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Electrochemically Mediated Atom Transfer Radical Polymerization from a Substrate Surface Manipulated by Bipolar Electrolysis: Fabrication of Gradient and Patterned Polymer Brushes**

*Naoki Shida, Yuki Koizumi, Hiroki Nishiyama, Ikuyoshi Tomita, and Shinsuke Inagi**

Abstract: *We report the first ever use of electrochemically mediated atom transfer radical polymerization (eATRP) employing a bipolar electrochemical method for the fabrication of both gradient and patterned polymer brushes. A potential gradient generated on a bipolar electrode allowed the formation of a concentration gradient of a* Cu^I *polymerization catalyst through the one-electron reduction of* Cu^{II}*, resulting in the gradient growth of poly(NIPAM) brushes from an initiator-modified substrate surface set close to a bipolar electrode. These polymer brushes could be fabricated in three-dimensional gradient shapes with control over thickness, steepness, and modified area by varying the electrolytic conditions. Moreover, by site-selective application of potential during bipolar electrolysis, a polymer brush with a circular pattern was successfully formed. Polymerization was achieved using both a polar monomer (NIPAM) and a nonpolar monomer (MMA) with the eATRP system.*

Recently, the technique of electroorganic synthesis has undergone remarkable development as a new strategy in the fields of organic chemistry, polymer chemistry, and materials science.[1] Based on the use of an electrochemical approach to enable facile control of chemical reactions through changing an applied potential, Matyjaszewski et al. have reported pioneering work on controlled polymerization, specifically electrochemically mediated atom transfer radical polymerization (eATRP), in which a Cu^I catalyst generated through electrochemical reduction of Cu^{II} is utilized.[2] Zhou and co-workers extended the eATRP method to the fabrication of polymer brushes from an initiator-modified substrate, using electrogenerated Cu^I diffused from a cathode surface incorporating a microgap.[3] By tilting the cathode toward the initiator-modified substrate, they successfully fabricated a three-dimensional (3D) gradient polymer brush exhibiting a gradual in-plane variation in the degree of polymerization. Gradient polymer brushes such as these are in great demand for biochemical applications, and the exploration of new classes of polymer brushes is of importance in the fields of both surface science and materials chemistry.[4]

A bipolar electrode (BPE) is a wireless electrode produced from the polarization of a conducting material in an external electric field generated by driving electrodes in a low concentration of a supporting electrolyte.[5] A BPE has unique characteristics, including multiple polarities and the ability to generate a potential gradient (Figure 1 a, bottom). We have previously reported the potential design of a BPE using an insulating wall between driving electrodes, and successfully utilized the resulting potential distributions (having linear, sigmoidal, or catenary-like slopes) to perform electrochemical reactions of conducting polymers on the BPE.[6] We were able to generate a concentration gradient of Cu^I on the BPE to promote the reaction of the azide-modified BPE surface with an alkyne derivative to give a molecular gradient.[6e] A Cu^I gradient on a surface is an effective means of controlling the polymerization rate during ATRP (Figure 1 b) on an initiator-modified surface, thus realizing the 3D gradient necessary to generate polymer brushes.

In the research reported herein, we aimed to establish a new method of fabricating 3D gradient polymer brushes and patterned polymer brushes based on the concept of bipolar electrochemistry. Bipolar electrolysis requires only a simple electrolytic setup, and enables ready manipulation of the potential distributions on the BPE. As a result, bipolar electrochemistry could become the leading methodology for the synthesis of gradient polymer brushes.

We prepared our eATRP experimental apparatus by sandwiching a glassy carbon (GC) plate acting as the BPE with an initiator-modified glass plate (see the Supporting Information), incorporating a microgap (D) (Figure 1 a, top). When a sufficient voltage was applied between the driving electrodes, an electric field was generated in the cell, generating a BPE at which simultaneous anodic (oxidation of water) and cathodic (reduction of copper(II) chloride) reactions occurred. These reactions were influenced by the potential distribution on the BPE as shown in Figure 1 a. Thus the concentration gradient of the Cu^I catalyst generated at the BPE produced a reaction field over which the concentration ratio $[Cu^I]/[Cu^{II}]$ varied slightly with position. In this manner, the polymerization rate gradually changed with position according to the reaction mechanism of ATRP (Figure 1 b). As a result, polymer brushes with 3D gradients were successfully obtained.

