Analysis of self-oscillating behaviors aimed at the development of a molecular robot with organic acids as fuel

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Abstract. We studied the transmittance self-oscillation of a polymer chain driven by an organic acid as the fuel. The self-oscillating polymer chain consists of 4-acryloylmorpholine (ACMO) and the Ru catalyst (\(\text{Ru(bpy)}_3\)) of the Belousov–Zhabotinsky (BZ) reaction. The transmittance self-oscillating behavior was affected significantly by the temperature. As the amplitude of the transmittance self-oscillation, which is reflected by the aggregation state, decreased with time, the oscillation period also decreased. This trend indicates that the polymer aggregation affects the rate of the BZ reaction significantly. The activation energy of the self-oscillating value was almost the same in the normal BZ reaction, which does not include \(\text{Ru(bpy)}_3\) complexes in the polymer chains. In addition, we demonstrated the effect of one BZ substrate (sodium bromate or malonic acid) on the transmittance self-oscillation period.

1. Introduction

Mechanical robots have actuators, sensors, and intelligence, and these three essential components are independent yet connected to each other. On the other hand, living organisms also have actuators, sensors, and intelligence, but it is impossible to clearly separate three essential components. Moreover, a living organism has specific functions, such as a self-motion, self-repairing, self-reproduction, and self-organization [1], and it is difficult to imitate these four functions using a mechanical framework. In recent years, molecular robots consisting of organic substances have been investigated with the aim of building a robot like a living organism. These molecular robots have been developed by using DNA, proteins, gels, and polymers [2–12]. Molecular robots assembled using DNA are of particular interest because it has become possible to synthesize various DNA structures [13–20]. However, molecular robots made of DNA nanostructures have several technical problems; for example, (1) it is difficult to drive these robots dynamically, such as polymer robots, and, (2) from the viewpoint of the cost, large DNA nanostructures are not realistic. On the other hand, by careful choice of polymeric material, large molecular robots can be developed [21, 22].

In many previous investigations, polymer based molecular robots have been fabricated by using stimuli-responsive polymers [23–25]. To date, stimuli-responsive polymers driven in response to various external stimuli, such as light, temperature, magnetic fields, and electric fields, have been developed [26–31]. In particular, temperature responsive polymers have been heavily studied because temperature control is convenient for chemists. To drive and control a robot made of stimuli-responsive polymers, external devices to control the external stimuli are necessary. That is, stimuli-responsive polymer-based robots are dependent on external control devices, as well as batteries as the energy source. This means that we cannot make small, self-sustaining ant-like robots.
In this study, to develop a molecular robot with the autonomous motion like a living organism, we synthesized a self-oscillating polymer chain [32–34] that is driven by the consumption of an organic acid (malonic acid (MA)) induced by the Belousov–Zhabotinsky (BZ) reaction [35–40]. In the BZ reaction, an organic substrate, such as malonic acid, is oxidized by an oxidizing agent (sodium bromate) in strongly acidic conditions in the presence of a catalyst. The solubility of the Ru catalyst that is covalently bonded to the polymer chains periodically changes, induced by the BZ reaction. The change in the solubility of the Ru catalyst moiety results in the periodic aggregation and disaggregation of the polymer chain. This behavior can be observed as the transmittance self-oscillations of the polymer chains [41–43]. In other words, the self-oscillating polymer chain autonomously converts chemical energy into mechanical energy.

Hara et al. studied self-oscillating polymer chains and gels to fabricate molecular robots. In particular, many studies have been published concerning self-oscillating polymer systems for operation under biological conditions. To drive the polymer under the biological conditions, Hara et al. synthesized a temperature-responsive N-isopropyl acrylamide (NIPPAm)-based polymer chain that was incorporated into a pH control site (acrylamide-2-methylpropane sulfonic acid (AMPS)) or a cationic capture site (methacrylamidopropyltrimethylammonium chloride (MAPTAC)) for an anionic oxidizing agent (bromate ions). As a result, these polymer systems underwent an aggregation–disaggregation self-oscillation under acid-free or oxidant-free conditions [44, 45]. Moreover, Hara et al. succeeded in the development of a novel self-oscillating polymer chain that underwent the self-oscillation in the presence of a BZ substrate (malonic acid) [46]. Subsequently, by improving the polymer structure, Hara et al. succeeded in the development of a novel self-oscillating polymer gel that undergoes self-oscillation under acid-free conditions [47]. In the process of these investigations, Hara et al. clarified that the NIPAAm-based AMPS-containing self-oscillating polymer chain has a high potential that can cause many types of self-oscillating behavior. For example, AMPS-containing self-oscillating polymer chains can switch the transmittance self-oscillation by external temperature control [48]. Moreover, NIPAAm-based AMPS-containing polymer gels undergo large displacements. By using the large displacement of the gel, a self-walking gel and a matter transport system were realized [49–51]. In addition, to improve the frequency of the self-oscillation, Hara et al. developed nonthermoresponsive self-oscillating polymer systems, such as the NIPAAm-based polymer chains [52–54]. In these polymer systems, the transmittance self-oscillation occurs at elevated temperatures. Furthermore, to reduce the cost of the self-oscillating polymer chain, a self-oscillating polymer chain with an Fe catalyst moiety, instead of the expensive and scarce Ru(bpy)_3 catalyst, was developed [55–57].

