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Control of wave formation pattern in self-oscillating gel by addition of hydroquinone in the Belosov-Zhabotinsky reaction solution

Do Sung Huh[a] (✉), Jong Kon Kang[a], Young Joon Kim[a], Ryo Yoshida[b]

[a]Department of Chemistry, Inje University, Kimhae, Kyungnam 621-749, South Korea
[b]Department of Materials Engineering, Graduate School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
E-mail: chemhds@inje.ac.kr

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Summary

We have investigated the effect of solution composition on the pattern of traveling wave formation in self-oscillating gel in which a metal catalyst for the Belousov-Zhabotinsky(BZ) reaction is covalently bonded to the gel matrix. The reaction solution contains all reactants for the BZ reaction except the catalyst. The gel was synthesized by the co-polymerization of N-isopropylacrylamide(NIPAAm) and $Ru(bpy)_3^{2+}$catalyst monomer. To vary the composition of the environmental solution for the oscillation reaction, we added a small amount of hydroquinone to the BZ solution since hydroquinone is a good reagent inducing a characteristic wave pattern in the BZ type oscillation system. The experimental results show that the pattern of wave formation in the self-oscillating gel is influenced greatly by a change of the environmental condition of the solution composition for the oscillation reaction without other environmental change such as temperature and pH.

Introduction

The Belousov-Zhavotinsky(BZ) reaction is known as an oscillating reaction generating periodical redox changes of catalyst.[1,2] In spatially distributed reacting media, an excited pulse of the oxidized catalyst, i.e., "chemical wave", evolves and propagates due to the diffusion of $HBrO_2$ as an intermediate. Such a chemically excitable system has become a model case for investigation with relation to the phenomena of spatio-temporal pattern formation in chemical and biological systems.[3] The chemical waves using the BZ reaction have been well studied in homogeneous[4] and inhomogeneous[5] reaction mixtures.

Polymer gel is a cross-linked polymer network swollen in solvent, and many kinds of polymeric gels undergoing abrupt volume change in response to external stimuli, such as a change in solvent composition[6] or temperature,[7,8] pH,[9] and electric field,[10] have been developed over the last two decades. Gels consisting of NIPAAm which swell by cooling and deswell by heating have been widely studied.[11,12]

Recently, a novel “self-oscillating” gel that autonomously swells and deswells periodically without any external stimuli has been obtained by coupling a gel with the oscillating dynamics of the BZ reaction.[13,14] It is prepared by a copolymer gel of a temperature-responsive NIPAAm, in which $Ru(bpy)_3^{2+}$ is covalently bonded to the polymer chain as a catalyst of the BZ reaction.[15] Such self-oscillating behavior may create new possibilities for polymer gels as new functional materials demonstrating rhythmical motion or self-beating.

However, gels that spontaneously oscillate with volume changes under non-oscillating BZ reaction solution have not been realized yet. Thus, the response of the gel properties to the condition of solution composition is interesting subject and it should be studied extensively.

In this report, we have studied on the pattern of wave initiation in the self-oscillating gel in which a metal catalyst for the BZ reaction is covalently bonded to the gel matrix. In the self-oscillating gel, we observed a pattern change of wave initiation by changing the condition of the solution composition.

To change the condition of the solution composition for the oscillation reaction, a small amount of hydroquinone was added to the BZ solution since hydroquinone is a good reagent inducing a characteristic wave pattern in the BZ type oscillation reaction system using 1,4-cyclohexanedione/BrO_3^-/Fe^{2+}/H^+.[16,17] Recently, many kinds of characteristic temporal and spatio-temporal phenomena have been observed in the reaction system.[18,19] In a very recent investigation, Huh et. al. found that hydroquinone could play an important role in characteristic pattern formations in that kind of reaction system.[20] Suzuki et. al have studied the effect of hydroquinone on the equilibrium size change in phase transition behavior of an N-isopropylacrylamide gel.[21] They used the gels being immersed in the aqueous solution of dilute hydroquinone for 3 days.

Experimental

Preparation of poly[NIPAAm-co-Ru(bpy)$_3$] Gels.

