Design of Mass Transport Surface Using Self-Oscillating Gel

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Novel conveyor gels exhibiting autonomous peristaltic motion without external stimuli were prepared by copolymerizing temperature-responsive N-isopropylacrylamide (NIPAAm), ruthenium tris(2,2’-bipyridine) (Ru(bpy))3 as the catalyst for the Belousov–Zhabotinsky (BZ) reaction and 2-acrylamido-2-methylpropanesulfonic acid (AMPS). The prepared bulky gel had an aggregative structure of its microgels when the AMPS feed ratio was low due to the effect of the poor solvent in the polymerization process. That structure highly improved the swelling–deswelling kinetics and generated swelling–deswelling amplitude more than 10% of the gel thickness, which was approximately 10 times larger than that of the gel with a homogeneous network structure. Further, we attempted to transport an object by utilizing the peristaltic motion of poly(NIPAAm-co-Ru(bpy))3-co-AMPS gel. A cylindrical poly(acrylamide) (PAAm) gel was transported as a model object on the poly(NIPAAm-co-Ru(bpy))3-co-AMPS gel surface wave when the gel had the aggregative structure of its microgels.

Key words: gel, peristaltic motion, mass transport

1. INTRODUCTION
How to transport micro- and/or nanosized materials is one of the fundamental issues in nanotechnology and biotechnology. Recently, for these purposes, several new methods utilizing soft functional materials have been proposed; for example, photoinduced mass transport system utilizing a photoisomerizable polymer film,1 cargo transport system through sequential regulation of volume phase transitions of temperature-responsive poly(NIPAAm) gel,2 etc. These functional surfaces and mass transport systems, however, need an external drive mechanism and there is no report of mass transport systems using complete synthetic materials which involves a driven mechanism in themselves. In order to realize such a novel mass transport system, we have attempted to utilize a "self-oscillating gel". The gel is composed of temperature-responsive component, N-isopropylacrylamide (NIPAAm) and ruthenium tris(2,2’-bipyridine) (Ru(bpy))3 as a catalyst for the Belousov–Zhabotinsky (BZ) reaction.3,4 The BZ reaction shows autonomous oscillations of redox potential under appropriate acidic conditions containing organic acid, oxidizing agent and metal catalyst. When poly(NIPAAm-co-Ru(bpy))3 gel is immersed in the catalyst-free BZ solution, the BZ reaction occurs in the gel. In the case that the length of the gel is much longer than the wavelength of the chemical wave, a train of excited pulses of the oxidized state (i.e., "chemical waves") spontaneously evolves and propagates in the gel by the reaction–diffusion mechanism. As the redox changes of the catalyst moiety (Ru(bpy))3−2 Ru(bpy)3+) affect the swelling ratio of the gel through the changes in hydrophilicity of polymer chains, the poly(NIPAAm-co-Ru(bpy))3 gel exhibits peristaltic motion.5,6 That is, locally swollen (or shrunk) states propagate in the gel with the propagation of chemical wave like locomotion of worms.1 In our previous study, it was reported that it was effective to copolymerize 2-acrylamido-2′-methylpropanesulfonic acid (AMPS) to poly(NIPAAm-co-Ru(bpy))3 gel network to generate large amplitude of volume change of the self-oscillating gel.3 In this paper, for the design of mass transport surface, the influence of the AMPS feed ratio on the swelling-deswelling properties of poly(NIPAAm-co-Ru(bpy))3-co-AMPS) gels and mass transportability of the gels were investigated.

2. EXPERIMENTAL SECTION
Materials
Ruthenium(4-methyl-4′-vinyl-2,2′-bipyridine)bis(2,2′-bipyridine) bis(hexafluorophosphate) (Ru(bpy)3 monomer) was synthesized according to the procedure reported by Spiro et al.9 and Belt et al.10 NIPAAm (Kanto Chemical) was purified by recrystallization in toluene/hexane. All the other reagents were of JIS special grade and used as received.