In this study, for the purpose of the development of an autonomous molecular robot, we synthesized a 4-acryloylmorpholine (ACMO)-based self-oscillating polymer chain, and analyzed in detail the self-oscillating behavior. The ACMO-based self-oscillating polymer gel has already been utilized as the main-chain of a self-oscillating polymer gel [57], but the detailed self-oscillating behavior has not been analyzed. To demonstrate the influence of the temperature and the concentration of the BZ substrates on the self-oscillating behavior, we measured the transmittance self-oscillation of the ACMO-based polymer chain by changing the temperature and the concentration of the BZ substrates. Moreover, the activation energy of the self-oscillation was calculated by utilizing the period of the transmittance self-oscillation at four different measuring temperatures. We believe that detailed analysis of the self-oscillating behavior is very important for the development and control of an autonomous molecular robot.

2. Method

2.1. Measurement of the isosbestic point of poly(ACMO-co-Ru(bpy)_3)

The isosbestic point of the poly(ACMO-co-Ru(bpy)_3) solutions was determined by measuring the absorbance in the oxidized and reduced states. By using sodium chloride, the ionic strength of the
polymer solutions was adjusted to be the same in both states. For the oxidized state measurements, a 3.0 wt.% polymer solution including 0.1 M NaCl, 0.3 M sodium bromate (NaBrO₃), and 0.4 M nitric acid (HNO₃) was prepared. For the reduced state, the polymer solution (3.0 wt.%) contained 0.3 M NaCl, 0.1 M MA, and 0.4 M HNO₃. As a result of the measurements of the isosbestic point of the poly(ACMO-co-Ru(bpy)₃) solutions in the reduced and oxidized states (see Figure 1), we adopted a wavelength of 548 nm for all other measurements in this study.

**Figure 1.** Chemical structure of poly(ACMO-co-Ru(bpy)₃).

2.2. Measurement of the lower critical solution temperature (LCST) of poly(ACMO-co-Ru(bpy)₃)

The lower critical solution temperatures (LCST) for the poly(ACMO-co-Ru(bpy)₃) solutions in the reduced and oxidized states were measured by UV-vis spectrophotometry at the isosbestic point (wavelength: 548 nm) (Figure 2) at temperatures from 15 to 60 °C. To equalize the total ionic strength of the polymer solutions in the reduced and oxidized states, NaCl was dissolved in the polymer solutions. For the oxidized state measurement, the 3.0 wt.% polymer solution contained 0.1 M NaCl, 0.3 M NaBrO₃, and 0.4 M HNO₃. On the other hand, for the reduced state, a polymer solution (3.0 wt.%) including 0.3 M NaCl, 0.1 M MA, and 0.4 M HNO₃ was prepared.

2.3. Measurement of the transmittance of the self-oscillations

To measure the transmittance self-oscillations, we prepared a 3.0 wt.% poly(ACMO-co-Ru(bpy)₃) solution containing the three BZ substrates, NaBrO₃, MA, and HNO₃. The transmittance measurement was monitored by UV-vis spectrophotometry at the isosbestic point (wavelength: 548 nm) under constant temperature conditions to measure the autonomous aggregation–disaggregation changes of the polymer solutions.

