Self-Oscillating Nano-Gel Particles

T. Sakai¹, R. Yoshida¹, S. Ito¹ and T. Yamaguchi²

¹Department of Materials Engineering, Graduate School of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
²National Institute of Advanced Industrial Science and Technology, Japan
Phone&Fax: 81-03-5841-7112, e-mail: sakai@bmw.t.u-tokyo.ac.jp

Introduction: We have ever prepared the novel self-oscillating gel system produced by the Belousov-Zhabotinsky (BZ) reaction. The gels were composed of crosslinked NIPAAm chain to which Ru(bpy)₃, as a catalyst for the BZ reaction, was covalently bonded[1]. When the polymer chain is dissolved in the aqueous solution containing BZ substrates except for the catalyst, periodical soluble-insoluble changes of the polymer occur[2]. In this study, we prepared the submicron-sized gel particles by emulsion polymerization for the purpose of the application to nano-actuator. Swelling-deswelling oscillations of the nano-gel particles were measured. Further, in order to analyze the oscillating profile of the gel beads, we compared the following three systems: (i) conventional BZ solution with nonpolymerized catalyst, (ii) the polymer solution with polymerized catalyst by NIPAAm, and (iii) the suspension of nano-gel particles. Through this analysis, the polymerization effect of catalyst and the cross-linking effect of polymer chains are discussed.

Experimental: The nano-gel particles of NIPAAm with Ru(bpy)₃, was prepared by emulsion polymerization as follows; Purified NIPAAm (3.80g), Ru(bpy)₃ monomer (0.422g), NaDBS (0.700g), MBAAm (0.700g) and AIBN (0.169g) were dissolved in 200mL of H₂O, and polymerized at 60°C for 24h. Diameter changes of poly(NIPAAm-co-Ru(bpy)) gel beads were measured as a function of temperature under the different conditions of reduced Ru(II) state and oxidized Ru(III) state by dynamic light scattering (DLS). Ru(bpy)₃Cl₂ (0.33mM) or the linear poly(NIPAAm-co-Ru(bpy)) (0.50wt%) or the nano-gel beads (0.25wt%) was dissolved in the aqueous solution containing the reactants of the BZ reaction (malonic acid, NaBrO₃, and HNO₃). Under constant temperature and stirring conditions, the time course of transmittance was monitored by the spectrophotometer by using 570nm for the polymer solution and the gel suspension, and 480nm for the conventional BZ solution.

Results and Discussion: Fig.1 shows the diameter changes of poly(NIPAAm-co-Ru(bpy)) gel beads. Generally, the diameter under oxidized state is larger than that under reduced state because the hydrophilicity of the gel beads increases in oxidized state. But in higher temperature, gel beads in reduced state aggregate because of high hydrophobicity, and the diameter becomes larger than that of oxidized state. Fig.2 shows the oscillation profiles of transmittance for the gel beads suspension at constant temperature. Self-oscillation based on swelling-deswelling changes with nano-order size was observed. As the temperature increases, the transmittance decreases and the period becomes short. As a result of comparing the period among the three systems under the same substrate concentrations, the period increased in the following order: (i) < (ii) < (iii). From this result, polymerization of catalyst and cross-linking of polymer chains are found to affect the self-oscillating behavior through cooperative effect.

References
Abstract

**Nano-gel particles** composed of crosslinked copolymer of N-isopropylacrylamide and ruthenium catalyst for the Belousov-Zhabotinsky reaction were prepared by emulsion polymerization. In the aqueous solution containing the BZ substrates, **self-oscillation of gel beads in nanometer scale** was achieved. By comparing the oscillating behavior of conventional BZ solution, the linear polymer solution, and the suspension of gel beads, the polymerization effect and the crosslinking effect was clarified. These self-oscillating gel beads have a potential for use in nano-machines as an oscillator.
Design of self-oscillating gel

Built-in Self-Oscillating Circuit in Gel
Belousov-Zhabotinsky (BZ) reaction (More than 80 elementary BZ reactions)

Oscillation

HBrO₂ → Ru(bpy)³⁺ → Br⁻ → BrO₃⁻ → Ru(bpy)²⁺ → Ru(bpy)³⁺

MA

NIPAAm

Catalyst of BZ reaction

Self-oscillating in closed system

Reduced state Ru(bpy)³⁺

Oxidized state Ru(bpy)³⁺

Deswelling

Swelling

Reference

Application

- Heart muscle-mimetic materials
- Self-oscillating micro actuator, micropump, etc.
Purpose

Achievement of Self-Oscillation in Polymer System in Nano-Order Scale.