We prepared the copolymer gels consisting of *N*-isopropylacrylamide chains, with covalently bonded $Ru(bpy)_3$ residues(Fig. 1) by the method of Yoshida et. al.[13] NIPAAm(99.9%, Sigma-Aldrich Co.) was purified by recrystallization from its toluene solution with n-hexane. We purchased $Ru(bpy)_3^{2+}$ with a double bond [ruthenium(4-vinyl-4’-methyl-2,2’-bipyridine)bis(2,2’-bipyridine)bis(hexafluorophosphate)] from the Fuji Molecular Ltd.(99.8%, Japan). *N,N*’-methylenebisacrylamide(99.8%, Sigma-Aldrich Co) was used as a cross-linker and .) and *N,N*’-azobisisobutyronitrile(99.8%, Sigma-Aldrich Co.) was used as an initiator, respectively.

Reaction Solution for the BZ Reaction.

The working solutions of the BZ reaction were prepared from stock solutions of 0.6 M NaBrO (99.9% Sigma-Aldrich Co.), 0.2 M malonic acid(99.8%, Sigma-Aldrich Co.) and 2 M nitric acid (Sigma-Aldrich Co.). 0.2 M hydroquinone(99.8%, Sigma-Aldrich Co.) solution was prepared as an additional reductant.

Monitoring of Chemical Waves in the Gels.

Chemical waves were observed under a microscope(Leica, model Mz75) equipped with a color CCD camera(Tosiba, model). Images from the CCD camera were processed to a computer(IBM 586) equipped with an image acquisition board(Image-Pro Expresses). The image of the colored wave pattern was adjusted into black and white using a color treatment program.

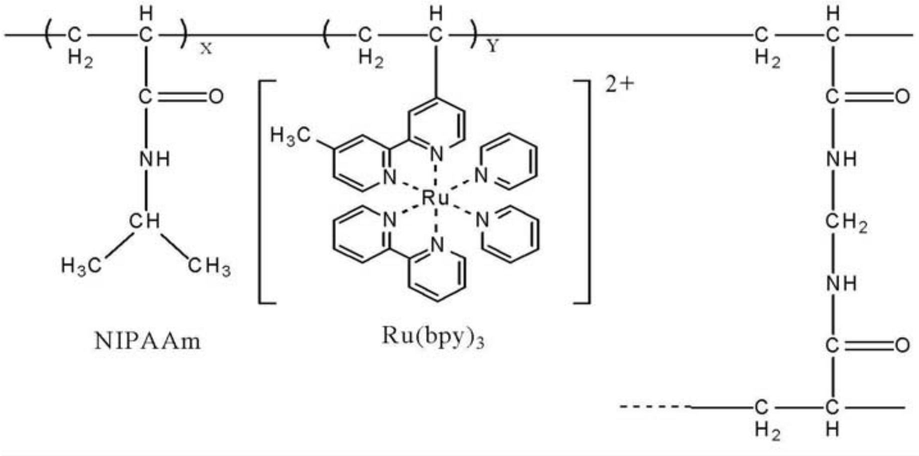

Figure 1. The chemical scheme for the poly[NIPAAm-co-Ru(bpy)$_3$ gel.

Results and Discussion

A one-dimensional cylindrical piece of poly[NIPAAm-co-Ru(bpy)$_3$] gel was immersed in the aqueous solution (in an about 5 mL chamber) containing three reactants (MA, $NaBrO_3$, HNO_3) of the BZ solution. Figure 2 shows a typical pattern of wave propagation in the gel obtained in the BZ reaction solution at 20°C. By coupling the chemical oscillation reaction with the diffusion of a reaction intermediate ($HBrO_2$) through the gel phase, a periodical redox pattern (white is the oxidized state; black is the reduced state) develops along the length of a cylindrical gel.

