

Autonomous polymer actuators

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Abstract: In this paper, in order to design the autonomous polymer actuators for soft robots and microfluidic devices, the effect of the molecular structure of the polymer chain on the self-oscillating behavior and the oscillation period was investigated by utilizing two-types of polymer chains; one is consist of N-isopropyl acrylamid (NIPAAm) and Ru catalyst of the BZ reaction, the other has NIPAAm and Ru catalyst, Acrylamide-2-methylpropanesulfonic acid (AMPS) with anionic charge as a solubility control site. As a result of the measuring the transmittance self-oscillation, it is clarified that the self-oscillating behavior is much affected by the molecular structure of the polymer chain. Moreover, this paper demonstrated the effect of the initial concentration of the three substrates of the Belousov-Zhabotinsky (BZ) reaction on the period of the aggregation-disaggregation self-oscillation.

Keywords: BZ reaction, molecular robot, soft actuator, oscillation period, self-oscillating polymer chain

1 INTRODUCTION

The self-oscillating polymer system can cause the aggregation-disaggregation self-oscillation synchronized with the periodically solubility change of the metal catalyst moiety in the polymer. [1-3] The cyclic solubility change of the metal catalyst is induced by the Belousov-Zhabotinsky (BZ) reaction. The BZ reaction is well known as an oscillating reaction accompanying spontaneous redox oscillations. [4-6] The overall process is the oxidization of an organic substrate by an oxidizing agent in the presence of the catalyst under acidic conditions. The solubility of the Ru catalyst changes with the oxidant state. In order to convert the cyclic solubility change of the Ru catalyst into the aggregation-disaggregation self-oscillation, the poly(Nisopropylacrylamide) (poly(NIPAAm)) covalently bonded to the Ru catalys was synthesized. As a result, the polymer chain caused the aggregation-disaggregation self-oscillation under the constant temperature conditions with the coexistence of the BZ substrates other than the metal catalyst. Therefore, the driving environment of the polymer chain was strongly restricted in the BZ reaction field. In my previous studies, in order to modify the driving environment, the molecular structure of the self-oscillating polymer chain was modified. As a result, the novel self-oscillating polymer chain can cause the aggregation-disaggregation self-oscillation only in the presence of malonic acid. [7] That is because the novel self-oscillating polymer chain has both a pH control and an oxidant supply sites in the self-oscillating polymer chain. In the process of this study, the self-oscillating polymer system with a negatively charged acrylamide-2-methylpropanesulfonic acid (AMPS) has a lot of potentials to control the self-oscillating behavior. [8-12] By utilizing this potential, the self-oscillating polymer system can cause an on-off switching of the self-oscillation by controlling the external temperature and a viscosity self-oscillation under acid-free condition.

In this paper, in order to design the autonomous polymer actuators for soft robots and microfluidic devices, the effect of the molecular structure of the polymer chains on the self-oscillating behavior and the oscillation period was investigated by utilizing two-types of polymer chains; one is consist of N-isopropyl acrylamid (NIPAAm) and Ru catalyst of the BZ reaction, the other has NIPAAm and Ru catalyst, Acrylamide-2-methylpropanesulfonic acid (AMPS) with anionic charge as a solubility control site. As a result of the measuring the transmittance self-oscillation, it is clarified that the self-oscillating behavior is much affected by the molecular structure of the polymer chain. Moreover, it is demonstrated the effect of the initial concentration of the three substrates of the BZ reaction on the period of the aggregation-disaggregation self-oscillation.

2 EXPERIMENTAL SECTION

Polymerization of poly(NIPAAm-co-Ru(bpy)₃)

poly(NIPAAm-co-Ru(bpy)₃) (Figure 1) was synthesized by utilizing N-isopropyl acrylamid (NIPAAm) and Ru(bpy)₃ monomer (ruthenium (4-vinyl-4'-methyl-2,2'-bipyridine)bis(2,2'-bipyridine)bis(hexafluorophosphate)) and 2,2'-azobisisobutyronitrile (AIBN) as an initiator by radical polymerization in an ethanol solution under a total monomer concentration of 20 wt% at 60°C. The feed composition (wt%) was as follows; NIPAAm : Ru(bpy)₃ = 10 : 90. The resulting reaction mixture was dialyzed against water for 4 days followed by ethanol for 3 days, and then freeze-dried.

Polymerization of poly(NIPAAm-co-Ru(bpy)₃-co-AMPS)

Using NIPAAm, Acrylamide-2-methylpropanesulfonic acid (AMPS), Ru(bpy)₃ monomer and AIBN, poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) (Figure 2) was synthesized by radical polymerization in a mixture of ethanol and water (1:1 wt/wt%) under a total monomer

concentration of 20 wt% at 60 °C. The feed composition (wt%) was as follows; NIPAAm : Ru(bpy)₃ : AMPS = 40 :10 : 50. The resulting reaction mixture was dialyzed against water for 4 days followed by ethanol for 3 days, and then freeze-dried.

