

Large deformation of self-oscillating polymer gel

Shingo Maeda,* Terukazu Kato, Yuji Otsuka, and Naoki Hosoya

Department of Engineering Science and Mechanics, Shibaura Institute of Technology, Toyosu, Tokyo 135-8548, Japan

Matteo Cianchetti and Cecilia Laschi

The BioRobotics Institute, Scuola Superiore Sant'Anna Polo Sant'Anna Valdera, Viale Rinaldo Piaggio 34 56025 Pontedera, Italy

(Received 5 September 2015; published 5 January 2016)

A self-oscillating gel is a system that generates an autonomous volume oscillation. This oscillation is powered by the chemical energy of the Belousov-Zhabotinsky (BZ) reaction, which demonstrates metal ion redox oscillation. A self-oscillating gel is composed of Poly-*N*-isopropylacrylamide (PNIPAAm) with a metal ion. In this study, we found that the displacement of the volume oscillation in a self-oscillating gel could be controlled by its being subjected to a prestraining process. We also revealed the driving mechanism of the self-oscillating gel from the point of view of thermodynamics. We observed that the polymer-solvent interaction parameter χ is altered by the redox changes to the metal ion incorporated in the self-oscillating gel. The prestraining process leads to changes in χ and changes in enthalpy and entropy when the self-oscillating gel is in a reduced and oxidized state. We found that nonprestrained gel samples oscillate in a poor solution ($\chi > 0.5$) and prestrained gel samples oscillate in a good solution ($\chi < 0.5$).

DOI: [10.1103/PhysRevE.93.010501](https://doi.org/10.1103/PhysRevE.93.010501)

I. INTRODUCTION

In molecular biology, the functioning of mechanisms characteristic of the phenomena of life have been demonstrated by using molecules. Research in this area has demonstrated significant progress [1]. Recently, a holistic approach that could capture the phenomenon of life using system biology has been proposed [2]. The autonomous functions of living organisms are particularly interesting phenomena within this research area. Examples of these include heartbeats and bowel peristalses. In order to understand such autonomous functions it is important to be able to construct simple chemical models as part of experimental systems. In such chemical models the experimental system converting chemical energy into mechanical energy and generating autonomous motion is noteworthy. For example, self-running oil droplets driven by chemical reactions [3–5] and self-actuating water droplets driven by oscillating reactions [6,7] have been observed. In addition to the motion of droplets, self-motion of hydrogels coupled with reaction diffusion systems has been reported in experimental systems [8–14]. In particular, it is known that when the Belousov-Zhabotinsky (BZ) reaction [15] is induced inside hydrogels, they undergo periodic volume oscillations and peristaltic motion (self-oscillating gel) [8,11–14]. As a whole, the BZ reaction is an oxidation reaction of malonic acid in the presence of a metal ion. During this oxidation process, a redox oscillation of the metal ion is generated. A self-oscillating gel is synthesized chemically by means of incorporating a metal ion with a hydrogel [8,12–14]. Hydrogels are composed of networks formed of crosslinking chains of molecules and can contain solvents such as water. As a result of environmental changes, hydrogels are able to absorb and release solvents, thereby changing their volume drastically. In other words, the solubility of the polymer chains in these solvents is dependent on environmental changes. For example, the poly(*N*-isopropylacrylamide) (PNIPAAm)

gel, known as a thermosensitive gel, displays a continuous or discontinuous transition of solubility at around 33°C. Hydrogels have been studied in physicochemical research and also in order to identify their potential technological applications [16–21].

The swelling ratio of a self-oscillating gel in its reduced state of $[\text{Ru}(\text{bpy})_2(4\text{-vinyl-4-methylbpy})]^{2+}$ ($[\text{Ru}]^{2+}$; bpy = 2,2-bipyridine) is different from that in its oxidized state ($[\text{Ru}]^{3+}$). The volume of the gel in the oxidized state is larger than that in the reduced state. Hence, under isothermal conditions, the gel repeats the periodical swelling-deswelling motion due to the BZ reaction. Although self-oscillating gel is a unique material that can function autonomously, from an engineering point of view the utility of that motion is disadvantaged by the fact that only a small displacement is produced. In 1996, a self-oscillating gel displacement of approximately 10 μm was reported [8]. One of the authors synthesized self-oscillating gel with a microdomain structure by using a methanol-water mixture solution as a synthetic solvent [12,13]. It is known that this mixture solution is the specific poor solvent for PNIPAAm gels [22]. As a result, one of us realized 100 μm of displacement and succeeded in observing peristalsis in self-oscillating gel. Lately, morphological changes in self-oscillating gel from the point of view of modeling and simulation have been reported [23,24]. In this paper, we found that the displacement of self-oscillating gel could be controlled by prestraining the gel and revealed the thermodynamic properties of the effects of the prestraining process from equilibrium swelling experiments.

