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Functional Surfaces

Self-Oscillating Polymer Brushes**

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Functional surfaces have attracted much attention owing to their various potential applications. Typical examples of functional surfaces are superhydrophobic surfaces that imitate the structure of a lotus leaf[1] and slippery surfaces that mimics a pitcher plant.[2] Moreover, functional surfaces prepared by modifying stimuli-responsive polymers can change their physiochemical properties dynamically in response to external stimuli (such as temperature,[3] light,[4] pH,[5] and solvent[6]), and they are applied to cell culture,[7–9] pattern construction,[10] separation systems,[11,12] control of fluid behavior,[13] and self-cleaning surfaces.[14] Externally driven directional actuation of surface microstructures embedded in stimuli-responsive gels were also reported.[15,16] On the other hand, if functional surfaces exhibiting autonomous changes without external stimuli are realized, they would be highly useful, especially for applications in closed spaces. So far several autonomous functional surfaces have been prepared by immobilizing biomacromolecules,[17] or demonstrated by utilizing the Marangoni effect.[18] However, construction of autonomous systems composed of artificially designed synthetic materials will make them more versatile and expand the range of their uses. As a relevant example, chemo-mechano-chemical self-regulating systems with catalyst-bearing microstructures embedded in stimuli-sensitive gels were reported.[19] Herein we report an autonomous functional surface prepared by grafting self-oscillating polymers as polymer brushes.

As a polymer with an autonomous function, we have developed a self-oscillating polymer that involves a built-in system of energy conversion from chemical oscillation to mechanical oscillation.[20,21] For the polymer design, we focused on the Belousov–Zhabotinsky (BZ) reaction, which autonomously generates redox oscillation and exhibits a temporal rhythm and spatiotemporal patterns that propagate as excited pulses of the oxidized state (chemical waves).[22,23] The self-oscillating polymer consists of *N*-isopropylacrylamide (NIPAAm) and tris(2,2′-bipyridine)ruthenium, $[Ru(bpy)_3]$, covalently bonded to the polymer chains as a catalyst for the BZ reaction. When the polymer gel is immersed in an aqueous solution containing all of the substrates of the BZ reaction except for the catalyst, the reaction occurs in the gel phase with the aid of the catalytic function of the incorporated $[Ru(bpy)_3]$ unit. Oscillating redox changes of the catalyst moiety induces the hydration/dehydration changes of the polymer chains because the hydrophilicity of the polymer changes with a change in charge number and the LCST shifts to higher temperature in the oxidized state.[24] As a result, mechanical swelling–deswelling oscillation of the gel is induced at a constant temperature. Since the first report in 1996,[20] we have systematically studied the self-oscillating polymers and the gels as well as their applications to biomimetic actuators, functional fluids, and so on.

When the gel size is large, chemical waves spontaneously evolve and propagate in the gel owing to the reaction-diffusion mechanism. Then locally swollen and shrunken regions propagate with the chemical waves, and peristaltic motion similar to that of a living worm or intestine can be induced. By utilizing peristaltic motion of the self-oscillating gel, autonomous mass transport has recently been demonstrated.[25–27]

Recently, surface-modification techniques for polymer chains have made much progress with the development of new polymer synthesis methods. In particular, surface-initiated atom-transfer radical polymerization (SI-ATRP) is one of the most effective modification methods for preparing a well-defined dense polymer brush structure, or polymer brush, on substrates.[28–31] Polymer brushes on substrates exhibit the same unique properties as those of the grafted polymers owing to the significantly higher graft density compared to other polymer grafting methods. Thus, a self-oscillating polymer brush prepared by SI-ATRP can be expected to create a new self-oscillating surface with autonomic function like a cilia, which will lead to potential applications to transporting systems for nanomaterials or flow control in microfluidics.

Herein, we prepared the self-oscillating polymer brush on glass substrates by SI-ATRP (Figure 1). Along with characterization of the polymer brush, the chemical wave, which propagates in the polymer brush layer, was observed. To the best of our knowledge, this self-oscillating polymer brush is the first achievement of an autonomic functional surface composed of a synthetic polymer.

