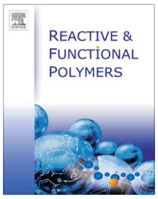
Reactive & Functional Polymers 73 (2013) 945–950

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react



Self-oscillation of polymer and photo-regulation by introducing photochromic site to induce LCST changes

Tatsuya Yamamoto, Ryo Yoshida *

Department of Materials Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

ARTICLE INFO

Article history:
Available online 14 March 2013

Keywords:
Polymer solution
Self-oscillation
The Belousov–Zhabotinsky reaction
Photochromism
Spirobenzopyran

ABSTRACT

We have developed polymers and gels with autonomous self-oscillating function by utilizing the Belousov–Zhabotinsky (BZ) reaction. The self-oscillating polymer is composed of poly(N-isopropylacrylamide), in which ruthenium tris(2,2′-bipyridine) is copolymerized as a catalyst for the BZ reaction. Under the coexistence of the reactants, the polymer undergoes spontaneous cyclic soluble–insoluble changes or swelling–deswelling changes (in the case of gel) without any on–off switching of external stimuli. In this study, spirobenzopyran was introduced into the self-oscillating polymer as the photochromic site. Under acidic condition necessary for the BZ reaction, photochromism of the spirobenzopyran occurs and the lower critical solution temperature of the polymer solution shifts to lower temperature with isomerization by photo-irradiation. As a result, on–off switching of the soluble–insoluble self-oscillation for the polymer solution is possible by photo-irradiation.

1. Introduction

Stimuli-responsive polymers and gels have been studied actively as functional soft materials for application to mechanical softactuators, etc. In most of previous studies, the mechanical actuating systems were driven by on–off switching of external stimuli (e.g., temperature, pH, light, electrical field and so on). In contrast to these conventional stimuli–responsive polymers and gels, we developed "self-oscillating" polymer gel that undergoes an autonomic and periodical swelling/deswelling oscillation like a beating heart under constant condition without any external stimuli in closed solution, which was firstly reported in 1996 [1]. The self-oscillating polymer gel was realized by copolymerizing ruthenium tris(2,2′-bipyridine) ($Ru(bpy)_3$) into poly(N-isopropylacrylamide) (PNIPAAm) gel. $Ru(bpy)_3$ was used as a catalyst for the Belousov–Zhabotinsky (BZ) reaction, which is well known as oscillating chemical reaction to generate spontaneous periodical redox changes of the catalyst with rhythm and spatial pattern [2,3]. As the valence change of the polymerized ruthenium catalyst causes the shift of the phase transition temperature of the gel as well as the swelling ratio due to hydrophilicity change of the polymer, under proper constant temperature, the gel swells at the oxidized Ru(III) state and deswells at the reduced Ru(II) state. When the gel is immersed in an aqueous acidic solution containing the substrates for the BZ reaction except for the catalyst (malonic acid and sodium bromate), periodical swelling/deswelling oscillation is spontaneously induced by the BZ reaction occurring in the gel. In the case of polymer solution, self-oscillation of optical transmittance due to soluble–insoluble changes of the polymer can be observed [4,5]. So far we have expanded the self-oscillating polymers and gels to several functional material systems [6] such as biomimetic actuators (artificial cilia [7], self-walking gel [8], intestine-like motion [9], etc.), mass transport surface [10–12], functional fluids to cause transmittance and viscosity oscillations [13–16].

The period and amplitude of the gel or polymer oscillation can be controlled by changing substrate concentration and temperature. Further, on–off regulation of the self-oscillation by external stimuli such as temperature change, addition and removal of organic acid, photo-irradiation is possible [6]. In particular, $Ru(bpy)_3$ has photo-sensitivity at the reduced state. By photo-irradiation, it creates the other reaction pathway to stop or cause the oscillation by producing an intermediate to act as an inhibitor (Br^-) or an activator ($HBrO_2$), depending on the composition of the BZ solution [17]. By utilizing such photochemical characteristics of the BZ reaction, we experimentally demonstrated photo-regulation of self-oscillating motion of the gel [18,19]. And also, Balazs et al. [20–22] demonstrated light-guided motility of the gel by theoretical model simulation.

In this photo-regulation system utilizing the photo-sensitivity of $Ru(bpy)_3$, there is no difference in hydrated state of the polymer chains (consequently swelling state of the gel) between photo-irradiated and non-irradiated conditions. On the other hand, here we design photo-regulated self-oscillating systems based on hydration and dehydration change of the polymer by photo-irradiation. For this purpose, spirobenzopyran (Sp) was introduced

---

* Corresponding author. Tel./fax: +81 3 5841 7112.
E-mail address: ryo@cross.t.u-tokyo.ac.jp (R. Yoshida).