Preparation of Gels
NIPAAm, Ru(bpy)3 monomer, AIBN and methylenebisacrylamide (MBAAm) were dissolved in methanol purged with dry nitrogen gas previously. AMPS was dissolved in distilled water purged with dry
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nitrogen gas previously. Then the two kinds of solution were mixed (mixture ratio of solvents was 50/50 v/v) and injected into the space between two PET sheets separated by a silicon rubber sheet (thickness: 1 mm) and backed by glass plates for preparing gel sheets. The pre-gel solution was injected into glass capillaries (inner diameter: 744 µm) for preparing cylindrical gels. The gelation was carried out for 24 h at 60 ºC. After gelation, all the gels were immersed in methanol to remove unreacted compounds for 1 day. The cylindrical gels were removed from the glass capillaries by HF treatment. Then the gels were soaked in methanol/distilled water mixture (75/25, 50/50, 25/75, 0/100 v/v) for 1 day each. Two kinds of poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) gels with different AMPS feed ratio (1.75, 10 mol %) were prepared (PNRA₀.₇₅, PNRA₁₀ gel, respectively). The precursor feed composition was summarized in Table I.

Table I. Feed compositions and sample ID of poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) gels.

<table>
<thead>
<tr>
<th>Sample ID*</th>
<th>PNRA₀.₇₅</th>
<th>PNRA₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIPAAm [mg]</td>
<td>762.0</td>
<td>697.1</td>
</tr>
<tr>
<td>Ru(bpy)₃ [mg]</td>
<td>94.5</td>
<td>94.5</td>
</tr>
<tr>
<td>MBAAm [mg]</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>AMPS [mg]</td>
<td>25.4</td>
<td>145.1</td>
</tr>
<tr>
<td>AIBN [mg]</td>
<td>11.5</td>
<td>11.5</td>
</tr>
<tr>
<td>C [wt %]</td>
<td>16.7</td>
<td>17.6</td>
</tr>
</tbody>
</table>

*The prepared gels were labeled as PNRAₓ where x indicated the AMPS feed ratio (mol % based on precursors amount of NIPAAm, Ru(bpy)₃, MBAAm and AMPS)

Weight percentage of total monomer of the pre-gel solution

Equilibrium Swelling Measurements

For the measurement of temperature dependence of swelling ratios, the cylindrical poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) gels were cut into approximately 5 mm in length. The gel samples were immersed in cerium sulfate solutions. Two kinds of cerium sulfate solutions (one solution contained 5 mM Ce₃(SO₄)₂ and 0.894 M HNO₃ and the other contained 5 mM Ce₃(SO₄)₂ and 0.894 M HNO₃) were used to maintain the gel in the oxidized Ru(III) state and the reduced Ru(II), respectively. The gel samples were equilibrated in the solution at a temperature ranging from 10 ºC to 50 ºC. The diameters of the cylindrical gel samples were measured by a microscope (Leica, MZ16). The swelling ratios were defined as the diameters of the gel normalized by the inner diameter of the glass capillary used in gelation process.

Evaluation of Transportability of Self-Oscillating Gel

A model object, cylindrical poly(acrylamide) (PAAm) gel was used. The PAAm gel was prepared from the aqueous solution of AAm, MBAAm and APS. The feed composition (wt %) was AAm/MBAAm/APS = 91.8:2.0:8.0 and the total monomer concentration was 7 wt %. The PAAm gel was synthesized in a glass capillary with inner diameter of 1063 µm at 60 ºC for 24 h. The cylindrical PAAm gel was taken out of the glass capillary and then rinsed thoroughly with water several times.

The poly(NIPAAm-co-Ru(bpy)₃-co-AMPS) gel sheets were immersed in the catalyst-free BZ solution containing HNO₃ (0.5 ~ 1 M), NaBrO₃ (30 ~ 120 mM) and CH₂(COOH)₂ (40 ~ 62.5 mM) at 18 ºC. Then the cylindrical PAAm gel (length: ca. 1.5 mm) was put on the cylindrical PAAm gel sheet. The propagation of the chemical waves and the motion of the cylindrical PAAm gels were observed and
3. RESULTS AND DISCUSSION