As the first step, the free self-oscillating polymer was prepared by ATRP and its oscillating behavior was investigated. Poly(NIPAAm-*co*-NAPMAm) was synthesized by ATRP, and then $[Ru(bpy)_3]$ with a succinimidyl group was

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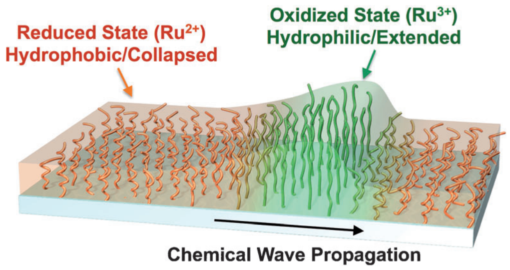
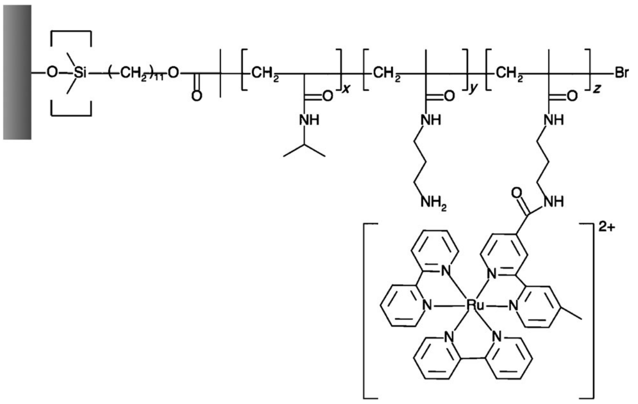


Figure 1. Illustration of the self-oscillating polymer brush in operation.

introduced into the polymer by the reaction with the amino group of NAPMAm (Scheme 1, Supporting Information, Figure S1). The composition ratio of poly(NIPAAm-*co*-NAPMAm) was determined to be 89.5:10.5 from ^{1}H NMR (Supporting Information, Table S1), which was approximately the same as that of the feed composition. The molecular weight M_w was 7.17×10^3 and the polydispersity index (M_w/M_n) was 1.24 from GPC. The conjugation ratio of [Ru(bpy)$_2$(bpy-mOSu)] to poly(NIPAAm-*co*-NAPMAm) were determined to be 74 % by UV/Vis spectroscopy, which was calculated based on the molecular weight of each unit (NIPAAm. NAPMAm, [Ru(bpy)$_3$]). Thus, the composition ratio of NIPAAm:NAPMAm:[Ru(bpy)$_3$]NAPMAm was determined to be 89.5:2.7:7.8 by ^{1}H NMR and UV/Vis spectroscopy. The conjugated [Ru(bpy)$_3$] ratio (7.8 mol %) was higher than the ratio (ca. 1 mol %) of the self-oscillating polymer directly prepared by copolymerizing NIPAAm and the [Ru(bpy)$_3$] monomer through radical polymerization.[32]



Scheme 1. Structure of the self-oscillating polymer brush.

Figure 2 shows the temperature dependence of the optical transmittance of the poly(NIPAAm-*co*-NAPMAm-*co*-[Ru(bpy)$_3$]NAPMAm) solution in the reduced Ru^{II} state and oxidized Ru^{III} state at 574 nm wavelength, which is an isosbestic point of the [Ru(bpy)$_3$] moiety. Owing to the characteristics of the thermosensitive NIPAAm component, the transmittance suddenly decreases as temperature increases, demonstrating an LCST. When the [Ru(bpy)$_3$] site is kept in an oxidized state, the LCST shifts higher than that of the reduced state because the hydrophilicity of the polymer increases owing to the charge increase of the copolymerized catalyst.[24]

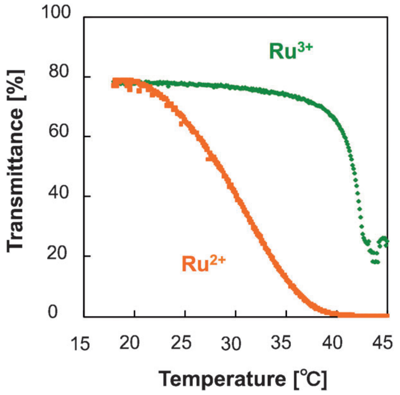


Figure 2. Temperature dependence of optical transmittance for poly(NIPAAm-*co*-NAPMAm-*co*-[Ru(bpy)$_3$]NAPMAm) solutions under the different conditions involved, namely the reduced Ru^{II} state (in 1 mM $Ce_2(SO_4)_3$ containing 0.3 M HNO_3 solution) and oxidized Ru^{III} state (in 1 mM $Ce(SO_4)_2$ containing 0.3 M HNO_3 solution).

From the deviation of the LCST between the Ru^{II} and Ru^{III} states, the polymer undergoes periodic soluble–insoluble changes with periodic redox changes caused by the BZ reaction at constant temperature. Figure 3 shows the oscillation profiles of the optical transmittance for the poly(NIPAAm-*co*-NAPMAm-*co*-[Ru(bpy)$_3$]NAPMAm) solution at 25 °C and 30 °C. The average oscillation periods were 0.9 min and 0.6 min, respectively. As temperature increases, the oscillation period becomes shorter owing to the increase in the reaction kinetics of the BZ reaction. These results suggested that the self-oscillating conformational change of the poly(NIPAAm-*co*-NAPMAm-*co*-[Ru(bpy)$_3$]NAPMAm) prepared by ATRP occurred successfully.