1381-5148/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.reactfunctpolym.2013.02.015

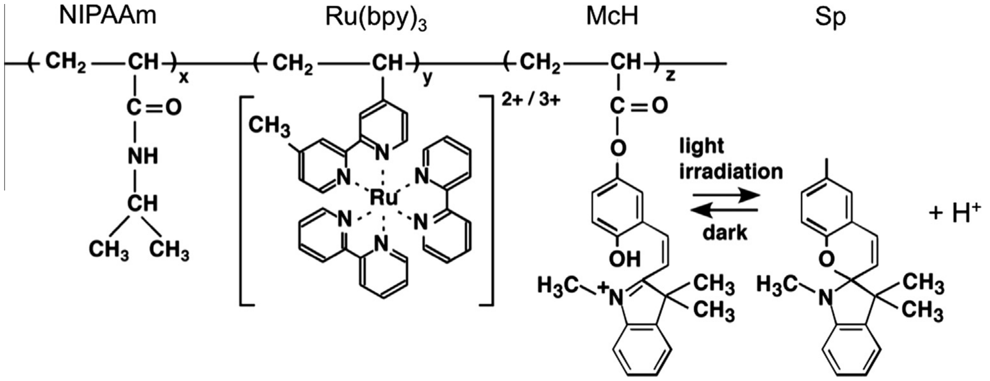


Fig. 1. Chemical structure of poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-Sp) (PNRS).

into the poly(NIPAAm-*co*-Ru(bpy)$_3$) as a photochromic site (Fig. 1). Change in the chemical structure and charge state of the site with photo-isomerization leads to the change in hydrophilicity of the polymer chain. When the polymer is dehydrated by photo-irradiation, the BZ reaction stops because the dehydrated polymer becomes globule state and inhibits the contact between the ruthenium catalyst and the BZ substrates. Such a system enables different temporal and spatial photoregulaton of self-oscillation from the previous photo-regulation systems. For example, by irradiating patterned light on the surface of the self-oscillating gel sheet, patterned relief of swollen region is left on the surface as a waveguide. Chemical wave propagates along the path with the peristaltic motion on the relief surface. If an object is put on the relief surface, it would be transported along the path. We can rewrite the pattern by swelling gel again in the dark. The transport path can be changed on demand temporally and spatially. In this study, as a fundamental study for that purpose, on–off regulation of soluble-insoluble self-oscillation by photochromism was attempted for the poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-Sp) solution. The self-oscillating behaviors in response to photo-irradiation were investigated.

2. Experimental

2.1. Materials

NIPAAm (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was purified by recrystallization from toluene–hexane followed by drying under a vacuum and was stored at 7 °C. 1′,3′,3′-Trimethyl-6-hydroxypiro(2*H*-1-benzopyran-2,2′-indoline) (Acros Organics, Geel, Belgium), acryloyl chloride (Wako Pure Chemical Industries, Ltd., Osaka, Japan), tetrahydrofuran, dehydrated (THF, Kanto Chemical Co., Inc., Tokyo Japan), azobisisobutyronitrile (AIBN, Wako Pure Chemical Industries, Ltd., Osaka, Japan), methanol, dichloromethane, hexane (all from Kanto Chemical Co., Inc., Tokyo Japan) were used without further purification. Ruthenium(4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine) bis(hexafluorophosphate) (Ru(bpy)$_3$ monomer) was synthesized according to the previous work [1].

2.2. Synthesis of poly(NIPAAm-co-Ru(bpy)$_3$-co-Sp)

Firstly, acrylated spirobenzopyran monomer was synthesized. A solution of 1.25 g (4.27 mmol) of 1′,3′,3′-trimethyl-6-hydroxypiro(2*H*-1-benzopyran-2,2′-indoline) and 0.7 mL (5 mmol) of triethylamine in dry THF (25 mL) was stirred at 0 °C. A total of 0.5 mL (5 mmol) of acryloyl chloride was added to the mixture. The mixture was stirred at 25 °C for 17 h. After the solvent was removed in vacuo, ethyl acetate and saturated aqueous sodium hydrogen carbonate were added and the aqueous phase was extracted with ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous magnesium sulfate, and filtered. After evaporation of the solvent, the residue was purified by silica gel column chromatography (41% hexane, 57% dichloromethane and 2% methanol as the eluent) to give the acrylated spirobenzopyran monomer (1.02 g, 2.95 mmol, 69%).

Poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-Sp) (PNRS) was synthesized in MeOH solution by free-radical polymerization with AIBN as an initiator. The NIPAAm monomer (1.87 g, 16.5 mmol), the acrylated spirobenzopyran monomer (58.4 mg, 0.168 mmol), Ru(bpy)$_3$ monomer (151 mg, 0.168 mmol), and AIBN (27.6 mg, 0.168 mmol) were dissolved in MeOH (8.4 mL) degassed with nitrogen gas for 30 min. The solution was polymerized at 60 °C for 20 h. The resulting reaction mixture was dialyzed against MeOH for 1 week and then freeze-dried. The molecular weight was determined by gel permeation chromatography at 40 °C with dimethylformamide as the eluent. The number-average molecular weight, M_n, estimated from polystyrene standards was 148,700. NMR and UV–visible absorbance measurement revealed that the molar fraction of the Ru(bpy)$_3$ and the spirobenzopyran units in the synthesized PNRS was about 1 mol%, respectively, which agreed with the molar ratio of the initial monomers in the solution.

2.3. Measurements of absorption spectra for PNRS solutions

The absorption spectra of PNRS in aqueous solution (0.1 wt.%) containing HCl with various concentrations were measured at 20 °C in the dark by UV–Vis spectrometer (Shimadzu, Model UV-2500) equipped with thermoregulated cell holder. The PNRS solutions were kept in the dark for 1 day at 8 °C to ensure open-ring state before the measurements.

The change in absorption spectra with photo-isomerization of spirobenzopyran at high proton concentration was measured for the aqueous solution of PNRS at 20 °C. The light irradiation to the sample solution was carried out with Hg light source (Hamamatsu Photonics LC5). In the spectroscopic measurement, the light was guided to the well-stirred sample solution in a thermoregulated cell holder in the spectrometers, through a set of filters and a fiber light guide. The wavelength and total intensity of the irradiating light were 400–440 nm and 50 mW/cm^2, respectively.

2.4. LCST measurements of PNRS solutions

Optical transmittance of the PNRS solution was measured as a function of temperature under different conditions of spirobenzopyran (closed-ring and open-ring structures) and Ru(bpy)$_3$ (reduced and oxidized states). The open-ring state was made in the dark and the closed-ring state was made under photo-irradiation. To maintain the reduced Ru(II) state and the oxidized Ru(III) state, $Ce_2(SO_4)_3$ and $Ce(SO_4)_2$ were used as a reducing and oxidizing agent, respectively. The light irradiation to the sample solutions was carried out by using the Hg light source. The wavelength and total intensity of the irradiating light were 400–440 nm and 30 mW/cm^2, respectively. The sample solutions were prepared by adding 1.5 mL of 0.3 M HNO_3 solution containing 1 mM $Ce_2(SO_4)_3$ or 1 mM $Ce(SO_4)_2$ to 1.5 mL of polymer solution (0.1 wt.%) containing 0.3 M HNO_3 kept in the dark for 1 day at 8 °C. The measurements were carried out by using a spectrophotometer equipped with an electronically controlled thermostated cell holder and magnetic stirrers. The optical transmittance (%) of the solution at 570 nm was recorded by raising temperature at a rate of 1 °C/min.

2.5. Measurements of optical transmittance oscillations

The PNRS (0.1 wt.%) was dissolved in the aqueous solution containing the reactants of the BZ reaction; malonic acid (0.1 M), sodium bromate (0.25 M), and nitric acid (0.3 M). Under constant temperature and stirring conditions, the time course of transmittance was monitored. The $Ru(bpy)_3$ complex has different absorption spectra in the reduced Ru(II) state and the oxidized Ru(III) state as an inherent property. The solution exhibited the absorption maximum at 460 nm in the reduced Ru(II) state and at 420 nm in the oxidized Ru(III) state, and has an isosbestic point at 570 nm. Therefore, the 570 nm wavelength was selected to detect the signal derived from the coil–globule oscillation of the polymer. The photo-irradiation (400–440 nm and 100 mW/cm^2) to the sample solutions was carried out as mentioned above.