As a proof-of-concept, we demonstrated the surface-initiated polymerization of N-isopropylacrylamide (NIPAM)

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[*] N. Shida, Y. Koizumi, Dr. H. Nishiyama, Prof. Dr. I. Tomita, Prof. Dr. S. Inagi
Department of Electronic Chemistry, Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 226-8502 (Japan)
E-mail: Inagi@echem.titech.ac.jp
Homepage: http://www.echem.titech.ac.jp/~inagi/e-index.html

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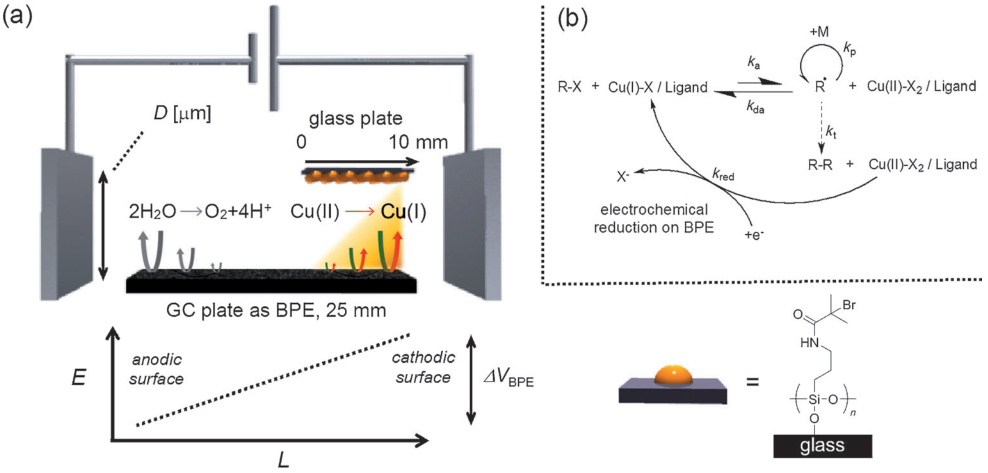

Figure 1. a) Illustration of the electrochemical apparatus used for eATRP, applying a GC (20×25 mm) as the BPE set between Pt driving electrodes (20×20 mm). An initiator-modified glass plate was placed against the BPE, leaving a microgap of *D* µm, while the driving electrodes were set 55 mm apart. Bipolar electrolysis was carried out under ambient conditions in a H_2O/MeOH solution containing monomer, $CuCl_2$, and PMDETA. b) General eATRP scheme.

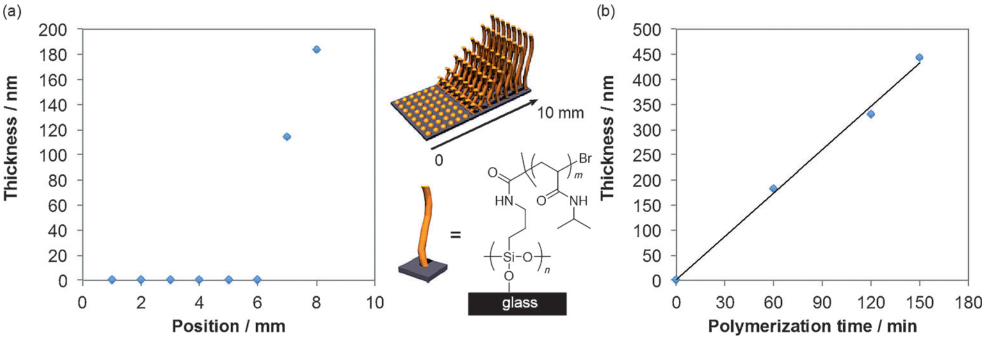

Figure 2. a) Film thickness profile at various positions along a poly(NIPAM)-tethered substrate. Electrolysis conditions: [NIPAM] = 3.2 M, [$CuCl_2$] = 2 mM, [PMDETA] = 10 mM, H_2O/MeOH = 1:1, ΔV_{BPE} = 1.4 V, electrolysis time = 60 min, *D* = 360 µm. b) Time course of the film thickness profile at the 8 mm position of a poly(NIPAM)-tethered substrate. Polymerization was reinitiated with the same glass substrate following each film thickness measurement.

