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Activation energy of the soluble-insoluble self-oscillation in an autonomous polymer chain

Tomoka Nakazumi[1] and Yusuke Hara[1, a]*

[1]Research 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.

[a]y-hara@aist.go.jp

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Abstract. In this study, we report the activation energy of the optical self-oscillation for a polymer chain that consisted of *N*-isopropylacrylamide (NIPAAm) (25 wt%), the Ru catalyst (5 wt%) of the Belouzov-Zhabotinsky (BZ) reaction, and acrylamide-2-methylpropanesulfonic acid (AMPS) (75 wt%). The AMPS moiety in the polymer chain has a negative charge and works as a solubility control site in the self-oscillating polymer chain (poly(NIPAAm-*co*-$Ru(bpy)_3$-*co*-AMPS)). The optical self-oscillation of the polymer chain at constant temperature was induced by the BZ reaction. In the BZ reaction, the $Ru(bpy)_3$ moiety in the polymer chain undergoes redox oscillation, and at the same time, the solubility of $Ru(bpy)_3$ changes periodically. Due to the cyclic redox change in the $Ru(bpy)_3$ moiety, the polymer chain underwent soluble-insoluble self-oscillation. The period of the self-oscillation for the poly(NIPAAm-*co*-$Ru(bpy)_3$-*co*-AMPS) decreased with increasing temperature, in accordance with the Arrhenius equation.

Introduction

The Belouzov-Zhabotinsky (BZ) reaction is a well-known self-oscillating redox reaction and the overall process of the BZ reaction is the oxidation of malonic acid (MA) by sodium bromate ($NaBrO_3$) in the presence of $Ru(bpy)_3$ under strong acidic conditions [1-9]. In the BZ reaction, the redox oscillation of the $Ru(bpy)_3$ and the solubility of the $Ru(bpy)_3$ changes periodically at the same time. To cause the soluble-insoluble self-oscillation of the polymer chain, we synthesized a polymer chain with the $Ru(bpy)_3$ moiety as the catalyst for the BZ reaction. In the BZ reaction, the solubility of the $Ru(bpy)_3$ moiety in the polymer chain changes periodically because the solubilities of the reduced and oxidized $Ru(bpy)_3$ are quite different: oxidized $Ru(bpy)_3$ is hydrophilic and the reduced species is hydrophobic [10-15]. In previous studies, Hara et al. clarified the activation energy of a self-oscillating polymer chain with 10 wt% acrylamide-2-methylpropanesulfonic acid (AMPS). To demonstrate the effect of the $Ru(bpy)_3$ content in the self-oscillating polymer chain on the activation energy, a polymer chain with 5 wt% $Ru(bpy)_3$ content was synthesized in this study. This is because the influence of the $Ru(bpy)_3$ content on the activation energy is important for the molecular design of the self-oscillating polymer system. In addition, in this study, we evaluated the amplitude of the optical self-oscillation for the AMPS-containing polymer chain with 5 wt% $Ru(bpy)_3$ at different temperatures.

Experimental Section

Synthesis of Poly (NIPAAm-*co*-$Ru(bpy)_3$-*co*-AMPS). Poly(NIPAAm-*co*-$Ru(bpy)_3$-*co*-AMPS) (Fig. 1) was synthesized by radical polymerization with a total monomer concentration of 20 wt% utilizing 2,2′-azobisisobutyronitrile (AIBN) as the initiator in a mixture of ethanol and water (1:1 wt/wt). The feed composition of the monomers was NIPAAm:$Ru(bpy)_3$:AMPS = 25:5:75 (wt%). The synthesized mixture was dialyzed by water and then by ethanol. After the dialysis process, the polymer solution was frizzed-dried.

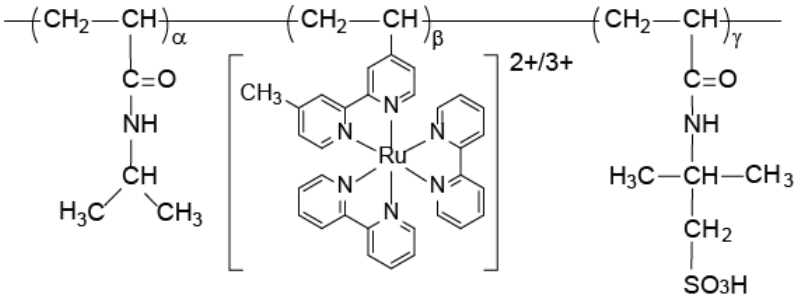

Fig. 1 Chemical structure of poly(NIPAAm-co-Ru(bpy)$_3$-co-AMPS).

Measurement of Soluble-Insoluble Self-oscillations. To measure the soluble-insoluble self-oscillation, we prepared 0.5 wt% poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) solutions containing fixed concentrations of the three BZ substrates: malonic acid (MA; 0.1 M), sodium bromate ($NaBrO_3$; 0.5 M), and sulfuric acid (H_2SO_4; 0.3 M). The soluble-insoluble self-oscillating behaviors of the polymer solution were measured at several temperatures (12, 15, 18, 21, 24, 27, and 30 °C) while being stirred. The 570 nm wavelength was used at all temperatures because this wavelength is the isosbetic point of the reduced and oxidized Ru(bpy)$_3$ moieties in the polymer chain [11-13]. In all measurements, the time course of the transmittance was monitored using a UV spectrophotometer.

