymer chain strongly interacts with the other reduced Ru one. Once the reduced Ru moiety strongly interacts with the other Ru one, the interaction hardly dissociates [20].

Figure 4. Oscillating profiles of transmittance at 14 ℃ for 0.5 wt% poly(VP-*co*-Ru(bpy)$_3$) solution in fixed nitric acid and malonic acid conditions ([HNO$_3$] = 0.3 M, [MA] = 0.1 M) (**A**) [NaBrO$_3$] = 0.1 M, (**B**) [NaBrO$_3$] = 0.2 M, (**C**) [NaBrO$_3$] = 0.3 M, (**D**) [NaBrO$_3$] = 0.4 M.
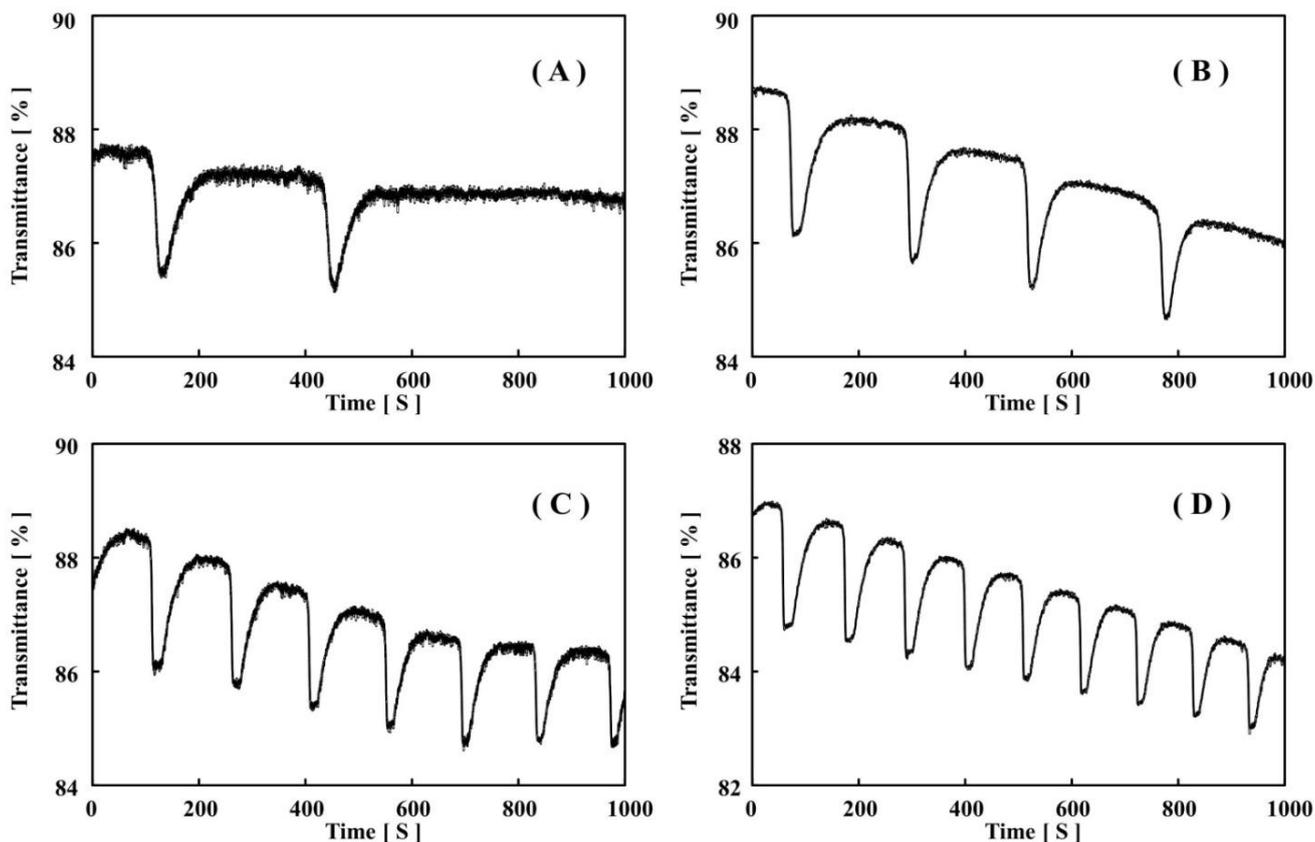
Figure 5. Dependence of amplitude of transmittance self-oscillation for polymer solution at 14 ℃ in the change in one BZ substrate under fixed concentrations of the other two BZ substrates: **MA** ([MA] = 0.04, 0.05, 0.06, 0.07, 0.08 and 0.09 M, fixed [NaBrO$_3$] = 0.3 M and [HNO$_3$] = 0.3 M); **NaBrO$_3$** ([NaBrO$_3$] = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 M, fixed [MA] = 0.1 M and [HNO$_3$] = 0.3 M); **HNO$_3$** ([HNO$_3$] = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 M, fixed [NaBrO$_3$] = 0.1 M and [HNO$_3$] = 0.3 M).
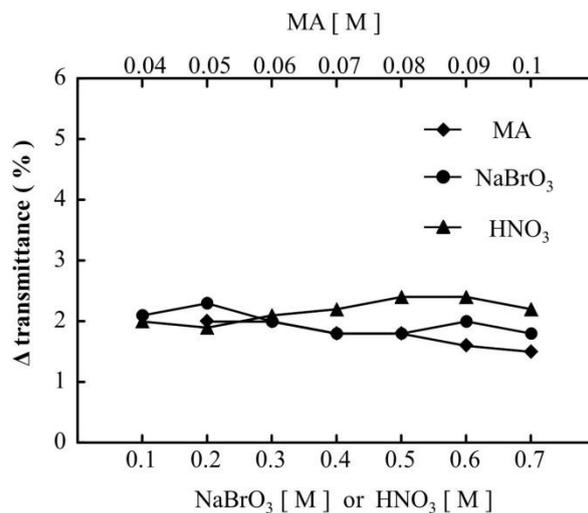
In the BZ reaction, the time in the reduced state is much longer than in the oxidized state. Therefore, the hydrophobic $Ru(bpy)_3^{2+}$ moiety in the polymer chain dominantly behaved for the determination of the polymer aggregation state in the self-oscillating behavior. For this reason, the mole fraction of the $Ru(bpy)_3^{2+}$ moiety in the polymer chain significantly affect the waveform of the transmittance self-oscillation. This influence can be explained by the overall process of the BZ reaction based on the Field-koros-Noyes (FKN) mechanism [15-18,20]. On the other hand, in the case of the VP-based polymer chain, the bipyridine ligands interacted with the VP based main-chain. The strength of the interaction of the bipyridine ligands in the oxidized state is higher than in the reduced state. That is, the polymer aggregation increased in the oxidized state. However, the time in the oxidized state is much shorter than in the reduced state. Therefore, the size of the polymer aggregation changed very slowly compared to the AMPS-containing polymer solution. Consequently, the degree of the damping for the Vp-based polymer solution is considerably small. Therefore, the amplitude is hardly affected by the initial concentration of the BZ substrates.