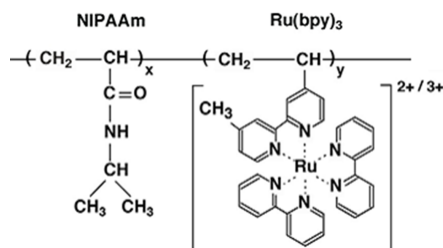


Figure 1. Chemical structure of poly(NIPAAm-co-Ru(bpy)₃)

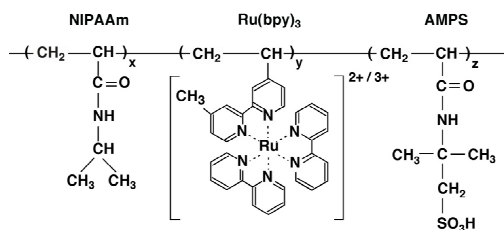


Figure 2. Chemical structure of poly(NIPAAm-co-Ru(bpy)₃-co-AMPS).

Measurement of transmittance self-oscillations.

The self-oscillating polymer solutions were prepared by dissolving the polymer (0.5 wt%) into an aqueous solution containing the three BZ substrates (nitric acid (HNO₃), sodium bromate (NaBrO₃) and malonic acid (MA)). The transmittance self-oscillations of the polymer solutions were measured under constant temperature (18 °C) and stirring condition. In order to detect the transmittance change which is based on the autonomous aggregation-disaggregation change, 570-nm wavelength was used. This is because 570-nm wavelength is the isosbestic point of the reduced and oxidized states of Ru(bpy)₃. [3, 7-9] The time course of the transmittance at 570 nm was monitored by a spectrophotometer.

3 RESULT AND DISCUSSION

Figure 3 shows self-oscillating behaviors of the poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) (Figure 3(A) and 3(B)) and the poly(NIPAAm-co-Ru(bpy)₃) (Figure 3(C) and 3(D)) solutions in the different concentrations of sodium bromate ([NaBrO₃] = 0.4 and 0.5 M) at 18 °C under the fixed concentration of malonic acid ([MA] = 0.1M) and nitric acid ([HNO₃] = 0.3 M). As shown in Figure 3(A) and 3(B), the amplitude of the transmittance self-oscillation for the AMPS-containing polymer solution is significantly stable. In contrast, the amplitude of the self-oscillation for the poly(NIPAAm-co-Ru(bpy)₃) is not constant.

