

Effect of strong acid on the self-oscillating behavior for the polymer chain with the $\text{Fe}(\text{bpy})_3$

Tomoka Nakazumi¹ and Yusuke Hara^{1, a*}

¹Research Institute for Sustainable Chemistry, ISC, National Institute of Advanced Industrial Science and Technology, AIST, Central 5-2, 1-1-1 Higashi, Tsukuba 305-8565, Japan.

^ay-hara@aist.go.jp

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Abstract. In this study, a self-oscillating polymer chain with $\text{Fe}(\text{bpy})_3$ as the catalyst of the Belousov-Zhabotinsky (BZ) reaction was synthesized to examine the influence of strong acid (due to its oxidizing power) on the self-oscillating behavior. The polymer chain with $\text{Fe}(\text{bpy})_3$ underwent a soluble-insoluble self-oscillation induced by the BZ reaction because the solubilities of the $\text{Fe}(\text{bpy})_3$ moiety in the reduced and oxidized states were different. The self-oscillation of the polymer chain with $\text{Fe}(\text{bpy})_3$ lasted a long time. During the long period of the self-oscillation, the oscillating period and amplitude of the self-oscillation were stable.

Introduction

In previous studies, self-oscillating polymer systems with a Ru catalyst moiety ($\text{Ru}(\text{bpy})_3$) such as the Belousov-Zhabotinsky (BZ) reaction [1-6] were developed [7-14]. The polymer chain with $\text{Ru}(\text{bpy})_3$ undergoes a soluble-insoluble self-oscillation induced by the BZ reaction under constant temperature conditions. In the BZ reaction, the redox state of the $\text{Ru}(\text{bpy})_3$ moiety in the polymer chain changes periodically and the solubility of the polymer chain changes at the same time because the oxidized and reduced states of $\text{Ru}(\text{bpy})_3$ have different solubilities. To apply the self-oscillating polymer system to devices such as an autonomous pump system, the cost of the $\text{Ru}(\text{bpy})_3$ moiety was regarded a problem because Ru is a rare metal. To reduce the cost of the metal catalyst moiety in the self-oscillating polymer system, Hara et al. first synthesized a self-oscillating polymer chain with an Fe catalyst moiety ($\text{Fe}(\text{bpy})_3$) for the BZ reaction [15, 16]. In this study, the optical self-oscillating behaviors of the polymer chain with $\text{Fe}(\text{bpy})_3$ were measured at constant concentrations of the three BZ substrates (malonic acid (MA; 0.1 M), sodium bromate (NaBrO_3 ; 0.2 M), and sulfuric acid (H_2SO_4 ; 0.2 M)) and at constant several temperatures ($T = 11, 12, 13, 15, 17$, and 19°C). In previous studies [15, 16], nitric acid was used as the strong acidic agent for the BZ reaction. In this study, we selected sulfuric acid as the strong acidic agent to confirm the influence of the oxidation power on the self-oscillating behavior of the polymer solution with $\text{Fe}(\text{bpy})_3$.

Experimental Section

Synthesis of Poly(NIPAAm-co- $\text{Fe}(\text{bpy})_3$). The polymer chain with $\text{Fe}(\text{bpy})_3$ was synthesized by radical polymerization with a total monomer concentration of 20 wt% (NIPAAm (9.0 g) and $[\text{Fe}(\text{bpy})_3]$ (1.0 g)), utilizing 2,2'-azobis-(2-methylbutyronitrile) (0.01 g) as an initiator, at 80°C for 5 h under N_2 bubbling. After synthesis, the reaction mixture solution was dialyzed for 30 d while changing ethanol frequently. The dialyzed poly(NIPAAm-co- $\text{Fe}(\text{bpy})_3$) solution was freeze-dried after replacing ethanol with water.