3. Results and discussion

For on–off regulation of self-oscillation of the polymer, we introduced photochromic site, spirobenzopyran, as a side chain of the self-oscillating polymer as shown in Fig. 1. Spirobenzopyran has a colored merocyanine state with an open-ring structure (Mc) and a colorless spiro form with a closed-ring structure (Sp), as well as the protonated forms of each state, McH and SpH, respectively. (In Fig. 1, the protonated form of merocyanine is expressed as McH.) Sumaru et al. [23,24] synthesized poly(*N*-isopropylacrylamide) modified with spirobenzopyran and found that the aqueous solution of the copolymer exhibited remarkable dehydration by photo-irradiation under acidic condition around pH = 4. In the dark, the spirobenzopyran residue forms a ring-opened and protonated structure with showing a yellow color. On the other hand, by irradiating blue light with 436 nm, the residue forms a ring-closed structure with dissociation of proton and becomes colorless. The photo-isomerization of the spirobenzopyran induces dehydoration of the polymer because the hydrophobicity increases due to disappearance of positive charge of the polymer chain. Further, they confirmed that the crosslinked polymer (hydrogel) rapidly deswelled by photo-irradiation in the acidic solution.

First, we investigated whether the photo-induced phase transition of the PNRS occurs or not at high proton concentrations necessary for the BZ reaction (around pH = 1). Fig. 2 shows the absorption spectra of the PNRS as well as the poly(NIPAAm-*co*-Sp) (PNS; Sp = 1 mol%), and the poly(NIPAAm-*co*-$Ru(bpy)_3$) (PNR; $Ru(bpy)_3$ = 1 mol%), which were prepared for comparison, at various pHs in the dark. The pH values were calculated from HCl concentration. Fig. 2a shows the absorption spectra of the PNS.