Spontaneous initiation of the waves tends to take place at the corner of the cylindrical gel because the oscillations take place earliest there after the gel is soaked into the solution, shown in Figure 2(a). Then the corner part acts as a source of oscillations (i.e., pacemaker). This pattern moves through the gel at a constant rate; thus, we observed the moving pattern as the train of chemical waves (i.e., wavetrain) as shown in Figure 2(a) – Figure 2(c). A chemical wave has nonlinear characteristics, which are annihilated when two waves collide as shown in Figure 2(d). The pattern of propagating chemical waves obtained in this study as shown in Figure 2 is much similar to the results obtained in the Ru(bpy)$_3^{2+}$-immobilized poly-N-isopropylacrylamide(PNIPAAm) gels[22] and poly[NIPAAm-co-Ru(bpy)$_3$] gels with BZ reaction solution by Yoshida et. al.[13]

However, the pattern of wave propagation in the gel soaked in the BZ reaction solution in which 0.009M of hydroquinone was added was much different compared with the wave propagation in the BZ solution using malonic acid alone. A typical pattern of the wave propagation in the gel soaked in the BZ solution with 0.009M of

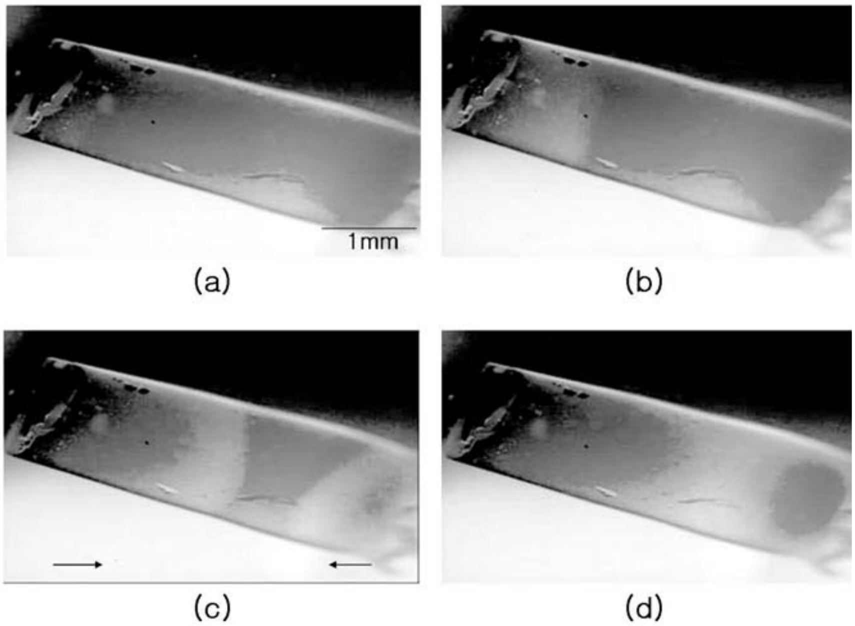

Figure 2. Snapshots of wave propagation in a cylindrical gel in the BZ reaction solution. Images (a), (b), (c), and (d) are taken respectively at 405, 445, 485 and 525 sec after soaking the gel into the solution. The initial compositions of the solution are: [MA] = 0.05 M, $[BrO_3^-]$ = 0.12 M, $[HNO_3]$ = 0.5 M. The arrow indicates the direction of wave propagation.

hydroquinone is introduced in Figure 3. Spontaneous initiation of waves appeared not from the outside(corner) but from the inner part(inside) of the cylindrical gel as shown in Figure 3(a). And the initiation part acts a pacemaker for the wave traveling into outside direction, as shown in Figure 3(b) – Figure 3(d). And a new pacemaker for a new wave appears continuously after the end of traveling in the gel. In another concentration of hydroquinone, some different pattern was obtained as shown in Figure 4. Two pacemakers for the wave initiation were formed at same time from the inside of the gel.

After initiation(Figure 4(a)), the two waves propagate(Figure 4(b) – Figure 4(c)), and lastly collide and annihilate(Figure 4(d). The position of wave initiation move a little into the outside of the gel in this system by the induction of the two waves.