3. Results and discussion

Figure 2 shows the relationship between the absorbance and wavelength of the poly(ACMO-co-Ru(bpy)₃) solutions in the reduced and oxidized states. The absorbance of the polymer solution in the reduced and oxidized states had two intersections at 399 and 548 nm in the range from 300 to 700 nm; that is, the isosbestic point of the polymer solutions in the reduced and oxidized state has two wavelengths. In this study, we adopted a wavelength of 548 nm in all measurements. For the transmittance self-oscillation of the polymer solutions detected at the isosbestic point, the self-oscillating behavior did not result in a color change of the Ru(bpy)₃ moiety but a change in the turbidity of the polymer solutions. That is, the transmittance self-oscillation reflects the changes in the solubility of the reduced and oxidized states. Therefore, by measuring the self-oscillating behavior, it is possible to discuss the dissolution state of the poly(ACMO-co-Ru(bpy)₃) chains induced by the BZ reaction. The turbidity of the polymer solution is attributed to the size of the polymer aggregates. As the solubility of the polymer chain decreased, the size of the polymer aggregates increased. Therefore, the transmittance self-oscillation is attributed to the aggregation–disaggregation self-oscillation arising from the different solubilities of the polymer chains in the reduced and oxidized states.
Figure 2. The relationship between absorbance and wavelength of the 3.0 wt.% \text{poly(ACMO-co-Ru(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.

Figure 3 shows the results of the transmittance measurements for \text{poly(ACMO-co-Ru(bpy)$_3$)}} in the reduced and oxidized states from 15 to 60 °C. As shown in Figure 3(A), the LCST of the polymer solution in the oxidized state was about 42 °C. In contrast, there was no LCST of the polymer solution in the reduced state because the transmittance value in the reduced state was stable over the measured temperature range. This result indicates that the LCST of \text{poly(ACMO-co-Ru(bpy)$_3$)}} is present only in the oxidized state. As shown in Figure 3, from 15 to 33 °C, the transmittance value in the oxidized state was higher than that in the reduced state. This different transmittance value between the reduced state and in the oxidized state is the driving force for the self-oscillation of the \text{poly(ACMO-co-Ru(bpy)$_3$)}} solutions. For this reason, in this study, the transmittance self-oscillations of the 3.0 wt.% \text{poly(ACMO-co-Ru(bpy)$_3$)}} solution were measured below 25 °C to detect the stable self-oscillating behaviors.

Figure 4 shows the transmittance self-oscillation of the \text{poly(ACMO-co-Ru(bpy)$_3$)}} solutions with a fixed concentration of the three BZ substrates (0.3 M NaBrO$_3$, 0.1 M MA, and 0.4 M HNO$_3$) at four constant temperature conditions (13, 19, 23, and 25 °C). Figure 5 shows the results of the amplitude and the period for the self-oscillation of the \text{poly(ACMO-co-Ru(bpy)$_3$)}} solutions at each temperature. As shown in Figure 4, the amplitude of the self-oscillation decreased with time. In addition, as the temperature increased, the damping arose earlier. At 13 °C, the amplitude reduction was much slower.
than that above 19 °C. In contrast, in the case of 19 and 23 °C, the amplitude value rapidly decreased with time (see Figure 5(C-1) and 5(D-1)). At 25 °C, the damping behavior occurred about 600 s from the start of the self-oscillation; subsequently, the self-oscillation stopped quickly. This phenomenon was attributed to the decreasing solubility of the polymer chain on increasing the measurement temperature. As shown in Figure 3, in the oxidized state, the transmittance value gradually decreased with increasing temperature. That is, when the aggregation size of the polymer chains increased, the polymer aggregation causes light scattering [53]. Therefore, the amplitude of the transmittance self-oscillation of the poly(ACMO-co-Ru(bpy)) solutions decreased more rapidly as the measuring temperature increased.