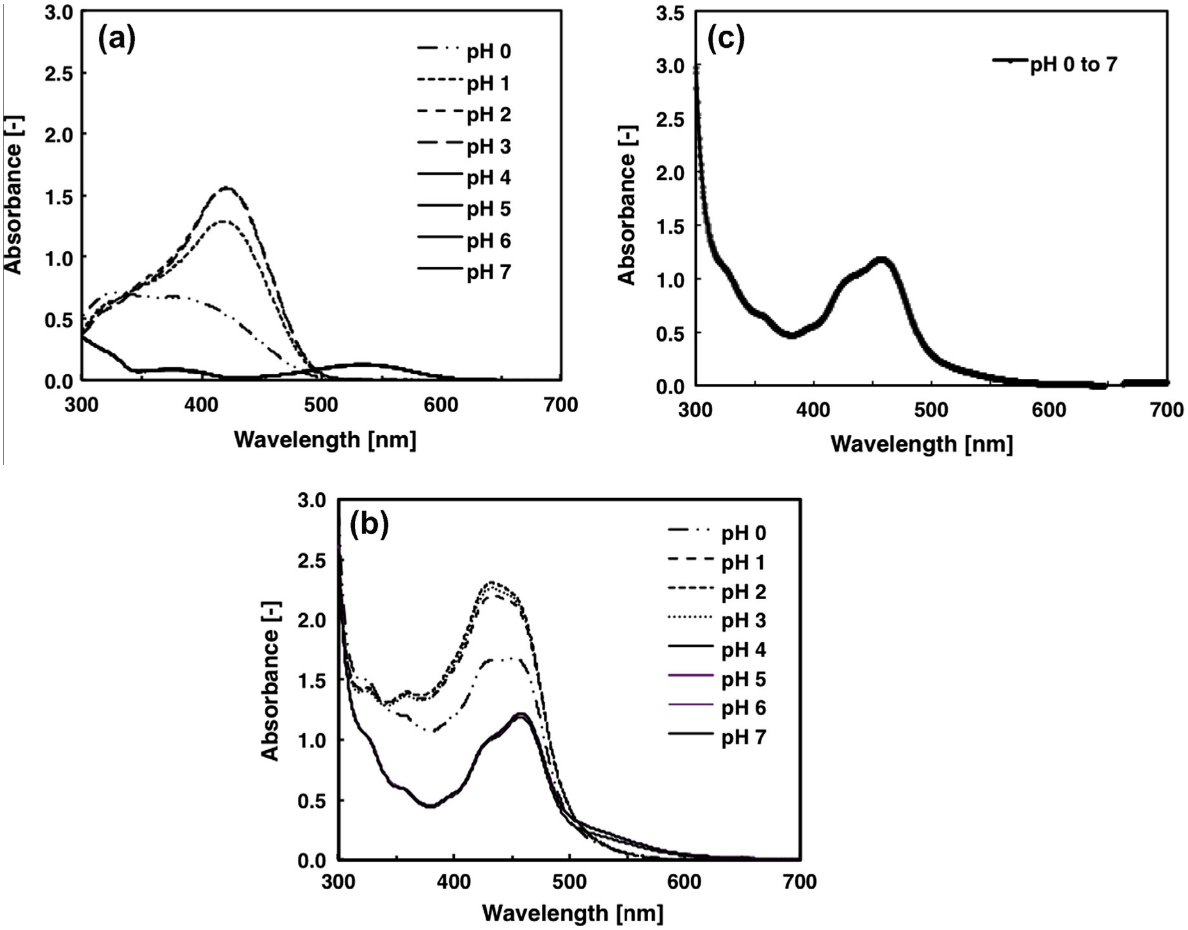


Fig. 2. Absorption spectra of the aqueous polymer solutions (0.1 wt.%) under various pHs at 20 °C under dark condition for (a) the PNS, (b) the PNRS and (c) the PNR.

Under the condition from pH = 7 to 4, the weak absorption band at 530 nm attributed to deprotonated Mc was found and the absorption band at 420 nm attributed to protonated McH [23] did not appear. On the other hand, under the condition from pH = 3 to 0, the absorption band for McH increased significantly although it decreased a little at pH = 0. It was found that spirobenzopyran forms McH structure even under strong acidic condition around pH = 1 which is necessary for the BZ reaction. The same tendency can be observed for the PNRS (Fig. 2b). Since there is no pH-dependence of the absorption spectra for PNR (Fig. 2c), the change in absorption spectra for the PNRS is due to photo-isomerization of spirobenzopyran.

Then, we investigated the behavior of photo-isomerization from Sp to McH state and vice versa under pH = 1. Fig. 3a shows the change in absorption spectra of the PNRS at pH = 1 under dark condition after dissolving the PNRS in the solution. Before being dissolved, the polymer is in solid state and the spirobenzopyran forms Sp structure. After dissolution, the absorbance at 420 nm which was attributed to McH structure increased with time (Fig. 3b). It was suggested that thermal isomerization from Sp to McH occurred. It took 20 h to complete the isomerization.

Fig. 4a shows the change in absorption spectra of the PNS solution by photo-irradiation after keeping the solution in the dark for 24 h. The absorbance at 420 nm decreased with time (Fig. 4b), which suggests that photo-isomerization from McH to Sp occurred. The rate was faster than the reverse process. About 50% of photo-isomerization occured in a few minutes and the most part completed in 1 h. From the results of Figs. 3 and 4, it was found that photochromism of spirobenzopyran occurs even under strong acidic condition necessary for the BZ reaction. The photo-isomerization is reversible, although the rate from Sp to McH is much slower than the rate of the reverse reaction.

In order to clarify the differences in solubility of the PNRS between reduced Ru(II) and oxidized Ru(III) states or between McH and Sp states of spirobenzopyran, the optical transmittance changes of the polymer solution was measured as a function of temperature (Fig. 5). Due to the characteristics of the thermosensitive NIPAAm component, the transmittance suddenly decreases as temperature increases, demonstrating a lower critical solution temperature (LCST). When the $Ru(bpy)_3$ site is kept in an oxidized state, the LCST shifts higher than that of the reduced state. The rise in the LCST by oxidation is due to an increase in hydrophilicity of the polymer by the charge increase of the polymerized catalyst. This phenomenon is identical with that generally observed in NIPAAm-based polyelectrolyte gels when their ionic charges increase. In both cases of the $Ru(bpy)_3$ site kept in an oxidized and reduced states, the LCST shifts lower with photo-irradiation inducing isomerization from McH to Sp. Charge disappearance or decreases with photo-isomerization from McH to Sp structure shifted the LCST lower. The LCST shift derived from the photo-isomerization of spirobenzopyran site (▲ ⇒ △) was larger than that derived from the valence decrease of the $Ru(bpy)_3$ site (▲ ⇒ •). That is, the increase