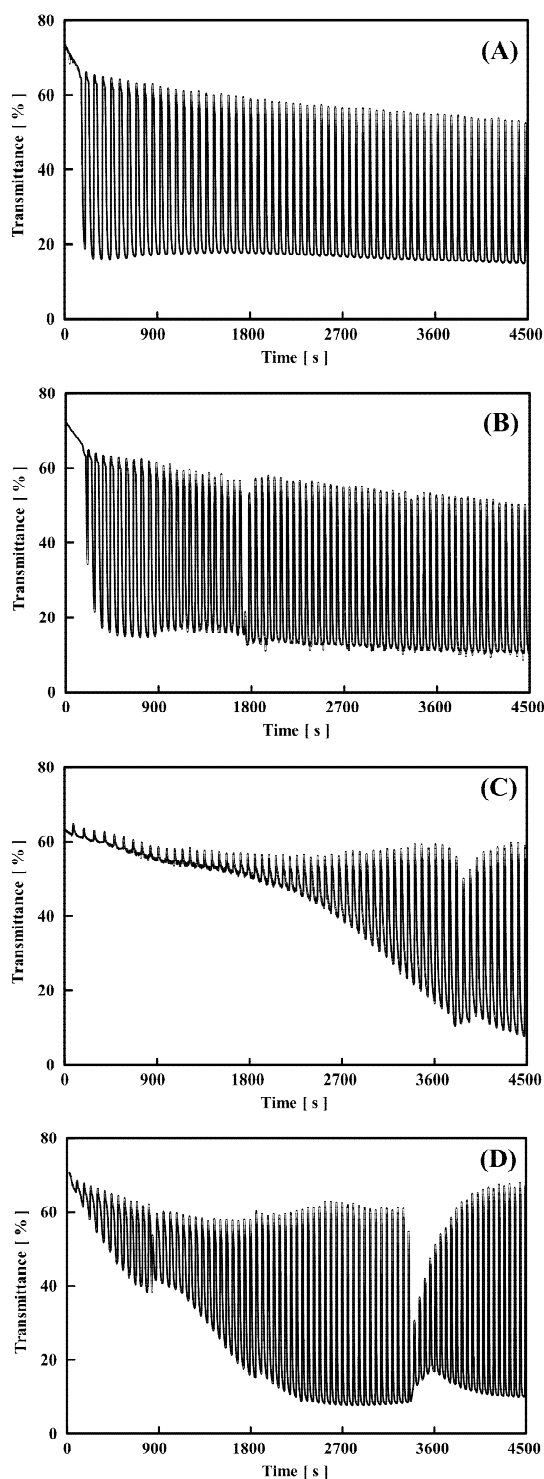


Figure 3. Oscillating profiles of transmittance at 18 °C for 0.5 wt% poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) ((A) and (B)) and poly(NIPAAm-co-Ru(bpy)₃) ((C) and (D)) solutions in the fixed nitric acid and malonic acid conditions ([HNO₃] = 0.3 M and [MA] = 0.1 M): (A) [NaBrO₃] = 0.4 M, (B) [NaBrO₃] = 0.5 M, (C) [NaBrO₃] = 0.4 M, (D) [NaBrO₃] = 0.5 M.

That is because the self-oscillating polymer chain without the AMPS moiety is easy to aggregate in the polymer solution because the solution containing three BZ substrates has the high ionic strength. On the other hand, the AMPS-containing polymer solution with the low polymer concentration is hard to aggregate due to the repulsive force of the AMPS moiety in the polymer chain. In my previous studies, in the polymer concentration above 1 wt%, the poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) chain is easy to aggregate due to the electrostatic attractive force among the polymer chains. [12-13]

This is because the polymer chain has the cationic Ru(bpy)₃ and the anionic AMPS moieties in the polymer chain. As shown in Figure 3(C) and 3(D), the amplitude of the self-oscillation gradually increased with time.

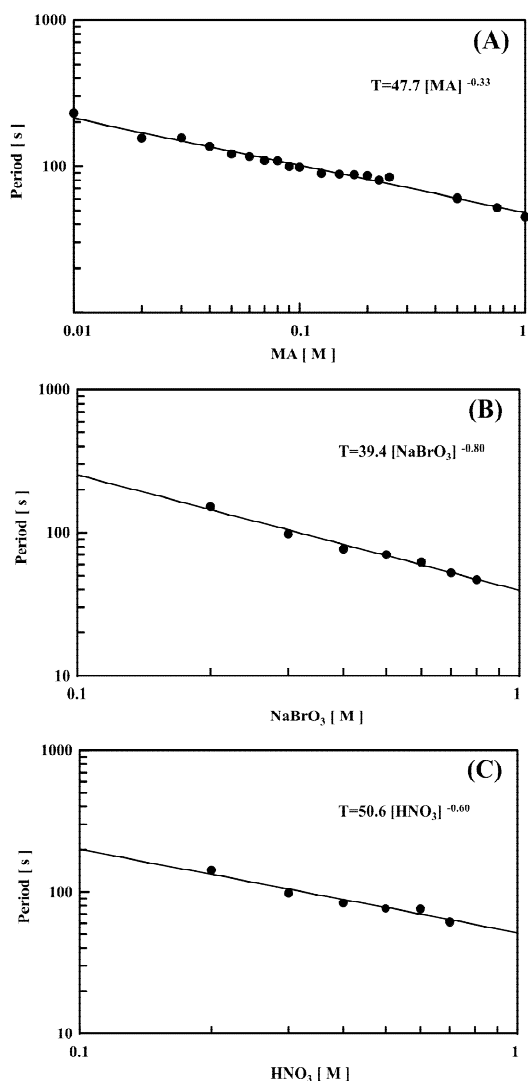


Figure 4. Logarithmic plots of period T (in s) for 0.5 wt% poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) solution vs initial molar concentration of one BZ substrate at a constant temperature ($T = 18\text{ }^{\circ}\text{C}$) under fixed concentrations of the other two BZ substrates: (A) $[\text{NaBrO}_3] = 0.3\text{ M}$ and $[\text{HNO}_3] = 0.3\text{ M}$; (B) $[\text{MA}] = 0.1\text{ M}$ and $[\text{HNO}_3] = 0.3\text{ M}$; (C) $[\text{MA}] = 0.1\text{ M}$ and $[\text{NaBrO}_3] = 0.3\text{ M}$.

This behavior indicates that the aggregated polymer chains gradually disaggregated in the self-oscillating behavior.