In the case of ionic gels [21], the osmotic pressure of those gels due to the effects of ions π_i is expressed as

$$\pi_i = \frac{(iC_p)^2}{4S} RT, \quad (1)$$

where i , C_p , S , R , and T are the valence of the gel, the concentration of the redox residue in the gel, the salt concentration of the solution, the gas constant, and the absolute temperature, respectively. Here, Eq. (1) is based on the hypothesis that

*maeshin@shibaura-it.ac.jp

$S \gg Cp$. At $T = 293$ K the difference in π_i between the reduced and oxidized states is extremely small, due to the difference in π_i being approximately 1.0 Pa, as can be seen from Eq. (1). Since the change in osmotic pressure resulting from the ionic effects is small, we conjecture that the volume change of the self-oscillating gel is due to the osmotic pressure of polymer-solvent mixing [21]. In this study, we were interested in observing a mechanical strain effect in the self-oscillating gel in its reduced and oxidized states.

II. MATERIALS AND METHOD

In this study, we synthesized poly(NIPAAm-co-[Ru]-co-AMPS) gel as a self-oscillating gel using radical polymerization, as reported previously [12,13]. The gels were prepared in the following manner. We added 0.4256 g of NIPAAm, 6 mg of *N,N*-methylenebisacrylamide, 53 mg of ruthenium(4-vinyl-4-methyl-2,2'-bipyridine)bis(2,2'-bipyridine) bis(hexafluorophosphate) $[\text{Ru}(\text{bpy})_3]^{2+}$ and 6.4 mg of 2,2-azobis(isobutyronitrile) to O_2 -free methanol (1.0 g). We then stirred the resulting solution for 30 min. Next, we added 13.5 mg of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) to O_2 -free pure water (1.0 g) and stirred the resulting solution. We mixed these solutions together and stirred them for 30 min. We then injected the mixed solution into glass capillaries with a diameter of 0.6 mm. We next put these glass capillaries into an oven at 60°C for 20 h. After gelation had occurred, we placed the synthesized cylindrical gel samples in methanol for 24 h. We finally washed the gel samples carefully in methanol-water mixtures (of 100:0, 75:25, 50:50, 25:75, and 0:100%) for one day each.

Figure 1 illustrates the experimental setup. We cut the samples of poly(NIPAAm-co-[Ru]-co-AMPS) gel into lengths of 20 mm. We then subjected the samples to prestraining with an external load (0.5 g). Since the BZ reaction generates complex chemical reaction networks, it is difficult to examine the nature of the poly(NIPAAm-co-[Ru]-co-AMPS) gel in its nonequilibrium condition.

First, we produced the reduced ($[\text{Ru}]^{2+}$) and oxidized ($[\text{Ru}]^{3+}$) states of the nonprestrained and prestrained poly(NIPAAm-co-[Ru]-co-AMPS) gel samples without the

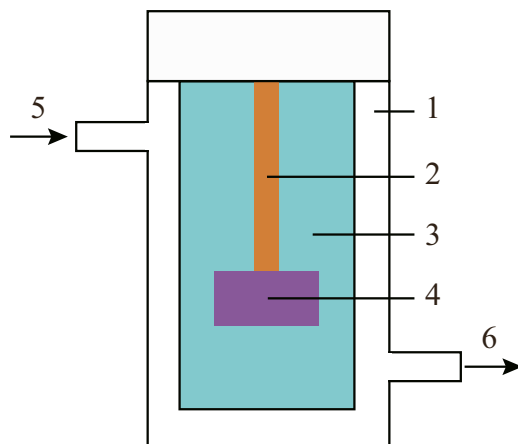


FIG. 1. Schematic illustration of the experimental setup. (1) Thermobath; (2) cylindrical gel; (3) BZ solution; (4) weight; (5) inlet flow of water; (6) outlet flow of water.