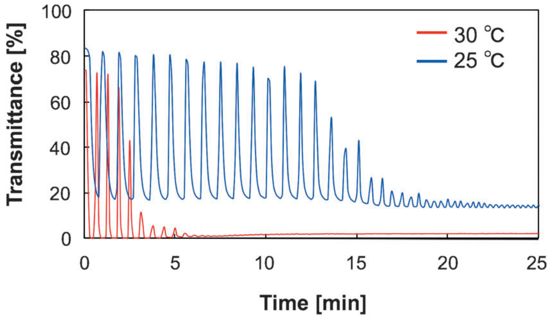


Figure 3. Oscillating profiles of optical transmittance for poly(NIPAAm-*co*-NAPMAm-*co*-[Ru(bpy)$_3$]NAPMAm) solution at 25 °C and 30 °C. The solution contains MA (0.1 M), $NaBrO_3$ (0.2 M), and HNO_3 (0.3 M).

Based on the synthesis of the free self-oscillating polymer by ATRP, the poly(NIPAAm-*co*-NAPMAm) grafted surface was prepared by SI-ATRP, and then [Ru(bpy)$_3$] with succinimidyl group was introduced into the polymer brush (Supporting Information, Figure S2). From XPS measurements, the carbon content increased after immobilizing the ATRP initiator onto the glass slides (Supporting Information,

Table S2). The carbon and nitrogen content increased after grafting the poly(NIPAAm-*co*-NAPMAm) onto them. Ru was detected after the introduction of [Ru(bpy)$_2$(bpy-mOSu)]. These results indicate that the poly(NIPAAm-*co*-NAPMAm-*co*-[Ru(bpy)$_3$]NAPMAm) brush surface was successfully prepared.

The molecular weight of the grafted poly(NIPAAm-*co*-NAPMAm) was determined by GPC after the grafted polymer was cleaved from the glass slide surfaces with hydrofluoric acid. M_n and polydispersity index (M_w/M_n) of the grafted copolymer was 7.15×10^3 and 1.47, respectively. Ellipsometry measurements also revealed that the thickness of the grafted polymer layer was 3.5 nm. From the obtained molecular weight and layer thickness, the graft density was estimated to be 0.31 chains nm^{-2}, indicating that the grafted polymer formed a dense polymer brush structure on the substrates.[33] Consequently, densely packed self-oscillating polymer brush could be formed on glass substrates through SI-ATRP. Furthermore, it was found from AFM observation that the polymer brush was uniformly grafted on the glass surface (Supporting Information, Figure S3).

Contact-angle measurements were carried out for the prepared surfaces in the reduced Ru^{II} state and oxidized Ru^{III} state (Figure 4). The substrates modified with the self-oscillating polymer were more hydrophobic than the glass slides because of the hydrophobicity of NIPAAm and the bipyridine ligands. The contact angle of the polymer brushes increased with increasing temperature in both Ru redox states. The reduced surface was slightly more hydrophobic than the oxidized surface in lower temperature range from 0 to 30 °C. However, the reduced surface dramatically increased its hydrophobicity above 32 °C and the difference in contact angles between the two states was approximately 10 degrees at 40 °C. There was no difference in contact angle for the unmodified glass slides in the Ce^{3+} and Ce^{4+} aqueous solutions (data not shown). From the LCST behavior (Figure 2), the polymer aggregates above 32 °C in the reduced state, which agrees with the result of the contact angle measurement. As the phase-transition temperature in the oxidized state is above 40 °C as shown in Figure 2, it is reasonable that a larger difference in contact angle between the redox states is observed at 35 and 40 °C in Figure 4. The result indicates that the hydrophilicity and wettability of the surface changes periodically by self-oscillation of the grafted polymer chains in the catalyst-free BZ reaction solution under appropriate temperature conditions.

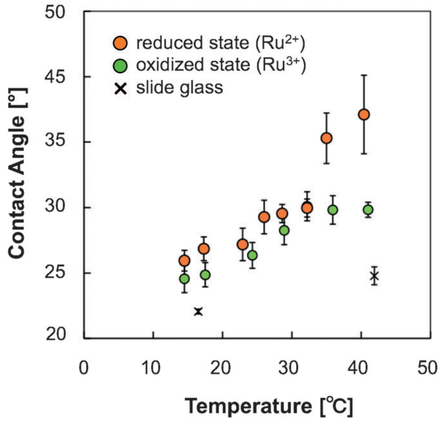


Figure 4. Temperature dependence of contact angle for poly(NIPAAm-*co*-NAPMAm-*co*-[Ru(bpy)$_3$]NAPMAm) grafted glass under the different conditions of reduced Ru^{II} state and oxidized Ru^{III} state.