Measurement of the Absorbance of Poly(NIPAAm-co- $\text{Fe}(\text{bpy})_3$). To clarify the isosbestic point of the poly(NIPAAm-co- $\text{Fe}(\text{bpy})_3$) solution, we measured the absorbance of the polymer chain as a function of the wavelengths in the reduced and oxidized states. To measure the reduced state, the 0.2 wt% polymer solution with $\text{Fe}(\text{bpy})_3$ contained 0.2 M sodium chloride (NaCl), 0.1 M malonic acid (MA), and 0.2 M sulfuric acid (H_2SO_4). In the oxidized state, the polymer solution (0.2 wt%)

contained 0.1 M NaCl, 0.2 M sodium bromate (NaBrO_3), and 0.2 M H_2SO_4 . The ionic strength of the polymer solution was adjusted using NaCl to be the same in the reduced and oxidized states.

Measurement of the Lower Critical Solution Temperature (LCST)

The lower critical solution temperature (LCST) for the polymer chain with $\text{Fe}(\text{bpy})_3$ in the reduced and oxidized states was measured via the isosbestic point measurement (604 nm wavelength). The LCSTs in the reduced and oxidized state were monitored by UV-vis spectrophotometry at temperatures ranging from 13 to 60 °C. In the reduced state, the 0.2 wt% polymer solution contained 0.2 M NaCl, 0.1 M malonic acid (MA), and 0.2 M H_2SO_4 . In the oxidized state, the polymer solution (0.2 wt%) contained 0.1 M NaCl, 0.2 M NaBrO_3 , and 0.2 M H_2SO_4 . NaCl was utilized to adjust the ionic strength of the polymer solution in the reduced and oxidized states.

Measurement of Transmittance Self-Oscillations

To measure the self-oscillation induced by the BZ reaction, the 0.2 wt% poly(NIPAAm-*co*- $\text{Fe}(\text{bpy})_3$) solutions including the three BZ substrates (MA (0.1 M), NaBrO_3 (0.2 M), and H_2SO_4 (0.2 M)) were prepared. As shown in Fig. 1, poly(NIPAAm-*co*- $\text{Fe}(\text{bpy})_3$) solution has an isosbestic point at 604 nm. This wavelength was different from the previous investigation because the polymer concentration, the strong acid and the concentrations of the oxidizing and reducing agents were different [15]. In this study, we used the 604 nm wavelength at several temperatures ($T = 11, 12, 13, 15, 17$ and 19 °C). The time course of the self-oscillation at 604 nm was monitored using a UV spectrophotometer.

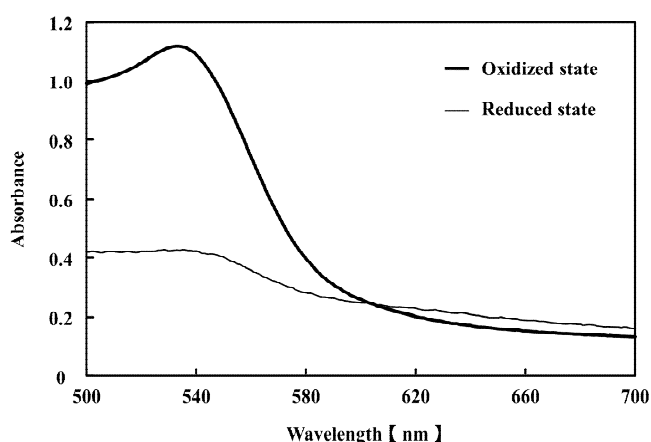


Fig. 1. Relationship between absorbance and the wavelength of the 0.2 wt% poly(NIPAAm-*co*- $\text{Fe}(\text{bpy})_3$) solutions in the reduced and oxidized states. MA and NaBrO_3 were used as the reducing and oxidizing agents, respectively. The ionic strength was adjusted to the same level in the reduced and oxidized state using NaCl.

Results and Discussion.

Fig. 1 shows the relationship between the wavelength and the absorbance of the poly(NIPAAm-*co*- $\text{Fe}(\text{bpy})_3$) solutions in the reduced and oxidized states. As shown in Fig. 1, the isosbestic point of the polymer solution with sulfuric acid as the strong acid agent for the BZ reaction was 604 nm. In this study, all measurements to measure the soluble-insoluble self-oscillation of the polymer solution were at 604 nm; this ignored the color change self-oscillation because the colors of $\text{Fe}(\text{bpy})_3$ in the reduced and oxidized states are different.