BZ reaction and measured the gel samples in the equilibrium condition to understand their physical properties. The volume of the gel samples was measured in the reduced and oxidized states. The oxidized state of the gel was produced using NaBrO_3 as an oxidizing agent. We submerged the gel samples in two solutions: $\text{HNO}_3 = 0.894$ M + $\text{NaBrO}_3 = 0.084$ M and $\text{HNO}_3 = 0.894$ M, respectively. The measurements were conducted in a thermobath to control the temperature.

Second, we measured the displacement of the nonprestrained and prestrained poly(NIPAAm-co-[Ru]-co-AMPS) gel samples driven by the BZ reaction. We submerged the gel samples into the solutions: $\text{HNO}_3 = 0.894$ M + $\text{NaBrO}_3 = 0.084$ M + malonic acid (MA) = 0.0625 M at $T = 293$ K.

III. RESULTS AND DISCUSSION

A. Temperature dependencies of the volume of poly(NIPAAm-co-[Ru]-co-AMPS) gel in thermal equilibrium

Figure 2 shows the swelling curve of the gel samples in thermodynamic equilibrium. At lower temperatures, in the

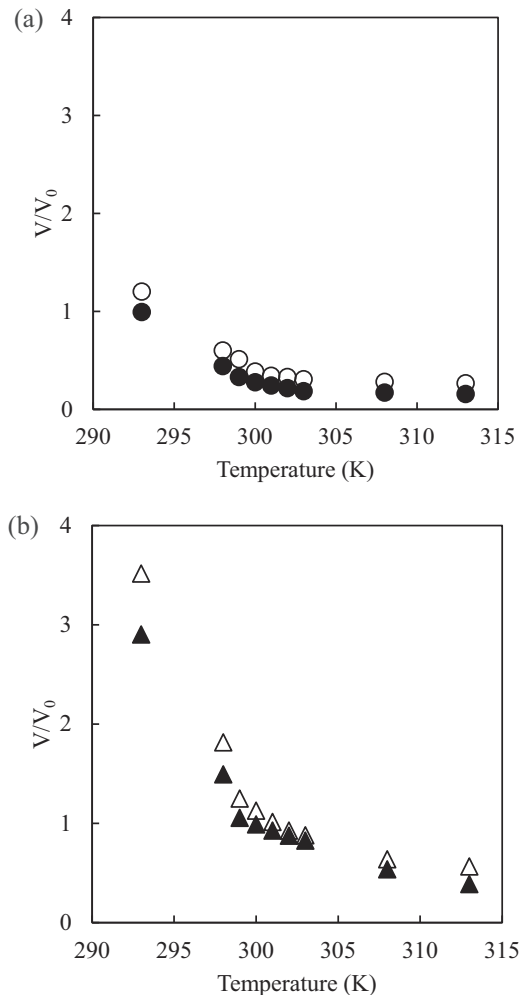


FIG. 2. Equilibrium swelling curve of gel samples as a function of temperature. (a) 0 g, (b) 0.5g of external load. Open circles indicate gel samples in an oxidized state (0 g). Closed circles indicate gel samples in a reduced state (0 g). Open triangles indicate gel samples in an oxidized state (0.5 g). Closed triangles indicate gel samples in a reduced state (0.5 g).

range of 293 ~ 299 K, the volume changes as the difference between the reduced and oxidized states of the prestrained poly(NIPAAm-co-[Ru]-co-AMPS) gel samples is larger than that of the nonprestrained gel samples. In particular, the changes in the volume of the prestrained gel samples resulting from the redox change was significantly larger at 293 K. As the volume change in the prestrained gel samples resulting from the redox change was small at temperatures over 300 K, the solubility change resulting from the prestraining process was small.