Results and Discussion

Fig. 2 shows the soluble-insoluble self-oscillating behavior of the poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) (see Fig. 1) solutions at 12 and 15 °C. The self-oscillating behavior is attributed to the different solubilities of Ru(bpy)$_3$ in the reduced and oxidized states [16]; the reduced Ru(bpy)$_3$ moiety in the polymer chain is hydrophobic, while oxidized Ru(bpy)$_3$ is hydrophilic. Therefore, the polymer chain with Ru(bpy)$_3$ undergoes soluble-insoluble self-oscillation induced by the BZ reaction. As shown in Figs. 2 and 3, the amplitudes of self-oscillation for the poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) at 12 and 15 °C increased with time. In a previous study, the amplitude of the AMPS-containing polymer chain was observed to decrease with time; therefore, the transmittance self-oscillation caused damping [16]. The decrease in amplitude with time is attributed to the low solubility of the reduced Ru(bpy)$_3$ moiety in the polymer chain. In the reduced state, the polymer chains aggregated owing to the hydrophobic interaction originating in the hydrophobic reduced Ru(bpy)$_3$ moiety. When the soluble-insoluble self-oscillation was repeated, the size of polymer aggregation increased and the amplitude of the self-oscillation decreased with time.

In the previous study [16], the polymer chain had 10 wt% Ru(bpy)$_3$ content, which was twice that in this study. Moreover, the AMPS content (which had hydrophilic nature) was 40 wt%; in this study, the polymer chain had 75 wt% AMPS content. Due to the lower content of the reduced Ru(bpy)$_3$ moiety and higher content of the AMPS domain, the hydrophilicity of the polymer chain is higher in this study. Therefore, we consider that the polymer chain does not undergo damping in the transmittance self-oscillation. The increasing amplitude of the AMPS-containing polymer solution in Fig. 2 is attributed to the disaggregation of the polymer chain in the self-oscillating behavior originating from the hydrophilicity of the polymer chain [16]. As shown in Fig. 2(B), the waveform of the self-oscillation was disturbed after ~1300 s. The disturbed waveform of the transmittance self-oscillation of the polymer solution was due to CO_2 bubbles generated by the BZ reaction. The amount of CO_2 bubbles was larger at 15 °C than at 12 °C because the rate of the BZ reaction depends on temperature (see Fig. 4). The CO_2 bubbles inhibit the long-term measurement of the self-oscillation.

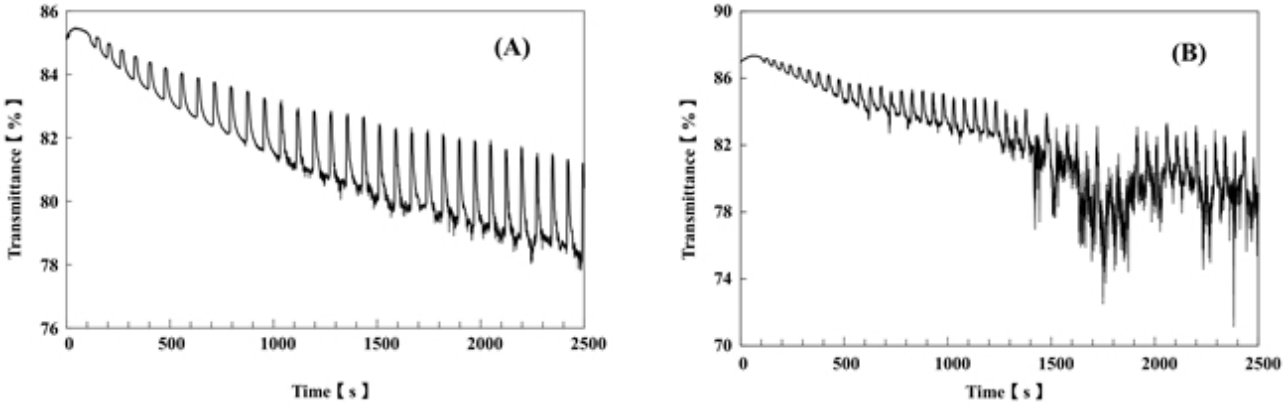

Fig. 2 Optical self-oscillations for 0.5 wt% poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) solutions at constant sulfuric acid, sodium bromate, and malonic acid ([H_2SO_4] = 0.3 M, [$NaBrO_3$] = 0.5 M, and [MA] = 0.1 M): (A) 12 °C, (B) 15 °C.

