Conducting Polymers

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Bipolar Patterning of Conducting Polymers by Electrochemical Doping and Reaction**

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When an isolated conducting substrate in a solution is subjected to a parallel electric field, it can become a bipolar electrode, that is, an electrode that simultaneously acts as both anode and cathode. This type of electrochemistry has made possible the studying of chemical reactions without physical contact to a circuit, for instance, in electrogenerated chemiluminescence applications.[1] Recently, Björefors and co-workers successfully created molecular gradients on a bipolar electrode.[2] For example, self-assembled monolayers on gold were converted to a gradient surface by the cathodic desorption of thiols. Reported electrochemical[3] or bipolar[4] patterning has all been based on deposition or desorption of organic/polymeric molecules or inorganic materials involved at the surface of a conducting substrate. The challenge to gradually convert the composition of molecular or polymeric film in-plane using a simple technique is quite important in view of the widely expanding research into polymer-based soft matter gradients.[5]

Conducting polymers generally have a high conductivity and show a significant color change when oxidized or reduced to have charges and counterions (dopants); therefore, they are candidates for conducting and electrochromic material applications. Herein, we investigate the novel bipolar patterning of a conducting-polymer film, that is, the electrochemical doping behavior of a conducting-polymer film on a bipolar electrode. Charge and dopant distributions with an in-plane gradient across the polymer film are expected. Based on electroorganic synthesis that utilizes electrogenerated species for organic reactions,[6] we recently developed a technique for the electrochemical modification of a conducting-polymer film triggered by electrochemical doping and subsequent chemical reaction.[7,8] For instance, the electrochemical chlorination of polythiophene films on an anode was successfully carried out using a nucleophilic salt such as Et_4NCl as a supporting electrolyte and chlorine source.[8,9] The desired substitution reaction proceeded not only at the surface but also within the bulk of the polymer film. Thus, we report the electrochemical polymer reaction of a conducting-polymer film on a bipolar electrode.

A poly(3-methylthiophene) (PT) film was prepared on an indium tin oxide (ITO) electrode by the potential-sweep method in 0.1 M Bu_4NPF_6/acetonitrile. After further dedoping of the film (dark red color), the substrate was used as a bipolar electrode, which was placed into a U-type electrolytic cell equipped with a platinum anode and a platinum cathode connected to a constant-current power supply (Figure 1).

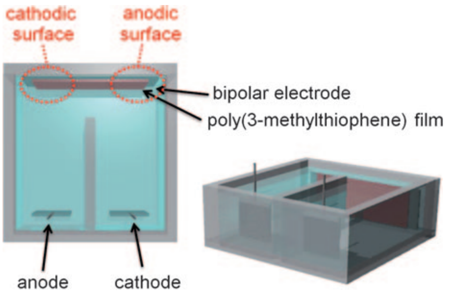

Figure 1. U-type electrolytic cell containing an anode, cathode, and bipolar electrode.

When the conductivity of an electrolytic medium is low, the isolated conducting substrate (bipolar electrode) becomes a less resistive path for a part of the current passing through the solution. On the bipolar electrode, one side facing the cathode acts as an anodic surface and the other side as a cathodic surface.

Electrochemical doping of the neutral PT film on the bipolar electrode was carried out in a non-nucleophilic Bu_4NPF_6/acetonitrile electrolytic solution. In a 0.005 M solution of the electrolyte, the PT film on the bipolar electrode exhibited a blue color with the passage of 1 mA current. The color change was derived from the formation of ionic states, namely, polaron (radical cation) and bipolaron (dication), in the polymer backbone.[10] The doping of the PT film gradually proceeded from the anodic side of the bipolar electrode after the passage of 0.05 C. When the doping process was ceased at an earlier stage (0.02 C), the interface of the color change was located closer to the anodic side (Figure 2). When the concentration of the electrolyte was high (0.1 M), it was necessary to pass a large current (10 mA) between the anode and the cathode to charge the PT film. However, under such severe conditions, detachment of the PT film from the ITO substrate was inevitable.