B. The Flory parameter χ of the poly(NIPAAm-co-[Ru]-co-AMPS) gel in thermal equilibrium

The Flory parameter χ is important to understanding the thermodynamic state of the system. We evaluated χ from the thermal equilibrium state of the gel samples [21]. The Flory χ parameter indicates a polymer-solvent interaction. As the Flory χ parameter increases the affinity between polymers and solvent molecules decreases. Thus, higher values of the Flory χ parameter lead to the contraction of the gel samples and a reduction in their volume. The thermal equilibrium state of the gel is expressed as follows:

$$\chi = -\frac{1}{\phi} - \frac{\ln(1-\phi)}{\phi^2} - \frac{1}{\phi^2} \left\{ \frac{V_1 N_c}{N_A V_0} \left[\left(\frac{\phi}{\phi_0} \right)^{\frac{1}{3}} - \frac{\phi}{2\phi_0} \right] - \pi_i \right\}, \quad (2)$$

where $\phi, \phi_0, V_1, N_c, N_A$, and V_0 are the polymer volume fraction, the polymer volume fraction at the gelation point, the molar volume of the solvent, the number of polymer chains, Avogadro's number, and the gel volume at the gelation point, respectively. Here, ϕ is defined as

$$\frac{\phi_0}{\phi} = \frac{V}{V_0}.$$

We assumed that monomers were completely polymerized and calculated ϕ_0 from the initial molar concentration of the monomers. In our experiments, ϕ_0 and N_c/V_0 are 0.078 and $1.17 \times 10^{25} (l^{-1})$, respectively. Thus, we determined χ as a function of temperature from Eqs. (1) and (2) and Fig. 2, as shown in Fig. 3.

The Flory parameter χ is a combination of the effects of the enthalpy change Δh and the entropy change Δs in the process

$$\chi = \frac{1}{k_B} \left(\frac{\Delta h}{T} - \Delta s \right), \quad (3)$$

where k_B is the Boltzman constant. From Eq. (3) we can see that the Flory parameter χ is a linear function of $1/T$. Figure 3 shows the Flory parameter χ as a function of the inverse absolute temperature. Table I shows Δh , Δs , and the Flory temperature (Θ) in low-temperature regions. Herein, the Flory temperature Θ is defined as $2\Delta h/(2\Delta s + k_B)$ [21]. At the Flory temperature Θ , the second virial coefficient of the osmotic pressure in the system vanishes. The Flory χ parameter becomes 0.5 at $T = \Theta$. When χ is less than 0.5, the system exhibits the presence of a poor solvent. When χ is more than 0.5, it exhibits the presence of a good solvent.

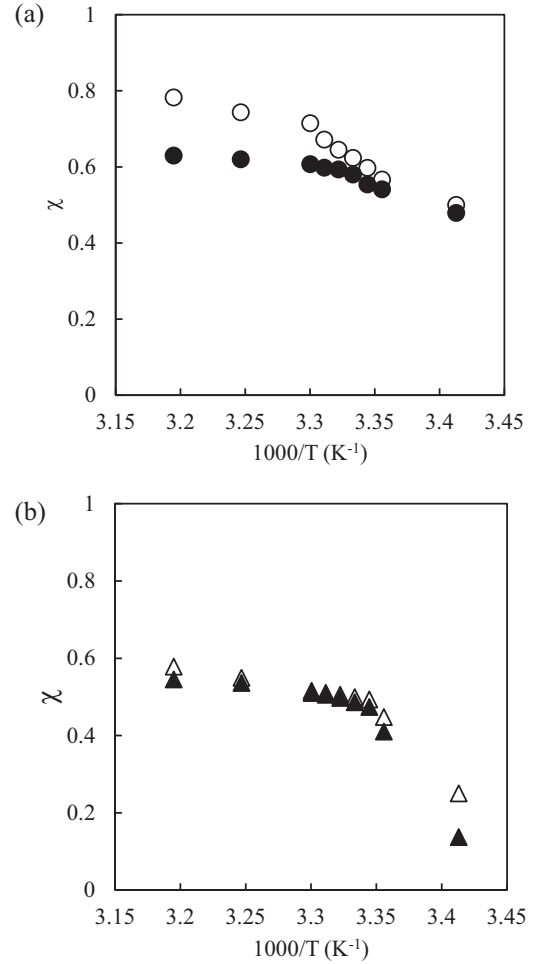


FIG. 3. Flory parameter χ as a function of inverse absolute temperature. (a) 0 g, (b) 0.5 g of external load. Open circles indicate gel samples in the oxidation state (load: 0 g). Closed circle indicate the gel samples in the reduced state (load: 0 g). Open triangles indicate gel samples in the oxidized state (load: 0.5 g). Closed triangles indicate gel samples in the reduced state (load: 0.5 g).