The LCST of the polymer solutions in the reduced and oxidized states (see Fig. 2) were measured at 604 nm while changing the temperature from 13 °C to 60 °C. In this LCST measurement, MA and NaBrO_3 were adopted as the reduced and oxidized agents, respectively. The

ionic strength of the 0.2 wt% polymer solution was adjusted using NaCl because the ionic strength of the solution affects the LCST and the transmittance self-oscillating behavior [15]. The LCST in the reduced state was about 28 °C and that in the oxidized state was about 15 °C.

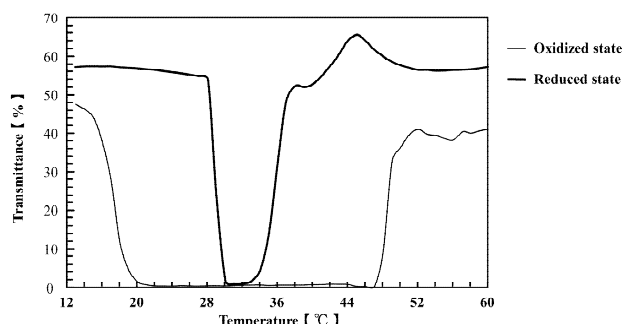


Fig. 2 Temperature dependence (13-60 °C) of transmittance at 604 nm for poly(NIPAAm-co-Fe(bpy)₃) solutions in the reduced and oxidized states.

In this study, we measured the transmittance self-oscillation of a 0.2 wt% poly(NIPAAm-co-Fe(bpy)₃) solution at constant concentrations of NaBrO₃, MA, and H₂SO₄, at different temperatures (T = 11, 12, 13, 15, 17, and 19 °C). At 15, 17, and 19 °C, there were no observations of transmittance self-oscillation. The LCST of the 0.2 wt% poly(NIPAAm-co-Fe(bpy)₃) solution in the oxidized state was about 15 °C. This result indicated that the polymer chain in the oxidized state above 15 °C had hydrophobic nature. The transmittance self-oscillation originates in the soluble-insoluble periodic change of the Fe(bpy)₃ moiety in the polymer chain. When the solubility of the polymer main-chain decreased in the oxidized state, the polymer chain easily aggregated. We consider that the decreasing flexibility of the polymer chain due to the low solubility inhibited the transmittance self-oscillation. Therefore, the self-oscillation could not be measured at temperatures above 15 °C [15].

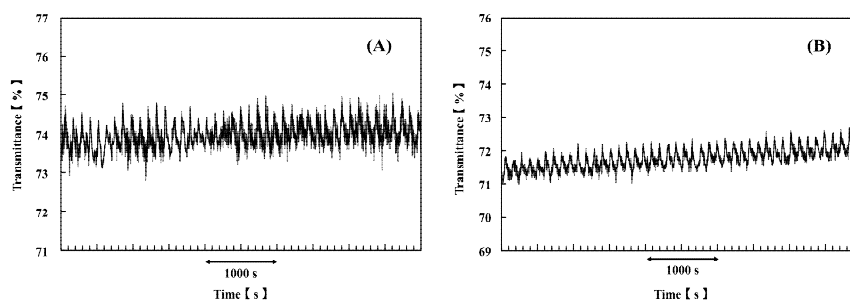


Fig. 3 Transmittance self-oscillation for 0.2 wt% poly(NIPAAm-co-Fe(bpy)₃) solutions at constant sulfuric acid, sodium bromate, and malonic acid condition ([H₂SO₄] = 0.2 M, [NaBrO₃] = 0.2 M, [MA] = 0.1 M): (A) 12 °C, (B) 13 °C.