on a glass substrate by eATRP, applying bipolar electrochemistry. In this process, a 3.2 M NIPAM solution in H_2O/MeOH (1:1) with $CuCl_2$ (2 mM) and *N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine (PMDETA, 10 mM) was used as the electrolyte. The microgap, *D*, was 360 µm in these trials. The applied potential difference between both poles of the BPE (ΔV_{BPE}) could be estimated using a well-known procedure (Figure S1). After applying a ΔV_{BPE} value of 1.4 V ($>\Delta V_{min}$[7]) for 60 min under ambient conditions, the glass plate was washed with distilled water, methanol, and acetone to remove physically adsorbed compounds. The formation of poly(NIPAM) on the glass substrate was confirmed by infrared reflection absorption spectroscopy (IR-RAS; Figure S5). Film thickness measurements at various positions with a stylus-type tester to generate a height-profile showed a gradient increase when moving toward the edge of the cathodic pole of the BPE (Figure 2a),[8] presumably resulting from the gradient change in the degree of polymerization. The polymerization rate during the ATRP process is proportional to the [Cu^I]/[Cu^{II}] ratio and so a [Cu^I]/[Cu^{II}] gradient generated on the cathodic side of the BPE will directly affect the polymerization rate gradient at various positions, resulting in the degree of polymerization also exhibiting a single gradient along the BPE.

To confirm the "living" nature of this polymerization system, we subsequently carried out the reinitiation of the polymerization. In these trials, the glass substrate still coated with the gradient poly(NIPAM) brush was again placed in the bipolar electrochemical cell and electrolyzed for an additional 60 min, after which the film thickness was measured. This same process was then repeated once more (30 min). As shown in Figure 2b,[9] the height of the polymer brush at the 8 mm position increased in a linear manner with increasing polymerization time, indicating that the surface-initiated eATRP proceeded in a living-like manner. Further kinetic investigation was carried out to compare the rate of brush growth at each position (Figure S9). As expected, a higher rate of polymerization was observed at more cathodic edge of the BPE.

To achieve fine tuning of the polymer brush film thickness, it is helpful to evaluate the effects of parameters such as the applied voltage (ΔV_{BPE}) and the microgap (*D*). Figure 3a demonstrates that, as higher voltages are applied to the BPE, the film thickness becomes slightly thicker in an increasingly steep manner. Extremely steep potential gradients, however, induce the generation of Cu^0 through the two-electron reduction of Cu^{II}, and therefore tuning of the applied voltage was deemed unsuitable for controlling the film thickness over a wide range. When the microgap was changed from 540 to 180 µm, the brush thickness obtained at the 5 to 8 mm positions following electrolysis for 60 min dramatically increased to as much as 510 nm (Figure 3b). Zhou et al. successfully estimated the proportional relationship between polymerization rate and the diffusion distance of Cu^I during eATRP,[3c] and found that the microgap has a significant effect on the polymerization rate in a BPE system. It is noteworthy that the polymer-modified area was clearly expanded when changing the *D* value due to the drastic increase in the [Cu^I]/[Cu^{II}] ratio at the surface of the glass substrate. These