In our experimental system, the wave with two pacemakers was generally obtained at lower concentration of hydroquinone. However, the wave pattern with pacemaker more than two was not obtained in our experimental condition although the position of pacemaker for the wave initiation in self-oscillating gel is controlled small by the existence of hydroquinone in the BZ solution. Similar results were obtained in other concentration systems, however a wave was not obtained in the solution in which hydroquinone is added more than about the concentration of 0.02 M. The temperature of solution was varied in order to check the effect of temperature on the pattern of wave formation. Although the pattern of wave formation was not effected greatly by a small temperature change in the condition that hydroquinone was not added, however the wave was not obtained in the temperature over than LCST of the gel(it was about 33 °C) because the gel deswelled greatly.

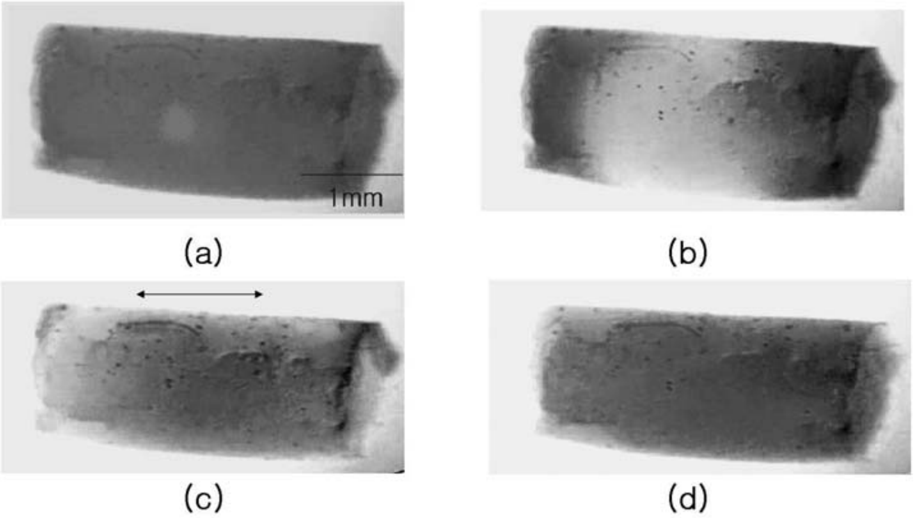

Figure 3. Snapshots of wave propagation in a cylindrical gel in the BZ reaction solution with hydroquine. Images (a), (b), (c), and (d) are taken respectively at 450, 475, 500 and 525 sec after soaking the gel into the solution. The initial compositions of the solution are: [MA] = 0.05 M, [hydroquinone] = 0.009 M, $[BrO_3^-]$ = 0.12 M, $[HNO_3]$ = 0.5 M.