A negative Δh indicates that the polymer chains have absorbed the water molecules. For example, for PNIPAAm gels, the hydrogen bonds between the amide group of PNIPAAm and water molecules result in large negative values for Δh . Both Δh and Δs are negative values for the nonprestrained and prestrained gel samples. As the $|\Delta h|$ of the prestrained

TABLE I. Parameter values from least-squares fit of the experimental data.

Samples ^a	Δh ($\times 10^{-20}$ J)	Δs ($\times 10^{-23}$ J/K)	Θ (K)
Ru(II)0	-2.3	-8.6	292.2
Ru(III)0	-1.7	-6.5	292.5
Ru(II)0.5	-4.9	-17	300.4
Ru(III)0.5	-6.7	-23	300.3

^aRu(II)0 and Ru(III)0 indicate nonprestrained gel samples in the reduced and oxidized states, respectively. Ru(II)0.5 and Ru(III)0.5 indicate prestrained gel samples in the reduced and oxidized states, respectively.

gel samples is much larger than that of nonprestrained ones, extensive absorption of water molecules by the polymer chains occurs only in the prestrained gel samples. Interestingly, Δh of the nonprestrained gel samples in the oxidized state is slightly smaller than that in the reduced state, and Δh of the prestrained gel samples in the oxidized state is observed to be larger than that in the reduced state. Moreover, $|\Delta s|$ of the prestrained gel samples was much larger than that of nonprestrained gel samples. It is assumed that these ordered structures were generated in the system due to water molecules forming hydrogen bonds with the polar groups of the polymer chains and becoming hydrated with the ionic groups. As a consequence, $|\Delta s|$ of the prestrained gel samples decreases. Δs of the nonprestrained gel samples in the oxidized state is slightly larger than that in the reduced state and Δs of the prestrained gel samples in the oxidized state is clearly smaller than that in the reduced state. Thus, when the gel goes from the reduced state to the oxidized state, the enthalpy and entropy of the nonprestrained gel samples increase. On the other hand, when the gel samples go from the reduced state to the oxidized state, the enthalpy and entropy of the prestrained gel samples decrease.

From the results of the Flory Θ of the gel samples, as shown in Table I, we found that the χ parameter of the nonprestrained gel samples changed in the poor solvent ($\chi > 0.5$) and the χ parameter of the prestrain gel samples changed in the good solvent ($\chi < 0.5$), following from the redox changes of the metal ion. On being immersed in nitric acid, which had high ionic strength, the nonprestrained gel samples became hydrophobic [25]. Thus, the nonprestrained gel samples were hydrated and dehydrated when the polymer chains were in a hydrophobic state and the hydrophobic interaction was dominant in the system. In contrast, the prestrained gel samples were hydrated and dehydrated when the polymer chains were in a hydrophilic state at lower temperatures.

C. Volume oscillation of poly(NIPAAm-co-[Ru]-co-AMPS) gel driven by the BZ reaction

From these results, it is expected that the displacement of the prestrained self-oscillating gel samples will become larger than that of the nonprestrained self-oscillating gel samples, driven by the BZ reaction. Figure 4 shows the oscillation profiles of the self-oscillating gel samples at $T = 293$ K. When the volume fraction of the gel is large, the redox potential of the metal ion in the BZ reaction is small. As a result, the displacement of the self-oscillating gel is small [12]. For this reason, we conducted the experiment at $T = 293$ K. The displacement of the prestrained self-oscillating gel samples was more than 1.0 mm, with the prestraining process greatly increasing the displacement of the gel.

Finally, we discuss the relationship between χ and ϕ of the gel samples. Figure 5 shows the relation between χ and ϕ of the poly(NIPAAm-co-[Ru]-co-AMPS) gel samples. When the BZ reaction occurs inside the poly(NIPAAm-co-[Ru]-co-AMPS) gel samples, we assume that the volume fraction ϕ is correlated with the change of the χ parameter. The trend of the gradient $d\chi/d\phi$ changes drastically around $\chi = 0.5$. According to our results [12], the gel samples are in a hydrophobic state at $\chi > 0.5$ and the redox potential of the metal ion in the