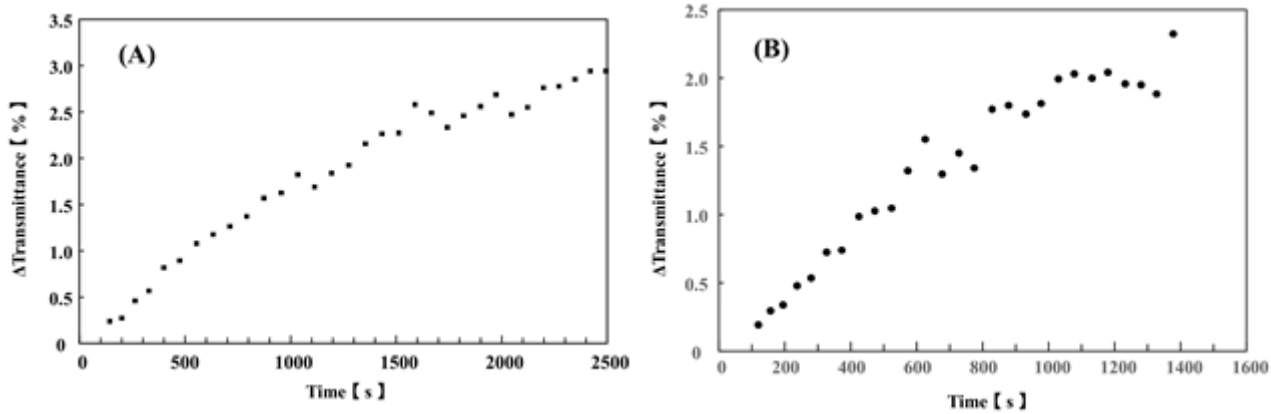

Fig. 3 Dependence of amplitude of optical self-oscillation for poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) solution at 12 °C (A) and 15 °C (B) at constant sulfuric acid, sodium bromate, and malonic acid ([H_2SO_4] = 0.3 M, [$NaBrO_3$] = 0.5 M, [MA] = 0.1 M).

Fig. 4 shows the period of the optical self-oscillation of the AMPS-containing polymer solution with constant concentrations of the three BZ substrates ([H_2SO_4] = 0.3 M, [$NaBrO_3$] = 0.5 M, [MA] = 0.1 M) as a function of temperature (12–30 °C). As shown in Fig. 4, the oscillating period of the AMPS-containing polymer solution decreased with increase in temperature, in accordance with the Arrhenius equation. The oscillating period and the experimental temperature (12–30 °C) have a linear relationship. From this linear relationship, the activation energy of the polymer solution was calculated to be 62.1 kJ/mol. The activation energy of the AMPS-containing polymer solution was almost the same as the BZ solution which does not include the self-oscillating polymer chain with Ru(bpy)$_3$ [17]. This result demonstrated that covalently bonding Ru(bpy)$_3$ to the AMPS-containing polymer chain does not inhibit the BZ reaction. Moreover, the activation energy of the polymer solution with 10 wt% Ru(bpy)$_3$ and 40 wt% AMPS was almost the same as the polymer chain used in this study [16]. This result suggested that the waveform of the transmittance self-oscillation does not affect the activation energy.

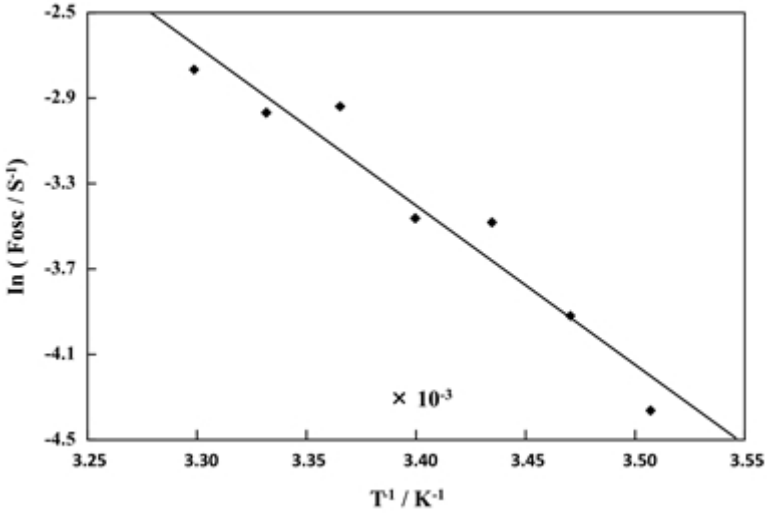

Fig. 4 Arrhenius dependence of the oscillating frequency (F_{osc}) of the optical self-oscillation of poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) on temperature (12–30 °C) with a fixed concentration of the BZ substrates ([H_2SO_4] = 0.3 M, [$NaBrO_3$] = 0.5 M, [MA] = 0.1 M).

Conclusion

In this study, we clarified the waveform and activation energy of the self-oscillation utilizing the AMPS-containing polymer solution. The Ru(bpy)$_3$ and the AMPS contents affected the waveform of the transmittance self-oscillation, but did not affect the activation energy. The generating CO_2 bubble inhibited measurement of the waveform of the self-oscillation. Therefore, in future, we plan to study the waveform of the self-oscillation of the polymer solution by using a BZ reaction that does not generate the CO_2 bubble.

Acknowledgments

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