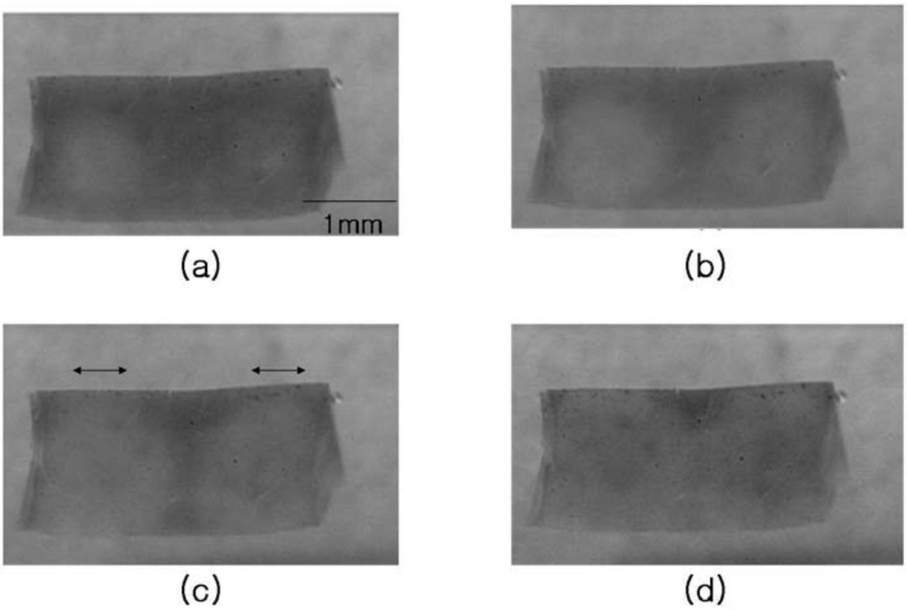

Figure 4. Snapshots of wave propagation in a cylindrical gel in the BZ reaction solution with hydroquinone. Images (a), (b), (c), and (d) are taken respectively at 485, 495, 505 and 515 sec after soaking the gel into the solution. The initial compositions of the solution are: [MA] = 0.05 M, [hydroquinone] = 0.005 M, $[BrO_3^-]$ = 0.12 M, $[HNO_3]$ = 0.5 M.

Table 1. The effect of hydroquinone concentration on the pattern of temporal oscillation in the BZ reaction using $Ru(bpy)_3^{2+}$ metal catalyst. The initial composition is; [MA] = 0.05 M, $[Ru(bpy)_3^{2+}] = 4.0 \times 10^{-5}$ M , $[BrO_3^-] = 0.12$ M, $[HNO_3] = 0.5$ M.

Concentration of H_2Q (M)	**Induction Time (min)**	**Temporal Oscillation Pattern**
0	2 - 3	Periodic oscillation
0.0 - 0.005	5 – 8	Bursting pattern(1^1)
0.005 - 0.01	17 - 18	Bursting pattern(1^2 or 1^3)
0.01 – 0.02	25 - 35	Small oscillation
More than 0.02	No oscillation	No oscillation

To understand the mechanism for the effect of hydroquinone to the pattern of wave formation in the self-oscillating gel, we have checked the variation of temporal oscillation pattern using similar BZ reaction system by changing the concentration of hydroquinone. In the reaction, $Ru(bpy)_3^{2+}$ was used as a metal catalyst for the BZ solution. The variation of temporal oscillation pattern is introduced in Figure 5. Figure 5(a) shows the oscillation pattern obtained in the BZ reaction solution in which hydroquinone is not added, and Figure 5(b) – 5(e) shows the oscillation patterns in the BZ reaction solution in which hydroquinone is added by varying the concentration. The patterns of Figure 5(b) and Figure 5(c) shows a periodic oscillation alternating small intensity and high intensity peak. However, an oscillation pattern was not obtained when hydroquinone is added more than a limit concentration as shown in Figure 5(e). Figure 5(d) shows a small intensity oscillation near the limit concentration of hydroquinone for the oscillation. The limit concentration of hydroquinone was dependent on the metal catalyst concentration also. The dependency of temporal oscillation pattern on the concentration of hydroquinone is summarized in Table 1.

By the table, the induction time for the regular oscillation increases by adding hydroquinone to the solution. The experimental results on the pattern of temporal oscillations show that hydroquinone can change the pattern of the BZ oscillation pattern, and in some case it plays a role as an inhibitor in the BZ reaction system.

We assume that the change in the pattern of temporal oscillation of the BZ reaction by addition of a small amount of hydroquinone is induced by an inhibition effect of hydroquinone to the Field-Körös-Noyes(FKN) mechanism[3] of the BZ reaction by the rapid oxidation of hydroquinone(H_2Q) to 1,4-benzoquinone(Q), as shown by the reactions of (R1) – (R3).

$$H_2Q + Br_2 \rightarrow Q + 2Br^- + 2H^+ \qquad (R1)$$

$$H_2Q + BrO_3^- \rightarrow Q + HBrO_2 + H_2O \qquad (R2)$$

$$H_2Q + HOBr \rightarrow Q + Br^- + H^+ + H_2O \qquad (R3)$$

The oxidation processes of (R1)-(R3) could perturb the oscillation condition in the FKN mechanism by changing the steady state concentration of reaction intermediates for the oscillation reaction. In order to support the assumption, we have tested an experiment using an inert gas such as nitrogen to protect the reaction system from the rapid oxidation process of hydroquinone catalyzed by oxygen gas. In the condition that nitrogen gas was bubbling, the temporal oscillation patterns were not influenced by the addition of hydroquinone. The patterns of temporal oscillation in that case are introduced in Figure 6. Normal periodic oscillations were obtained although hydroquinone was added to the solution as shown in Figure 6(a) and Figure 6(b). The concentration of hydroquinone in Figure 6(b) is so high, therefore the normal periodic oscillations can not be obtained without nitrogen gas bubbling by the results shown in Figure 5. The result means that the variation of oscillation pattern is completely induced by the reactions of hydroquinone added in the BZ reaction solution. And the perturbation by hydroquinone is catalyzed by oxygen.