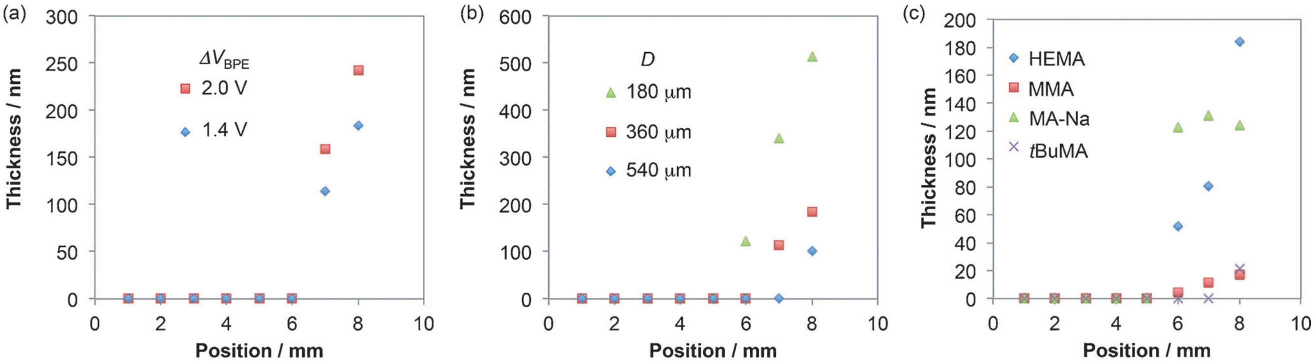

Figure 3. Film thickness profiles at various positions along polymer brushes. a) Electrolyzed at different applied voltages. Conditions: [NIPAM] = 3.2 M, [$CuCl_2$] = 2 mM, [PMDETA] = 10 mM, H_2O/MeOH = 1:1, reaction time = 60 min, D = 360 μm. b) Electrolyzed with different values of D. Conditions: [NIPAM] = 3.2 M, [$CuCl_2$] = 2 mM, [PMDETA] = 10 mM, H_2O/MeOH = 1:1, reaction time = 60 min, ΔV_{BPE} = 1.4–1.5 V. c) Polymerization of various monomers. Conditions: [monomer] = 3.2 M, [$CuCl_2$] = 2 mM, [PMDETA] = 10 mM, D = 360 μm, reaction time = 60 min, H_2O/MeOH = 1:1, ΔV_{BPE} = 2.0 V (for HEMA), H_2O/MeOH = 4/1, ΔV_{BPE} = 1.6 V (for MMA), H_2O/MeOH = 1:1, ΔV_{BPE} = 1.4 V (for MA-Na), D = 180 μm, reaction time = 180 min, H_2O/MeOH = 1:5, ΔV_{BPE} = 2.0 V (for *t*BuMA).

results indicated that facile control of the steepness, modified area, and thickness of the gradient polymer brush could be achieved by changing both the applied voltage and the D value. To visualize the height profile of the gradient brush (D = 180 μm), a 3D laser scanning microscope was employed (Figure S11a). A gentle height profile of the polymer brush was observed across several millimeters, corresponding to the height profile obtained by the stylus-type measurement.

We next investigated the surface-initiated eATRP of various monomers with the BPE. In contrast to the typical electrolytic procedure applied during surface-initiated eATRP, bipolar electrolysis is carried out using a low concentration of a supporting salt. This makes it possible to perform eATRP using nonpolar monomers such as methyl methacrylate (MMA), which is immiscible with polar solvents containing high concentrations of a supporting salt. We investigated the polymerizations of 2-hydroxyethyl methacrylate (HEMA, a polar monomer), MMA (a nonpolar monomer), and sodium methacrylate (MA-Na, an ionic monomer). The film thickness profiles of the obtained polymer brushes are presented in Figure 3c. HEMA showed very similar behavior to NIPAM, both of which are regarded as polar monomers. In the case of MMA, the gradient polymer brush was successfully formed, although the brush was relatively thin compared to the poly(NIPAM) and the poly(HEMA) brushes. This result can be explained by considering a previous report regarding the polymerization rates of these monomers during surface-initiated ATRP in water/methanol.[10] The results of these trials demonstrated that a wide range of monomers with varying polarities are applicable to eATRP with a BPE. Such versatility could allow the fabrication of complex polymer brush architectures, such as block copolymers. When the ionic monomer MA-Na was used, however, the obtained polymer brush did not exhibit a typical gradient slope. Although the GC plate worked adequately as the BPE under the optimal conditions during the eATRP, the current flow in the external circuit was approximately 100 mA, a value two orders of magnitude greater than the values observed with the other monomers (NIPAM, HEMA, and MMA). As well, over the course of 60 min of electrolysis, deposition of a large amount of Cu^0 on the driving cathode was observed due to the two-electron reduction of Cu^{II}. Ionic monomers such as MA-Na can act as supporting electrolytes in electrolysis systems, such that faradaic reactions including the Kolbe electrolysis[11] of MA-Na itself as an anodic reaction on the driving electrodes will proceed as well as those on the BPE. In the case of MA-Na, these side reactions on the driving electrodes made it impossible to control the potential distribution on the BPE. We also fabricated a gradient polymer brush of poly(*tert*-butyl methacrylate) (*t*BuMA) by the BPE method (Figure 3c). The following deprotection of *tert*-butyl groups from the brush with trifluoroacetic acid resulted in forming its anionic state,[4b] an equivalent of the product using MA-Na (Figure S10). Such an indirect pathway can overcome the unavailability of ionic monomers.

Finally, we investigated the fabrication of a patterned polymer brush with a BPE system. For this purpose, we employed an electrolytic system with an insulating cylinder, in which the BPE was situated under the cylinder and generated a circular potential distribution reflecting the diameter of the cylinder.[6c] As shown in Figure 4a, the driving anode and cathode were set inside and outside the cylinder (diameter: 1 mm), respectively. This configuration induced a circular cathodic surface in the region just under the cylinder. The Cu^I catalyst generated around the cathodic area of the BPE mesh (Pt) would diffuse to the glass substrate placed 130 μm apart from the Pt mesh and promote the surface-initiated polymerization, resulting in the site-selective formation of the polymer brush. The bipolar electrolysis was conducted in the same electrolyte as was used for the eATRP of NIPAM, applying a constant voltage (10.0 V) between the driving electrodes for 60 min (Figure 4b). Following the electrolysis, the successful formation of poly(NIPAM) was confirmed by both visual examination and optical microscopy. Rinsing the poly(NIPAM)-modified substrate with distilled water was