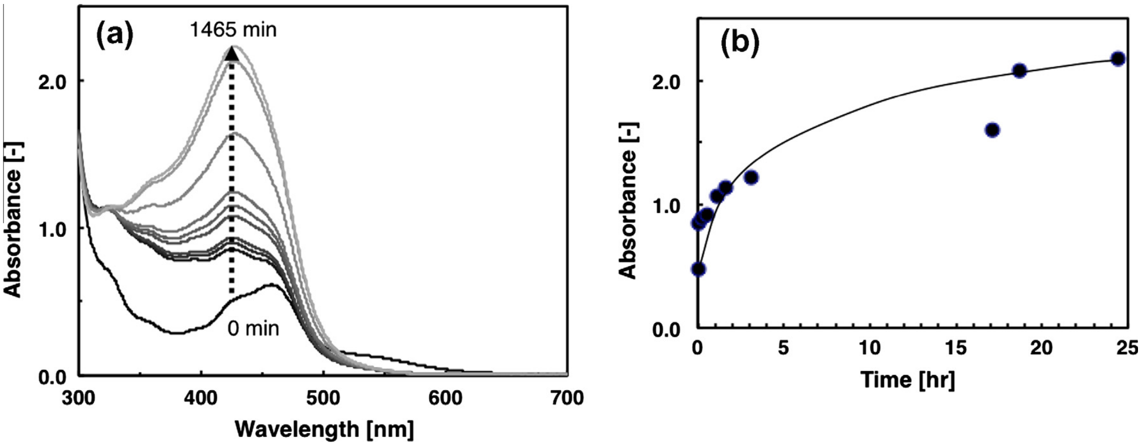


Fig. 3. Change in (a) the absorption spectra (each curve shows 0, 5, 15, 30, 70, 95, 185, 1025, 1120 and 1465 min, respectively) and (b) the absorbance at 420 nm of the PNRS aqueous solution (0.1 wt.%) at pH 1 and 20 °C in the dark after dissolving the PNRS in the solution.

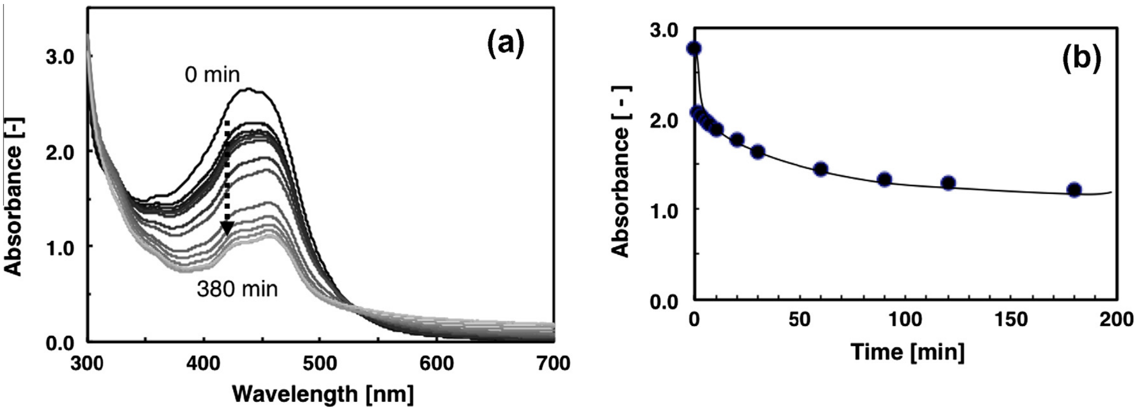


Fig. 4. Change in (a) the absorption spectra (each curve shows 0, 1, 3, 5, 7, 10, 20, 30, 60, 90, 120, 180, 280, 365 and 380 min, respectively) and (b) the absorbance at 420 nm of the PNRS aqueous solution (0.5 wt.%) at pH 1 and 20 °C by photo-irradiation from dark condition.

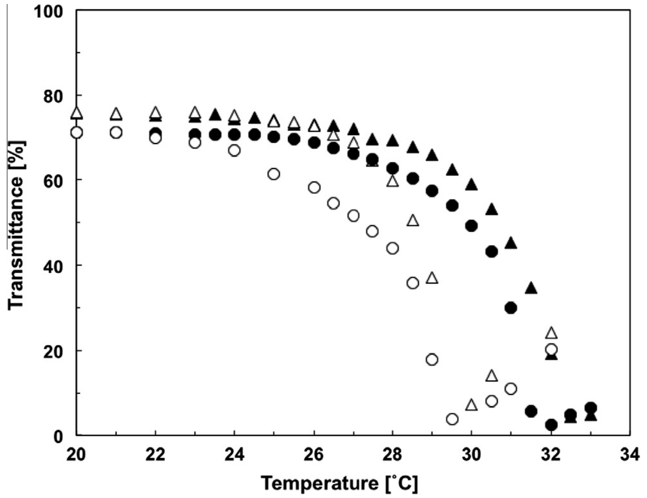


Fig. 5. Temperature dependence of optical transmittance for the PNRS solutions (0.1 wt.%) under the different conditions of reduced state Ru(II) in 1 mM Ce(III) and 0.3 M HNO_3 solution (circle) and the oxidized state Ru(III) in 1 mM Ce(IV) and 0.3 M HNO_3 solution (triangle). Open symbols: under photo-irradiation, closed symbols: in the dark.