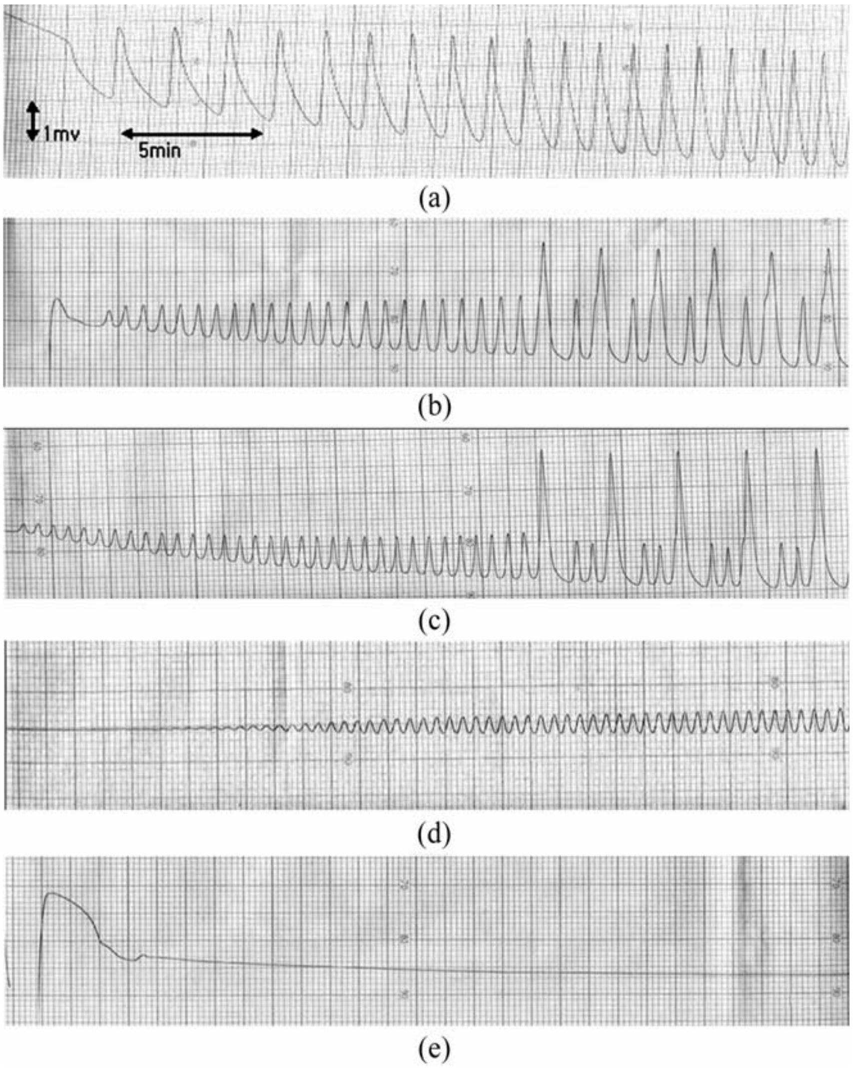

Figure 5. The comparison of temporal oscillation pattern between in the BZ reaction system by varying the concentration of hydroquinone. The initial compositions of the solution are [MA] = 0.05 M, $[Ru(bpy)_3^{2+}]$ = 4.0 x 10^{-5} M, $[BrO_3^-]$ = 0.12 M, and $[HNO_3]$ = 0.5 M, (a) [hydroquinone] = 0 M, (b) [hydroquinone] = 0.007 M, (c) [hydroquinone] = 0.01 M, (d) [hydroquinone] = 0.02 M, and (e) [hydroquinone] = 0.04 M.