- Preparation of Self-Oscillating Liner Polymer Chains
- Preparation of Self-Oscillating Nano-Gel Particles

Application to Self-Oscillating Nano-Machines.
Hierarchical synchronization in self-oscillating gel

Monomer
- Reduced state
- Oscillation
- Polymerization
- Oxidized state

(i) Conventional BZ reaction

Polymer
- Insoluble (reduced state)
- Oscillation
- Crosslinking
- Soluble (oxidized state)

(ii) Polymer solution

Miniature Gel
- Nano-Gel Particle
- Micro-Gel Particle
- Deswelling (reduced state)
- Oscillation
- Diffusion coupling
- Swelling (oxidized state)

(iii) Suspension of Gel Particle

Bulk gel
- [Ru(III)]
- Wave length
- Propagation of chemical wave

nm scale
μm scale
mm scale
Temperature dependence of transmittance for poly(NIPAAm-co-Ru(bpy)$_3$) solution

Measuring wavelength = 570nm (isosbestic point for reduced and oxidized states for Ru(bpy)$_3$)

- NIPAAm (3.8g)
- Ru(bpy)$_3$ monomer (5 or 10wt%)
- AIBN (0.16g)
- methanol (20mL)

- Freeze-thaw cycle 3 times
- Sealed in vacuo
- Polymelyzed at 60°C, 24h
- Purification (Dyalysis)

- LCST of oxidized state > LCST of reduced state
- Difference of LCST between reduced and oxidized states increases with Ru(bpy)$_3$ contents
Self-oscillation of polymer chains with rhythmical soluble-insoluble changes

Solution
[MA] = 0.1M
[NaBrO₃] = 0.25M
[HNO₃] = 0.3M
polymer concentration=0.5wt%

Oxidized state
(soluble, transparent)

Reduced state
(insoluble, opaque)

Transmittance oscillation with soluble-insoluble changes of polymer chains
Temperature dependence of diameter for poly(NIPAAm-co-Ru(bpy)$_3$) gel beads

Ce(IV) and Ce(III) were used to maintain oxidized Ru(III) and reduced Ru(II) state.

- **Diameter of oxidized state > Diameter of reduced state ($\leq 35^\circ$C)**
  - Hydrophilicity of polymer increase in oxidized state.
- **Diameter of oxidized state < Diameter of reduced state ($\geq 35^\circ$C)**
  - Gel particles aggregate in reduced state due to hydrophobicity.

**Materials:****
- Ru(bpy)$_3$ monomer (0.422g)
- NIPAAm (3.8g)
- AIBN (0.1688g)
- BIS (0.70g)
- NaDBS (0.70g)
- H$_2$O (200g)

**Methods:**
- Emulsion polymerization at 60°C for 4h.
- Dialysis (Et-OH for 3 days)
Oscillation profiles of transmittance for poly(NIPAAm-co-Ru(bpy)₃) gel beads suspension induced by the BZ reaction

Suspension
[MA]=0.1M, [NaBrO₃]=0.25M
[HNO₃]=0.3M, gel beads = 0.15wt%

Transmittance oscillation with swelling-deswelling changes
Dependence of oscillation period on initial substrate concentration

- (i) Conventional BZ solution
- (ii) Polymer solution
- (iii) Suspension of nano-gel particles

**Concentration dependence** of period are different among three systems.
T = $a \text{[MA]}^{-b} \text{[NaBrO}_3\text{]}^{-c} \text{[HNO}_3\text{]}^{-d}$: Empirical equation

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional BZ</td>
<td>2.97</td>
<td>0.414</td>
<td>0.794</td>
<td>0.743</td>
</tr>
<tr>
<td>Polymer</td>
<td>2.97</td>
<td>0.413</td>
<td>0.934</td>
<td>0.567</td>
</tr>
<tr>
<td>Gel beads</td>
<td>5.75</td>
<td>0.506</td>
<td>0.667</td>
<td>0.478</td>
</tr>
</tbody>
</table>

Oscillating period: Conventional BZ < Polymer < Gel beads

**Polymer**

Fixed charge on the polymer chain

$\rightarrow$ An increase in electrostatic repulsion between the charge site is suppressed.

$\rightarrow$ The change to oxidized state is restrained.

$\rightarrow$ Longer duration of reduced state $\rightarrow$ The period becomes longer

**Crosslinked polymer network (gel)**

Diffusion limitation of substrate from the outer solution to gel phase.

$\rightarrow$ Decreasing the effective concentration $\rightarrow$ The period becomes longer
The amplitude of the polymer solution is smaller than that of conventional BZ solution.

← Distance between the catalysts are defined in the polymer.
Conclusion

- **Periodical soluble—insoluble changes of the polymer** induced by the BZ reaction was measured as transmittance.

- **Periodic swelling-deswelling changes of nano-gel beads** can be observed as cyclic transparent and opaque changes for the suspension in the closed system.

  *Oscillating period: Conventional BZ < Polymer < Gel beads*

- **Polymerization effect of catalyst**
  
  Charges are fixed on the polymer chain.

- **Cross-linking effect of polymer chains**
  
  Polymers are forced to oscillate cooperatively.

  **Diffusion** of substrates from bulk phase to the gel phase becomes more difficult.