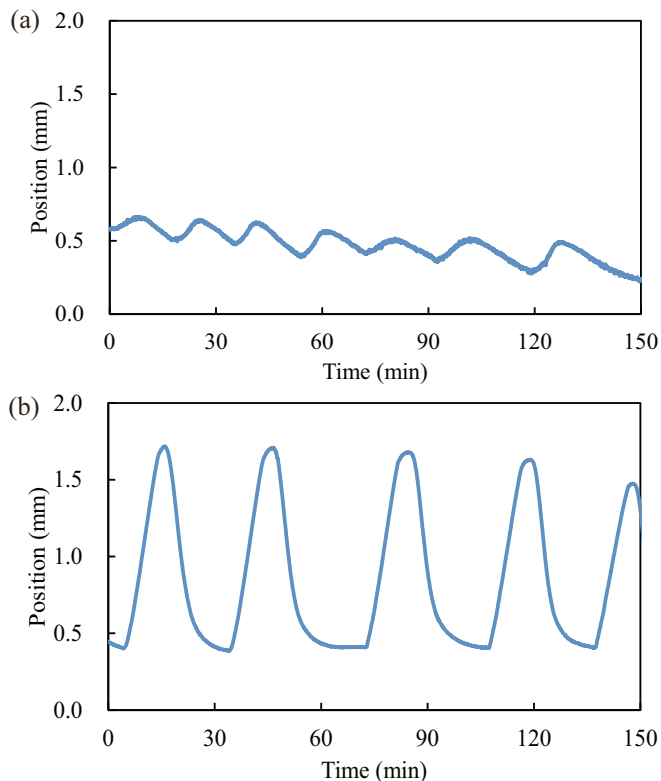


FIG. 4. Time profiles of the (a) nonprestrained and (b) prestrained self-oscillating gel samples. Outer solution: $[MA] = 0.0625$ M; $[NaBrO_3] = 0.084$ M; $[HNO_3] = 0.894$ M.

BZ reaction is extremely small. As a result, the displacement of the self-oscillating gel samples is also small. Hence, it is important for χ to be fixed at a value under 0.5 in order for large displacements of the gel samples to take place.

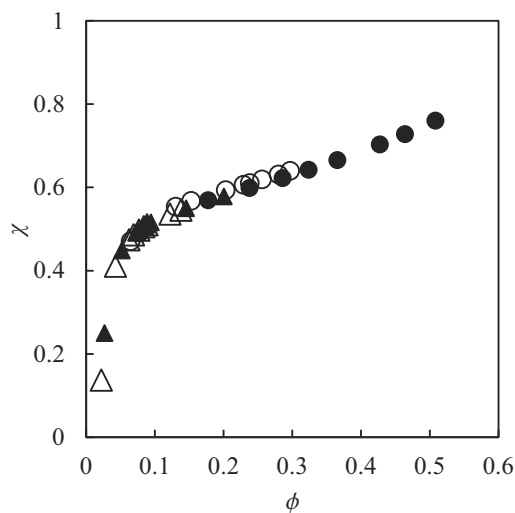


FIG. 5. Polymer solvent parameters χ and ϕ . Open circles indicate self-oscillating gel samples in the oxidized state (load: 0 g). Closed circles indicate gel samples in the reduced state (load: 0 g). Open triangles indicate self-oscillating gel samples in the oxidized state (load: 0.5 g). Closed triangles indicate self-oscillating gel samples in the reduced state (load: 0.5 g).

In this experiment the prestraining of the gel led to a large displacement at $\chi < 0.5$.

IV. CONCLUSIONS

In conclusion, we have revealed the effects of prestraining self-oscillating gel from the point of view of thermodynamics. The prestraining process results in significant changes in the enthalpy and entropy of self-oscillating gel samples in both the reduced and oxidized states. We have found that the swelling and deswelling mechanisms of prestrained gel samples are different from those of nonprestrained gel samples. A molecular level investigation would need to be carried out to ascertain further details. In recent research, self-oscillating gels that swell and deswell as a result of

changes in entropy and which swell in a reduced state and deswell in an oxidized state have been identified [26–28]. In the course of this research we have succeeded in controlling the swelling and deswelling of self-oscillating gel samples under the mechanical circumstances of their having been subjected to a process of prestraining. In the future, we would like to investigate the responses of self-oscillating gel to periodic external forces.