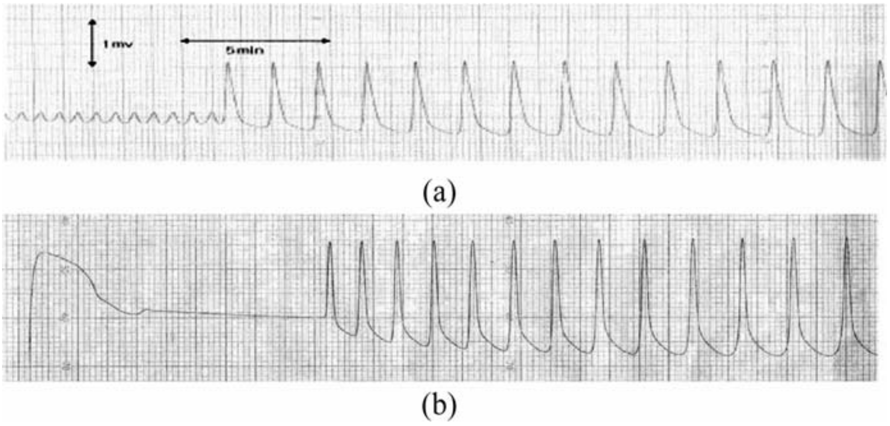

Figure 6. The pattern of temporal oscillation in the condition that nitrogen gas is bubbling. The initial composition of the solution are [MA] = 0.05 M, [$Ru(bpy)_3^{2+}$] = 4.0 x 10^{-5} M, [BrO_3^-] = 0.12 M, and [HNO_3] = 0.5 M, (a) [hydroquinone] = 0.01 M, (b) [hydroquinone] = 0.04 M.

Therefore the pattern change of wave formation in the gel system can also be interpreted by a similar reaction mechanism relating with hydroquinone in the oscillation reaction. The wave can not be initiated at the outside(corner) of the gel since the solution composition is inhibited by hydroquinone for the BZ reaction as shown in the batch experiment. However, reaction intermediates of solution phase should diffuse into the gel with the progress of reaction time. Then, the diffusion velocity of hydroquinone should be slower than other reaction intermediates because of hydrophobic property of hydroquinone.[21] A new reaction condition for the wave initiation will be formed in the inside of the gel in which the effect of hydroquinone in the solution composition is excluded as much as possible. This assumption is supported by the experimental results of the induction period for the wave initiation. The induction period for a wave in the gel soaked in the solution with hydroquinone always needs more times than the induction time needed for the system using malonic acid alone.

The effect of solution composition on the chemical waves in the self-oscillating gel with one-dimensional cylindrical type was well supported by the experimental results in the two-dimensional circular plate gels. The circular plate gels were made by broacher with about 10 mm diameter from the gel membrane. The thickness of the circular plate was controlled as about 0.7 mm in the synthesizing process. The waves propagated into one direction from the initiation of the outside part in the gel. After annihilation of the traveling waves, a new wave appeard and propagated with the same pattern. This pattern of wave propagation was much similar to the wave propagation obtained in a cylindrical shape gel. A wave initiates at the corner or outside of the gel in the cylindrical type gel.

However, a characteristic wave was induced in the gel soaked in the BZ reaction solution with a small amount of hydroquinone. A traveling chemical wave initiated spontaneously inside(center part) of the gel. A pacemaker for the traveling wave was formed inside of the gel. And from the pacemaker, a continuous wave evolved with a pattern of a concentric or spiral wave. Therefore the experimental results show that the initiation of wave formation depends on the BZ solution condition, i.e. a perturbation by the reaction of hydroquinone to the BZ reaction. It means that triggering of wave initiation in the oscillating gel can be controlled only by the variation of solution composition.

Conclusions

We have obtained an experimental result that the pattern of wave initiation and propagating mode in a gel in which a metal catalyst for BZ oscillation is covalently loaded in the gel matrix is influenced greatly by a small change in the condition of solution composition.

The experimental results show that the wave initiation pattern in the oscillating gel can be easily controlled by the environmental stimuli, especially to the condition of solution composition.

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