Figure 4 and 5 showed the logarithmic plots of the period against the initial concentration of one substrate under fixed the other two BZ substrates at the constant temperature ($T = 18\text{ }^{\circ}\text{C}$). As shown in Figure 4 and 5, all the logarithmic plots had a good linear relationship. Therefore, the period $[T(\text{s})]$ of the transmittance self-oscillation can be expressed as $a[\text{substrate}]^b$ where a and b are the experimental constants and bracket s assign the initial concentration. As shown in Figure 4 and 5, there are no saturation points in this experimental condition. In the case of the nonthermoreponsive polymer chain, the period of the self-oscillation have the saturation point at the $[\text{HNO}_3] = 0.3\text{ M}$. [14]

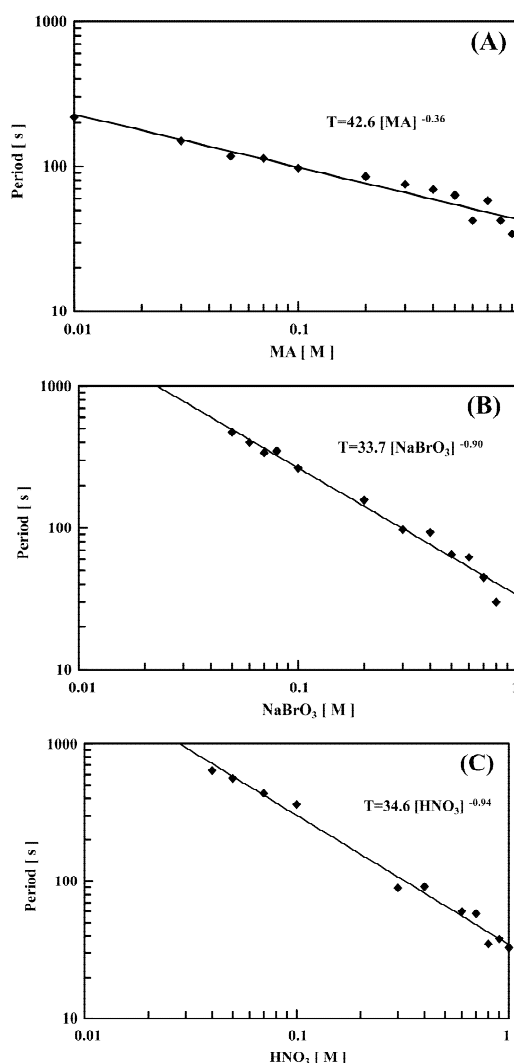


Figure 5. Logarithmic plots of period T (in s) of 0.5 wt% poly(NIPAAm-co-Ru(bpy)₃) solution vs initial molar concentration of one BZ substrate at a constant temperature ($T = 18\text{ }^{\circ}\text{C}$) under fixed concentrations of the other two BZ substrates: (A) $[\text{NaBrO}_3] = 0.3\text{ M}$ and $[\text{HNO}_3] = 0.3\text{ M}$; (B) $[\text{MA}] = 0.1\text{ M}$ and $[\text{HNO}_3] = 0.3\text{ M}$; (C) $[\text{MA}] = 0.1\text{ M}$ and $[\text{NaBrO}_3] = 0.3\text{ M}$.

As shown in Figure 4(C) and 5(C), the b value of the poly(NIPAAm-co-Ru(bpy)₃) is much larger than that of poly(NIPAAm-co-Ru(bpy)₃-co-AMPS). In the case of the poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) solution (Figure 4(C)), the aggregation-disaggregation self-oscillation do not occur in the condition under the [HNO₃] = 0.1 M. Moreover, in the case of the poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) solution (Figure 4(B)), there are no aggregation-disaggregation self-oscillation in the condition under the [NaBrO₃] = 0.1 M. These results indicate that the concentration range of the three BZ substrates for the AMPS-containing polymer solution where the self-oscillation occur is much narrower than that for the poly(NIPAAm-co-Ru(bpy)₃) solution. In addition, as shown in Figure 4(C) and 5(C), the period has the different aspect as compared to the conventional-type poly(NIPAAm-co-Ru(bpy)₃) gel [15]. In the case of the poly(NIPAAm-co-Ru(bpy)₃) gel, when increasing in the concentration of nitric acid, the period increased. However, in general, the period of the 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, I consider that the tendency of the Figure 4(C) and 5(C) is more natural tendency

4 CONCLUSION

In this study, in order to design the autonomous polymer actuators for soft robots and microfluidic devices, the effect of the molecular structure of the self-oscillating polymer chain on the self-oscillating behavior and the oscillation period was investigated by utilizing the poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) and the poly(NIPAAm-co-Ru(bpy)₃) solutions. As a result, the amplitude of the poly(NIPAAm-co-Ru(bpy)₃) is not stable due to the aggregation property of the polymer chains. On the other hand, the amplitude of the poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) is significantly stable. This result indicates that the AMPS-containing polymer chain is hard to aggregate originating in the repulsive force of the AMPS moiety in the polymer chain in the low polymer concentration. In addition, this paper demonstrated the period of the two-types of self-oscillating polymer solutions. The concentration range of three BZ substrates for the poly(NIPAAm-co-Ru(bpy)₃) solution where the self-oscillation occur is much wider than that for the poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) solution.

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