Figure 2 shows the effect of the different valence of ruthenium catalyst ion on the equilibrium swelling ratio. It was found that the swelling ratio increased with the increase of the AMPS feed ratio. This is because the increased \( \text{SO}_3^- \) group could attract more water as well as strong electrostatic repulsions between highly ionized \( \text{SO}_3^- \) groups facilitate the expansion of the gel network. In the Ce\((\text{SO}_4)_{3}\) solution, the gel keeps a tinge of orange, which suggests that the copolymerized Ru(bpy)\(_3\) remains in the reduced state. In the Ce\((\text{SO}_4)_{2}\) solution, which is a powerful oxidizing agent, the gel quickly turns from orange to green, suggesting that Ru(bpy)\(_3\) is oxidized. The phase transition temperature of the oxidized Ru(bpy)\(_3\) gel was higher than that of the reduced Ru(bpy)\(_3\) gel because the hydrophilicity of the oxidized Ru(bpy)\(_3\) gel increases due to the increase in the charge of the redox moiety. This deviation of the charge of the redox moiety. This deviation of the charge of the redox moiety. This deviation of the charge of the redox moiety. This deviation of the charge of the redox moiety. This deviation of the charge of the redox moiety.

Fig. 2 Temperature dependence of the equilibrium swelling ratio of poly(NIPAAm-co-Ru(bpy)\(_3\)-co-AMPS) gels. (○) PNRA\(_{10}\) gel, [Ce\((\text{SO}_4)_{3}\)] = 5 mM and [HNO\(_3\)] = 0.894 M; (□) PNRA\(_{10}\) gel, [Ce\((\text{SO}_4)_{3}\)] = 5 mM and [HNO\(_3\)] = 0.894 M; (■) PNRA\(_{25}\) gel, [Ce\((\text{SO}_4)_{3}\)] = 5 mM and [HNO\(_3\)] = 0.894 M; (□) PNRA\(_{75}\) gel, [Ce\((\text{SO}_4)_{3}\)] = 5 mM and [HNO\(_3\)] = 0.894 M. The swelling ratio is defined as the ratio of the diameter of the gel to the inner diameter of the glass capillary used in the gelation process.

The PNRA\(_{75}\) gel was opaque. In contrast, the PNRA\(_{10}\) gel was transparent. Figure 3 shows SEM micrographs of interior morphology of the poly(NIPAAm-co-Ru(bpy)\(_3\)-co-AMPS) gels. It was found that the prepared bulky PNRA\(_{75}\) gel was the aggregation of the microgels. In contrast, the PNRA\(_{10}\) gel exhibited homogeneous network structure. In general, a mixture of methanol and water (50/50 v/v) is a poor solvent for poly(NIPAAm). Therefore, when the AMPS feed ratio was low, the mixture became a poor solvent for poly(NIPAAm-co-Ru(bpy)\(_3\)-co-AMPS) gel. As a result, the growing microgels were supposed to deswell and aggregate each other in the gelation process. In contrast, when the AMPS feed ratio became completely high (ca. 10 mol %), the effect of poor solvent on the gelation process diminished and the resulted poly(NIPAAm-co-Ru(bpy)\(_3\)-co-AMPS) gel had a homogeneous network structure. The difference of the texture was attributed to the microstructure of the gel.

![Fig. 2](image2.png)

![Fig. 3](image3.png)

Fig. 3 SEM micrographs of the interior morphologies of poly(NIPAAm-co-Ru(bpy)\(_3\)-co-AMPS) gels. (a) PNRA\(_{75}\) gel and (b) PNRA\(_{10}\) gel.

The deswelling kinetics of poly(NIPAAm-co-Ru(bpy)\(_3\)-co-AMPS) gels were shown in Figure 4. It shows that the deswelling rate of the PNRA\(_{75}\) gel was faster than that of the PNRA\(_{10}\) gel. In the case of the PNRA\(_{10}\) gel, a skin layer was formed when the gel began to deswell, which is a well-known phenomenon caused by extrusion of solvent from gel surface. Due to the formation of the skin layer, the extrusion of solvent from inside is prevented and deswelling becomes slower. After showing the plateau period, the gel began to deswell gradually with an increase in the inner pressure. On the other hand, such a skin layer was not observed on the surface of the PNRA\(_{75}\) gel. This is attributed to the aggregative structure of the microgels. In the aggregative structure of the microgels as shown in Figure 3a, solvent was easily taken in and out through the flow channels formed among the microgels. As a result, the PNRA\(_{75}\) gel exhibited faster deswelling response.