To confirm the existence of [Ru(bpy)$_3$] within the polymer brush surface, the surface was observed by fluorescence microscope (excitation: 425 nm) in the reduced and oxidized states of [Ru(bpy)$_3$].[34] The fluorescence (585 nm) exhibited strong intensities only in the reduced state (see Figure S4 in Supporting Information), indicating that the self-oscillating polymer brush was successfully modified on the glass slides and that it is possible to observe the BZ reaction by fluorescence microscope.

The self-oscillating polymer brush grafted glass slides were immersed in a large amount of the catalyst-free BZ reaction solution (that is, an aqueous solution containing HNO$_3$, NaBrO$_3$, and malonic acid (MA)). However, a periodic change of the fluorescence intensity was not observed. This is because the intermediate products of the BZ reaction, and in particular HBrO$_2$, which acts as an activator of the oscillation, diffuses into the outer solution. To suppress this dilution effect, two glass slides with self-oscillating polymer grafted onto them were placed facing toward each other with a spacer of 50 μm thickness, and the catalyst-free BZ solution was injected into the small, enclosed space (Supporting Information, Figure S5).

In this case, periodic changes of fluorescence intensity were observed, although the oscillation was gradually dampened (Figure 5). This result suggests that diffusion of intermediate products into the outer solution was an important factor for generating the oscillating reaction on the polymer brush surface.

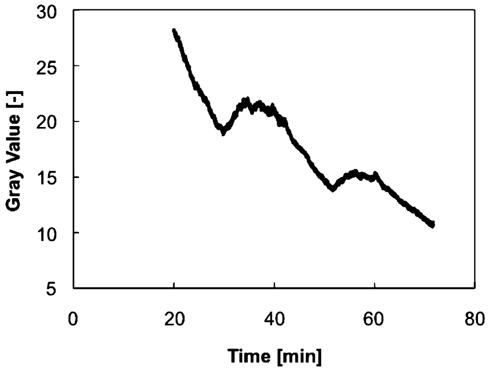


Figure 5. Oscillating profile of fluorescence intensity for self-oscillating polymer brush modified slide glass. The polymer brush surface contacts the solution containing MA (0.1 M), NaBrO$_3$ (0.15 M) and HNO$_3$ (0.81 M) at 18 °C.

From this result, we grafted the self-oscillating polymer onto the inner surface of a glass capillary (Supporting Information, Figure S6). Figure 6 (upper) shows the image observed by fluorescence microscope, which shows that the self-oscillating polymer brush was successfully modified onto the inner surface of the capillary. Then the catalyst-free BZ

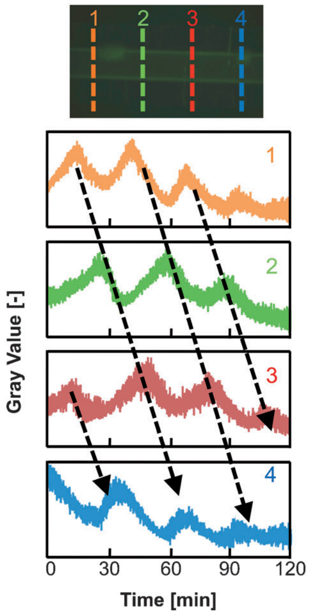


Figure 6. Top: Images of a glass capillary modified with the self-oscillating polymer as observed by a fluorescence microscope. Bottom: Oscillating profile of fluorescence intensity at each position for the self-oscillating polymer brush modified on the inner surface of glass capillary. The solution containing MA (0.1 M), $NaBrO_3$ (0.15 M), and HNO_3 (0.81 M) is enclosed in the capillary at 25 °C.

solution was fed into the capillaries and the BZ reaction on the inner surface was observed by fluorescence microscope. Spatiotemporal image analyses were performed in different locations (1–4) of the glass capillary and the oscillating profiles of the fluorescence intensity were compared (Figure 6). It was found that oscillations occurred at each position with a phase difference. This suggests that the chemical wave propagates in the self-oscillating polymer brush layer on the inner surface of the glass capillary.

In conclusion, we have prepared a self-oscillating polymer brush on glass a substrate by SI-ATRP. Grafting of the self-oscillating polymer onto the surface was confirmed by XPS measurements, AFM observations, and contact-angle measurement. The BZ reaction occurred on the self-oscillating polymer brush surfaces, and the propagation of the chemical wave was observed in the polymer brush layer on the inner surface of a glass capillary. Our next interest is to measure mechanical changes of the well-designed grafted polymer chains, which will be reported in the future. We were able to demonstrate a self-oscillating surface to generate spontaneous periodic changes by using synthetic polymers, as a novel autonomous functional surface which has potential applications in systems such as nanoscale transport systems.

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