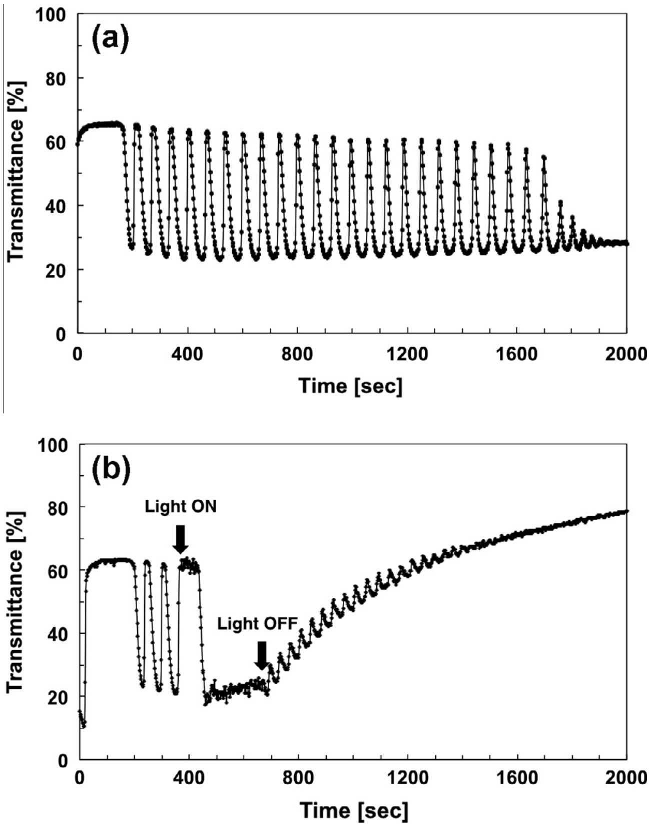


Fig. 6. Oscillating profile of the PNRS aqueous solution (0.1 wt.%) containing the BZ substrate ([MA] = 0.1 M, [$NaBrO_3$] = 0.25 M and [HNO_3] = 0.3 M) at 21.5 °C. (a) In the dark; (b) in response to on–off switching of photo-irradiation.

in hydrophobicity by photo-isomerization of spirobenzopyran to closed-ring structure has more effects than the decrease in valence of the ruthenium catalyst for LCST shifts.

By utilizing the photochromism, on–off control of self-oscillation by photo-irradiation was attempted. Fig. 6 shows the oscillating profile of the PNRS aqueous solution containing the BZ substrates. In the dark, stable oscillation with almost constant amplitude was observed for a long time (Fig. 6a). Fig. 6b shows the oscillating profile in response to on–off switching of photo-irradiation (irradiation period: from 370 s to 670 s). The oscillation stopped after photo-irradiation. It was suggested that this result was due to two possible mechanism; one is the photosensitivity of the reduced $Ru(bpy)_3$ catalyst. Due to the photochemical reaction by the excited state of the reduced catalyst, the inhibitor (Br^-) to stop oscillation is produced [14].

The other is due to lowering hydrophilicity and solubility of the polymer with photoisomerization of spirobenzopyran site. The reaction stops because the contact between the polymerized catalyst and the reactants dissolved in the solution is suppressed when the polymer becomes hydrophobic and insoluble. The observed decrease in optical transmittance after photo-irradiation suggests that stopping oscillation is due to aggregation of hydrophobic polymer chains. After turning light off, the transmittance gradually increased with showing smaller amplitude as compared with that before photo-irradiation. Once the polymer aggregates, it might be difficult to hydrate back to the initial soluble state. Actually, aggregated polymers were observed in the experiment. The small amplitude is attributed to the slow hydration of polymer chains. This result suggests that the on–off switching of self-oscillation was achieved dominantly by the change in polymer solubility due to photochromic isomerization from McH to Sp, not by photosensitivity of $Ru(bpy)_3$. The detailed analysis is under investigation. As a preliminary and control experiment, on–off switching of photo-irradiation was attempted for the poly(NIPAAm-*co*-$Ru(bpy)_3$) (PNR) solution. On–off regulation of oscillation was possible due to the photo-sensitivity of $Ru(bpy)_3$. In this case, immediately after stopping photo-irradiation, the same oscillating profile as that before photo-irradiation was observed, differently from Fig. 6b. This is because there is no difference in hydrated state of the polymer chains between photo-irradiated and non-irradiated conditions. Such a system, however, is not the aim of this study as mentioned in Introduction part. As mentioned before, the photo-regulated system with a change in hydrated state of polymer has some advantages to control mechanical oscillation temporally and spatially, and it is our final goal to create the systems by using the gel. In this study, it was demonstrated that such photo-regulated self-oscillating systems are possible.