When the cylindrical poly(NIPAAm-co-Ru(bpy)\(_3\)-co-AMPS) gels were immersed in the catalyst-free BZ solution, the BZ reaction occurred in the gel. The substantial large swelling–deswelling change was emerged in the PNRA\(_{75}\) gel but such a peristaltic motion with the propagation of the chemical wave was hardly observed in the PNRA\(_{10}\) gel and just the propagation of the chemical wave was observed. The swelling–deswelling amplitude of the PNRA\(_{75}\) gel obtained from the image analysis was 16±2% and that of the PNRA\(_{10}\) gel was 1.8±0.7%. Although the difference
of the equilibrium swelling ratio between the reduced and oxidized Ru(bpy)$_3$ states was larger in the PNRA$_{1.75}$ gel than in the PNRA$_{1.75}$ gel as shown in Figure 2, the generated amplitude of the PNRA$_{1.75}$ gel was lower than that of the PNRA$_{1.75}$ gel. When the BZ reaction occurs in the gel, the gel is not in the equilibrium state. Therefore, the swelling–deswelling kinetics becomes an important factor. The homogeneous PNRA$_{1.75}$ gel didn’t exhibit large amplitude because it couldn’t respond quickly enough to the redox change of the Ru(bpy)$_3$ moiety in several minutes as shown in Figure 4. In contrast, the PNRA$_{1.75}$ gel having the aggregative structure of the microgels could swell and deswell quickly during the propagation of the chemical wave and the amplitude was enlarged.

Fig. 4 Deswelling kinetics of poly(NIPAAm-co-Ru(bpy)$_2$-co-AMPS) gels in response to stepwise temperature change from 11 °C to 48 °C. (○) PNRA$_{1.0}$ gel, [Ce$_2$(SO$_4$)$_3$] = 5 mM and [HNO$_3$] = 0.894 M; (■) PNRA$_{1.75}$ gel, [Ce$_2$(SO$_4$)$_3$] = 5 mM and [HNO$_3$] = 0.894 M.

Figure 5 shows a transport phenomenon of the cylindrical PAAm gel on the PNRA$_{1.75}$ gel surface. The cylindrical PAAm gel was transported as it rolled on the gel surface with the propagation of the chemical wave. The swelling-deswelling amplitude of the PNRA$_{1.75}$ gel sheet was approximately 240 μm, and that was approximately 16% change of the gel thickness. The velocity and the period of the chemical wave were approximately 3 mm/min and 4 min, respectively. As the size of the PAAm gel was on the order of millimeters, the gravity, frictional force and contact force acting on the gel object were the important factors for mass transport. So, if the object materials aren’t adsorbed to the poly(NIPAAm-co-Ru(bpy)$_2$-co-AMPS) gel surface by an attracting force like hydrophobic interaction, mass transportation depends on the performance of the peristaltic motion of the poly(NIPAAm-co-Ru(bpy)$_2$-co-AMPS) gel surface. It was found that the aggregative structure of the microgels was a key to transport cylindrical gel object because the enlarged peristaltic motion could be useful for generating rotational movement of the cylindrical gel object. The influences of attractive interactions such as hydrophobic interaction and electrostatic interaction between an object and the self-oscillating gel on the mass transport phenomena are under investigation.

4. CONCLUSION

The effects of AMPS feed ratio on the structure and the swelling properties of the poly(NIPAAm-co-Ru(bpy)$_2$-co-AMPS) gel were investigated. When the AMPS feed ratio is low, the gel has the aggregative structure of its microgels and the deswelling kinetics and the swelling–deswelling amplitude of the peristaltic motion were greatly improved. Further, by utilizing the enlarged peristaltic motion of the poly(NIPAAm-co-Ru(bpy)$_2$-co-AMPS) gel having the aggregative structure of its microgels, we have succeeded in transporting cylindrical PAAm gel object on the poly(NIPAAm-co-Ru(bpy)$_2$-co-AMPS) gel surface without an external drive mechanism. The functional gel surface generating autonomous and periodic peristaltic motion has a potential for several new applications such as a conveyor to transport soft materials, a formation process for ordered structures of micro- and/or nanosized materials, a self-cleaning surface and so on.

5. REFERENCES


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