ACKNOWLEDGMENTS

This work was supported in part by JSPS KAKENHI Grants No. 23686043, No. 26630102, and No. 26630080. The authors are grateful to Mr. Aidan Butler for comments on the manuscript. We thank Eiko Maeda for helpful discussion.

-
- [1] Y. Masashi, K. Hiroki, K. Sadao, T. Yoko, K. Mieko, M. Youji, Y. Yoshio, G. Katsutoshi, and M. Tomoh, *Nature* **332**, 411 (1988).
- [2] H. R. Ueda, M. Hasegawa, and H. Kitano, *J. Theor. Biol.* **210**, 401 (2001).
- [3] Y. Sumino, N. Magome, T. Hamada, and K. Yoshikawa, *Phys. Rev. Lett.* **94**, 068301 (2005).
- [4] Y. Sumino, H. Kitahata, H. Seto, and K. Yoshikawa, *Phys. Rev. E* **76**, 055202 (2007).
- [5] M. K. Chaudhury and G. M. Whitesides, *Science* **256**, 1539 (1992).
- [6] H. Kitahata, N. Yoshinaga, K. H. Nagai, and Y. Sumino, *Phys. Rev. E* **84**, 015101 (2011).
- [7] J. Szymanski, J. Gorecki, and M. J. B. Hauser, *J. Phys. Chem. C* **117**, 13080 (2013).
- [8] R. Yoshida, T. Takahashi, T. Yamaguchi, and H. Ichijo, *J. Am. Chem. Soc.* **118**, 5134 (1996).
- [9] J. Boissonade, *Phys. Rev. Lett.* **90**, 188302 (2003).
- [10] V. Labrot, P. De Kepper, J. Boissonade, I. Szalai, and F. Gauffre, *J. Phys. Chem. B* **109**, 21476 (2005).
- [11] Y. Zhang, N. Zhou, N. Li, M. Sun, D. Kim, S. Fraden, I. R. Epstein, and B. Xu, *J. Am. Chem. Soc.* **136**, 7341 (2014).
- [12] S. Maeda and S. Hashimoto, *Macromol. Chem. Phys.* **214**, 343 (2013).
- [13] S. Maeda, Y. Hara, R. Yoshida, and S. Hashimoto, *Angew. Chem. Int. Ed.* **47**, 6690 (2008).
- [14] S. Maeda, Y. Hara, T. Sakai, R. Yoshida, and S. Hashimoto, *Adv. Mater.* **19**, 3480 (2007).
- [15] A. M. Zhabotinsky, *Chaos* **1**, 379 (1991).
- [16] T. Tanaka, D. Fillmore, S.-T. Sun, I. Nishio, G. Swislow, and A. Shah, *Phys. Rev. Lett.* **45**, 1636 (1980).
- [17] S. Maeda, T. Kato, H. Kogure, and N. Hosoya, *Appl. Phys. Lett.* **106**, 171909 (2015).
- [18] A. Saito, J. Kimura, Y. Fujii, and I. Nishio, *Phys. Rev. E* **88**, 062601 (2013).
- [19] D. L. Huber, R. P. Manginell, M. A. Samara, B.-I. Kim, and B. C. Bunker, *Science* **301**, 352 (2003).
- [20] M. Doi, *J. Phys. Soc. Jpn.* **78**, 052001 (2009).
- [21] P. J. Flory, *Principles of Polymer Chemistry*, 1st ed. (Cornell University Press, Ithaca, NY, 1953).
- [22] S. Hirotsu, *J. Phys. Soc. Jpn.* **56**, 233 (1987).
- [23] V. V. Yashin, O. Kuksenok, and A. C. Balazs, *Prog. Polym. Sci.* **35**, 155 (2010).
- [24] V. V. Yashin, K. J. Van Vliet, and A. C. Balazs, *Phys. Rev. E* **79**, 046214 (2009).
- [25] T. López-León and A. Fernández-Nieves, *Phys. Rev. E* **75**, 011801 (2007).
- [26] S. Nakamaru, S. Maeda, Y. Hara, and S. Hashimoto, *J. Phys. Chem. B* **113**, 4609 (2009).
- [27] S. Maeda and W. Oda, *Chem. Lett.* **41**, 1526 (2012).
- [28] I. Konotop, I. Nasimova, N. Rambidi, and A. Khokhlov, *Polym. Sci. Ser. B* **53**, 26 (2011).