Figure 6 shows the logarithmic plots of the period against the initial concentration of one substrate under fixed concentrations of the other two BZ substrates at the constant temperature ($T = 14$ °C). As shown in Figure 6, all the logarithmic plots had a good linear relationship. Therefore, the period [T(s)] of the transmittance self-oscillation can be expressed as a[substrate]^b where a and b are the experimental constants and brackets assign the initial concentration. As shown in Figure 6(A,B), there are no saturation points in this experimental condition. On the contrary, as shown in Figure 6(C), the period of self-oscillation has its saturation point at the [HNO$_3$] = 0.4 M. Moreover, in the conditions of Figure 6(C), the period had a different aspect as compared to the conventional-type poly(NIPAAm-*co*-Ru(bpy)$_3$) gel [27]. In the case of the poly(NIPAAm-*co*-Ru(bpy)$_3$) gel, when increasing the concentration of nitric acid, the period increased. However, in general, the period of self-oscillation decreased with increasing the initial concentration of the BZ substrates because of the increase in the collision frequency among the BZ substrates. Therefore, we consider that the relationship between the period and the [HNO$_3$] for the poly(Vp-*co*-Ru(bpy)$_3$) is more a natural tendency.

Figure 6. Logarithmic plots of period *T* (in s) *vs.* initial molar concentration of one BZ substrate at a constant temperature ($T = 20$ °C) under fixed concentrations of the other two BZ substrates: (**A**) [NaBrO$_3$] = 0.3 M and [HNO$_3$] = 0.3 M; (**B**) [MA] = 0.1 M and [HNO$_3$] = 0.3 M; (**C**) [MA] = 0.1 M and [NaBrO$_3$] = 0.3 M.
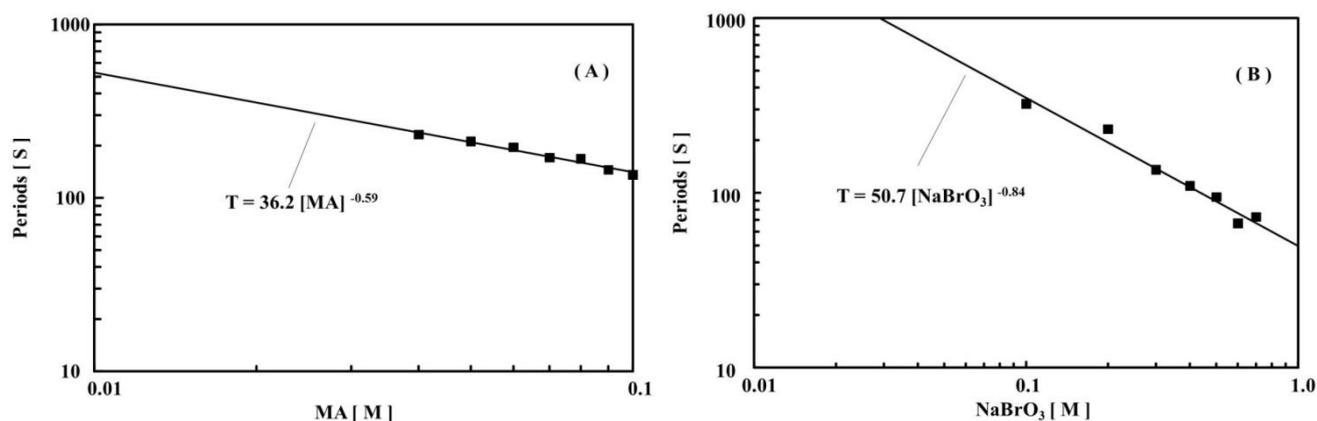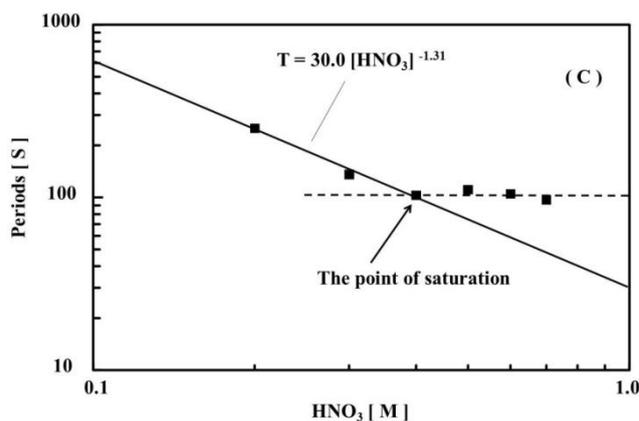
Figure 6. *Cont.*

4. Conclusions

In this study, we examined the influence of initial substrate concentrations of the BZ reaction on transmittance self-oscillation for the novel poly(Vp-*co*-Ru(bpy)₃) solution. As a result we noted that the width of the self-oscillation is much affected by the initial concentration of the BZ substrates. In addition, we clarified that the amplitudes of the transmittance self-oscillation is hardly affected by the initial concentrations of the BZ substrates. This tendency was not observed in the case of the AMPS-containing polymer solution. Furthermore, we demonstrated that the period of the transmittance self-oscillation can be controlled by the selection of the initial concentration of the BZ substrates.

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