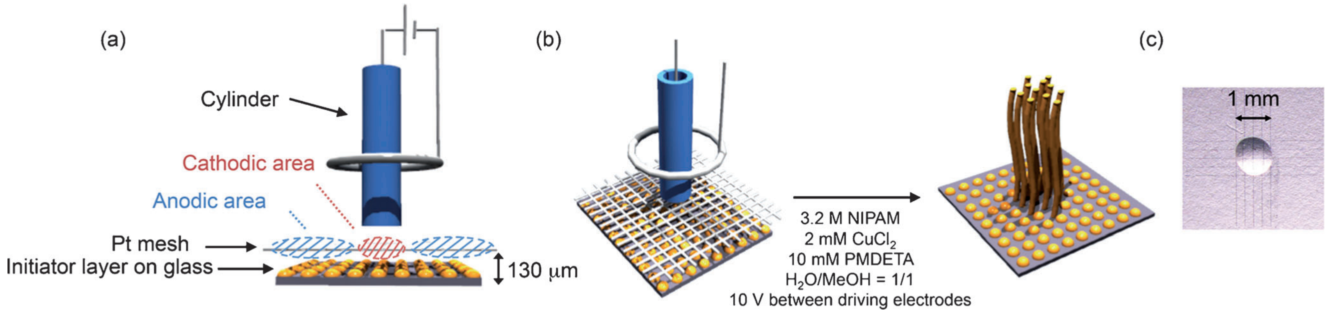

Figure 4. Illustration of the apparatus employed for polymer brush patterning. a) Side view of the system in which a Pt mesh electrode was placed under the cylinder without a gap and a glass substrate was placed 130 μm apart from the Pt mesh. b) Surface-initiated eATRP of NIPAM generating a bipolar electrochemical patterning. c) Optical micrograph of a water droplet adsorbed on the patterned poly(NIPAM) brush. Each ruled line spans 0.25 mm.

observed to leave a water droplet on that portion of the glass surface to which the hydrophilic poly(NIPAM) had been fixed site-selectively (Figure 4c), and the diameter of this droplet was in good agreement with that of the cylinder (1 mm). In contrast, following treatment of the substrate with hot water (60 °C), no water droplet was observed due to the phase transition of the grafted poly(NIPAM) above its lower critical solution temperature of 32 °C. The height profile of the patterned polymer brush across the diameter of the circle exhibited a trapezoidal shape with steep outer rims (Figures S7 and S11b), which reflected the potential distribution on the BPE as predicted by computational simulations (Figure S12). The negatively charged area of the BPE mesh located just under the cylinder evidently generated Cu^I that diffused to the surface of the glass substrate and acted as a catalyst for ATRP.

In conclusion, we have developed a new strategy for the fabrication of 3D gradient and patterned polymer brushes, based on the concept of applying bipolar electrochemistry to surface-initiated eATRP. In the case of the polymerization of NIPAM, the obtained polymer brushes clearly showed gradient height profiles due to the gradual change of the $[Cu^I]/[Cu^{II}]$ ratio and the attendant variations in the polymerization rate at various positions. Using this BPE strategy, we successfully controlled the film thickness, steepness, and area of modification of gradient polymer brushes by changing simple parameters. Moreover, a patterned polymer brush with a trapezoidal topology was successfully fabricated by using this same electrolytic apparatus in conjunction with an insulating cylinder. Because the BPE system does not require supporting salts, it is possible to be flexible with regard to the electrolytic media and monomers, and thus it is possible to fabricate more complex architectures within the polymer brush, such as block copolymers.

Keywords: electrochemistry · gradient material · patterning · polymer brushes · polymers

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[7] ΔV_{min}: minimum applied voltage to induce BPE (see the Supporting Information).

[8] Due to the limitation of the setup with the sandwiched structure of a BPE and a glass plate, it possesses an open edge at 10 mm position. A considerable amount of Cu^I catalyst generated on the BPE would diffuse outside from the microgap to result in complex polymerization behavior around the cathodic edge. For this reason, we did not discuss the film thickness at 9 mm position. The long-term stability of the concentration gradient of Cu^I at 5–8 mm area might be affected by oxygen diffused from the anodic part of the BPE.

[9] The plots in Figure 2b consist of an average of two independent trials as described in Figure S8.

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