Figure 5 shows the time dependence of the period for the transmittance self-oscillation of the poly(ACMO-co-Ru(bpy)) solutions at each temperature. As shown in Figures 5(A-2) and 5(B-2) (measuring conditions: 13 and 19 °C), the period of the self-oscillation gradually decreased with increasing self-oscillation number, while the period remained almost the same, except for the initial 10 cycles. Except for at 25 °C, the periods of the first 10 cycles were longer until the period stabilized. When the temperature rose, the stabilization time was shorter than at lower temperatures. At 23 °C (see Figure 5(C-2)), as the period decreased, the amplitude also decreased. Moreover, at 25 °C, the period sharply decreased in synchrony with the dramatic decrease in the amplitude. This result demonstrates that the period of the transmittance self-oscillation is affected by the amplitude of the transmittance self-oscillation. That is, as the size of the polymer aggregates increased in the self-oscillations, the amplitude decreased. As the same time, the density of the Ru(bpy)₃ moiety in the polymer aggregation increased. The density of the Ru(bpy)₃ moiety affected the reaction rate because the density of the substrates of the BZ reaction influences the reaction rates originating in the increasing collision rate among the reaction substrates. Therefore, the period of the self-oscillation was significantly influenced by the measuring temperature and the amplitude of the transmittance self-oscillation.
Figure 4. Transmittance self-oscillating profiles for 3.0 wt.% poly(ACMO-co-Ru(bpy)$_3$) solutions with fixed concentrations of HNO$_3$, NaBrO$_3$, and MA ([HNO$_3$] = 0.4 M, [NaBrO$_3$] = 0.3 M, and [MA] = 0.1 M) at four different temperatures: (A) 13 °C, (B) 19 °C, (C) 23 °C, and (D) 25 °C.
Figures 6 shows the Arrhenius dependence on the measuring temperature at a fixed concentration of two of the BZ reaction substrates. In Figure 6, the average periods were adopted by choosing the stable period region from Figure 5. As shown in Figure 6, the periods of the transmittance self-oscillation have a linear relationship; that is, the ACMO-based self-oscillating polymer chain follows the Arrhenius equation. The activation energy of the transmittance self-oscillation was about 67.0 kcal. This activation energy is almost the same value as that of the normal BZ reaction, which consists of a Ru(bpy)$_3$ catalyst that is not bonded to the polymer chain [58]. This result indicates that the Ru(bpy)$_3$ moiety that is bonded to the ACMO-main chain does not inhibit the BZ reaction. Furthermore, the activation energy of the poly(ACMO-co-Ru(bpy)$_3$) solutions is the almost same value as that of an NIPAAm-based [59] and a vinylpyrrolidone (VP)-based polymer chain [52], which have a nonthermoresponsive nature. In the previous investigation, a nonthermoresponsive VP main-chain was used to undergo the self-oscillation in high-temperature condition compared to the NIPAAm-based self-oscillating polymer system.

Figure 6. Arrhenius dependence on the temperature of self-oscillation for poly(ACMO-co-Ru(bpy)$_3$), oscillating frequency ($F_{osc}$), with a fixed concentration of the other three BZ substrates: [NaBrO$_3$] = 0.3 M, [MA] = 0.1 M, and [HNO$_3$] = 0.4 M.
have good linear relationships. Therefore, we expressed this relationship as \( T = a \text{[substrate]}^b \), where the \( T \) indicates the period and the brackets show the initial concentration, and \( a \) and \( b \) denotes the experimental constants. The values of \( a \) and \( b \) of the poly(ACMO-co-Ru(bpy)₃) solutions were almost the same as those of poly(NIPAAm-co-Ru(bpy)₃) and poly(VP-co-Ru(bpy)₃) solutions [52, 59]. The gradient of the graph in Figure 7(A) is steeper than that in Figure 7(B). This trend indicates that the effect of the concentration of NaBrO₃ for the oscillating period was larger than that of MA. Moreover, these results demonstrate that the period of the transmittance self-oscillation can be controlled by changing the BZ substrate conditions, as well as controlling the measuring temperature.

![Graphs showing the relationship between period \( T \) and concentration of NaBrO₃ and MA](image)

**Figure 7.** Relationship between period \( T \) (s) and initial molar concentration of one BZ substrate at constant temperature (\( T = 13 \) °C) with fixed concentrations of the other two BZ substrates: (A) \([\text{MA}] = 0.1 \text{ M and } [\text{HNO}_3] = 0.4 \text{ M}\); and (B) \([\text{NaBrO}_3] = 0.3 \text{ M and } [\text{HNO}_3] = 0.4 \text{ M}\).

### 4. Conclusions
In this study, we measured the transmittance self-oscillation of the poly(ACMO-co-Ru(bpy)₃) solutions as the function of the temperature and concentration of the BZ substrates. The amplitude of the transmittance self-oscillation was affected significantly by the measuring temperature. The amplitude of the self-oscillation decreased with time because the polymer chain aggregated in the self-oscillating behavior. As the size of the polymer aggregation increased with time, the period of the self-oscillation decreased. That is, the change in the density of the Ru(bpy)₃ moiety in the polymer aggregation increased the collision rate among the BZ substrates. Therefore, as apparent from the decreasing period, the reaction rate of the BZ reaction increased because of the increasing collision rate. The activation energy of the transmittance self-oscillation was almost the same value as the normal BZ reaction and the NIPAAm-based and VP-based self-oscillating polymer chains. Moreover, in this study, we have demonstrated that the period of the self-oscillation for the poly(ACMO-co-Ru(bpy)₃) solutions can be controlled by changing the concentration of the BZ substrates, as well as by changing the temperature.

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