Fig. 4 shows the amplitude of the transmittance self-oscillation for the poly(NIPAAm-co-Fe(bpy)₃) solution at constant concentrations of the BZ substrates at 12 and 13 °C. The amplitude of the self-oscillation at 12 °C was slightly larger than that at 13 °C (Fig. 4). In this self-oscillating condition, the polymer flexibility increased when decreasing the temperature because the LCST in the oxidized state of the polymer chain was about 15 °C. Therefore, we considered that the amplitude of the self-oscillation at 12 °C was slightly larger than at 13 °C.

Fig. 5 shows the time dependence of the period of the transmittance self-oscillation for the 0.2 wt% poly(NIPAAm-co-Fe(bpy)₃) polymer solution at constant concentrations of the three BZ substrates. The period of the self-oscillation was almost the same (120 s) because the self-oscillating period follows the Arrhenius equation [17].

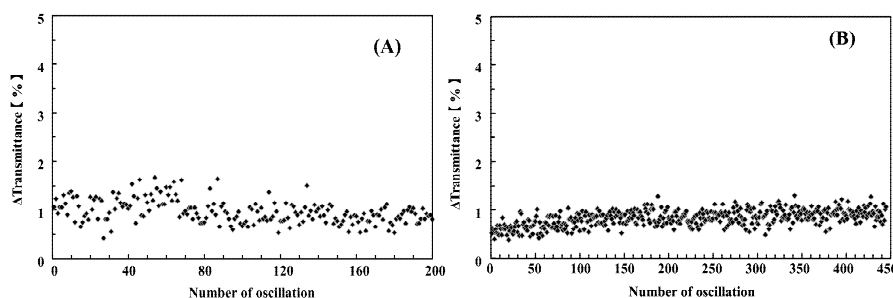


Fig. 4 Dependence of the amplitude of optical self-oscillation for 0.2 wt% poly(NIPAAm-*co*-Fe(bpy)₃) at constant sulfuric acid, sodium bromate, and malonic acid ([H₂SO₄] = 0.2 M, [NaBrO₃] = 0.2 M, [MA] = 0.1 M): (A) 12 °C, (B) 13 °C.

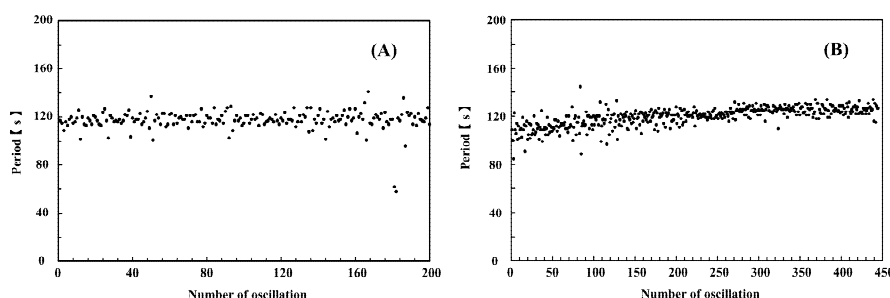


Fig. 5 Dependence of the period of optical self-oscillation for 0.2 wt% poly(NIPAAm-*co*-Fe(bpy)₃) at constant sulfuric acid, sodium bromate, and malonic acid ([H₂SO₄] = 0.2 M, [NaBrO₃] = 0.2 M, [MA] = 0.1 M): (A) 12 °C, (B) 13 °C.

Conclusion

The transmittance self-oscillation of the 0.2 wt% poly(NIPAAm-*co*-Fe(bpy)₃) solution was observed at 11, 12, and 13 °C. There was no observation of the transmittance self-oscillation above 15 °C because the LCST of the oxidized polymer solution was about 15 °C. Using sulfuric acid as the strong acid agent in the BZ reaction affected the solubility of the polymer chain with the Fe(bpy)₃ because the LCST in the oxidized state changed compared relative to the use of nitric acid. The self-oscillation of the 0.2 wt% poly(NIPAAm-*co*-Fe(bpy)₃) solution had a long lifetime with stable amplitude and period.

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