4. Conclusions

Spirobenzopyran was introduced into the self-oscillating polymer as a photochromic site. Even under strong acidic condition necessary for the BZ reaction, photochromism of spirobenzopyran occurs and the LCST of the polymer solution shifts to lower temperature with isomerization from McH to Sp. As a result, on–off switching of the soluble–insoluble self-oscillation for polymer solution is possible by photo-irradiation. This result suggests that spatio-temporal photo-regulation of self-oscillating mechanical motion is possible for the gel.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research in Priority Areas “New Frontiers in Photochromism” (No. 471) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

[1] R. Yoshida, T. Takahashi, T. Yamaguchi, H. Ichijo, J. Am. Chem. Soc. 118 (1996) 5134.
[2] R.J. Field, M. Burger (Eds.), Oscillations and Traveling Waves in Chemical Systems, John Wiley & Sons, New York, 1985.

[3] I.R. Epstein, J.A. Pojman, An Introduction to Nonlinear Chemical Dynamics: Oscillations, Waves, Patterns, and Chaos, Oxford University Press, New York, 1998.
[4] R. Yoshida, T. Sakai, S. Ito, T. Yamaguchi, J. Am. Chem. Soc. 124 (2002) 8095.
[5] Y. Hara, R. Yoshida, J. Phys. Chem. B 112 (2008) 8427.
[6] R. Yoshida, Adv. Mater. 22 (2010) 3463.
[7] O. Tabata, H. Kojima, T. Kasatani, Y. Isono, R. Yoshida, Int. Conf. MEMS 2003 (2003) 12–15.
[8] S. Maeda, Y. Hara, T. Sakai, R. Yoshida, S. Hashimoto, Adv. Mater. 19 (2007) 3480.
[9] Y. Shiraki, R. Yoshida, Angew. Chem. Int. Ed. 51 (2012) 6112.
[10] Y. Murase, S. Maeda, S. Hashimoto, R. Yoshida, Langmuir 25 (2009) 483.
[11] Y. Murase, M. Hidaka, R. Yoshida, Sens. Actuators B: Chem. 149 (2010) 272.
[12] R. Yoshida, Y. Murase, Colloids Surf. B: Biointerfaces 99 (2012) 60.
[13] D. Suzuki, T. Sakai, R. Yoshida, Angew. Chem. Int. Ed. 47 (2008) 917.
[14] D. Suzuki, H. Taniguchi, R. Yoshida, J. Am. Chem. Soc. 131 (2009) 12058.
[15] Y. Hara, R. Yoshida, J. Chem. Phys. 128 (2008) 224904.
[16] T. Ueno, K. Bundo, Y. Akagi, T. Sakai, R. Yoshida, Soft Matter 6 (2010) 6072.
[17] T. Amemiya, T. Ohmori, T. Yamaguchi, J. Phys. Chem. A 104 (2000) 336.
[18] S. Shinohara, T. Seki, T. Sakai, R. Yoshida, Y. Takeoka, Chem. Commun. (2008) 4735.
[19] S. Shinohara, T. Seki, T. Sakai, R. Yoshida, Y. Takeoka, Angew. Chem. Int. Ed. 47 (2008) 9039.
[20] P. Dayal, O. Kuksenok, A.C. Balazs, Langmiur 25 (2009) 4298.
[21] P. Dayal, O. Kuksenok, A.C. Balazs, Soft Matter 6 (2010) 768.
[22] V.V. Yashin, O. Kuksenok, P. Dayal, A.C. Balazs, Rep. Prog. Phys. 75 (2012) 066601.
[23] K. Sumaru, M. Kameda, T. Kanamori, T. Shinbo, Macromolecules 37 (2004) 4949.
[24] M. Kameda, K. Sumaru, T. Kanamori, T. Shinbo, Langmuir 20 (2004) 9315.