To quantify the doping, energy-dispersive X-ray (EDX) analysis of the doped PT film on ITO was performed after rinsing with acetonitrile.[11] The observed amounts of ele-

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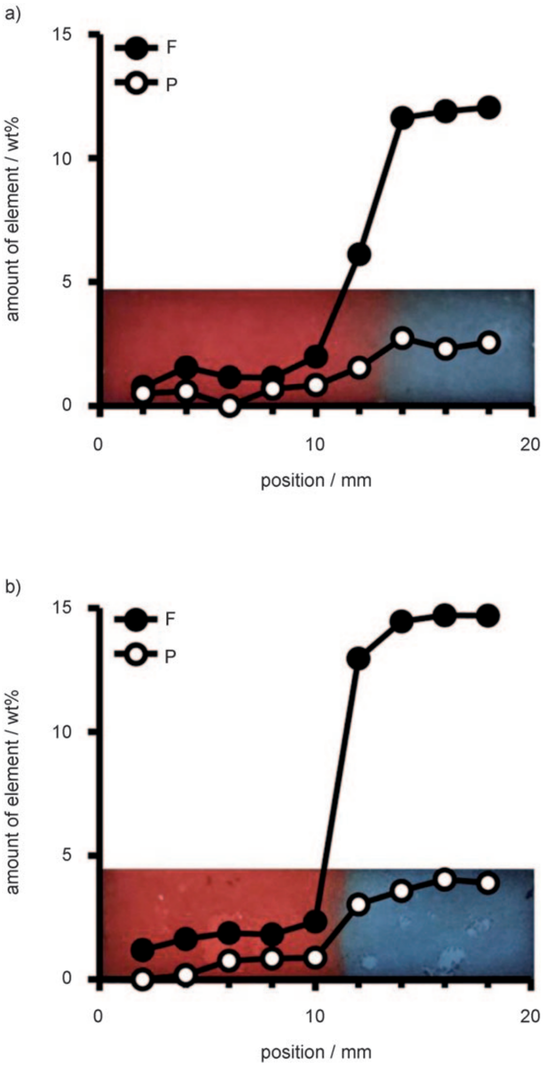

Figure 2. Photographs of the PT film produced by bipolar patterning and the amounts of phosphorus (P) and fluorine (F) contained at each distance from the cathodic side of the doped film after charging with a) 0.02 and b) 0.05 C in 0.005 M Bu_4NPF_6/acetonitrile. Dark red area: neutral PT; blue area: anodically doped PT.

ments comprising the PF_6^- anion, which was included as a dopant, were plotted at each position (Figure 2). The profiles showing the contents of phosphorus and fluorine correspond well to the color change within the doped PT film. Starting from the cathodic side of the film at 2 mm, the dopant contents were negligible. Between 10 and 14 mm the contents gradually increased, which reflected the potential gradient on the bipolar electrode. Closer to the anodic side (> 16 mm), the amount of dopant was maintained constant.

If a charged polymer film is unstable in the presence of reactive reagents in an electrolytic cell, a subsequent chemical reaction takes place that will modify the polymer film. In the case of poly(thiophene) derivatives, selective chlorination onto the 3- or 4-positions of the repeating thiophene unit occurred when they were anodically charged in the presence of Et_4NCl as the supporting electrolyte.[8,9] Therefore, we investigated the electrochemical chlorination of the PT film on a bipolar electrode. Using the electrolytic cell setup shown in Figure 1, a PT film on ITO as the bipolar electrode was placed into an acetonitrile solution containing 0.005 M Et_4NCl. A constant current (1 mA) was passed between the platinum anode and cathode for 0.2 C. The bipolar electrode was then removed from the cell and treated by cathodic dedoping at −0.3 V (vs. SCE) to remove chloride anions attached as the dopant from the PT film.

Figure 3 illustrates the appearance of the partially chlorinated PT films and the chlorine content from EDX analysis after the passage of various amounts of charge (0.05, 0.1, and 0.2 C). Although the doped area on the film cannot be distinguished by its appearance, the EDX results provided clear evidence of the successful introduction of chlorine atoms into the film on the anodic surface, which reflects the potential gradient of the bipolar electrode. The chlorine atoms must be substituted covalently onto the 4-position of the repeating 3-methylthiophene unit, as we have reported previously.[8] The degree of chlorination at the anodic surface increased during the course of charge passed, in keeping with the composition gradient. The highest chlorination area was observed in the sample charged with 0.2 C, and represents approximately 80 % chlorine substitution per repeating thiophene unit (Figure 3 c). In addition, the chlorinated area exhibited a slightly yellow emission under UV irradiation, whereas the non-chlorinated area did not.

Chlorine substitution on poly(thiophene) derivatives often imparts a tolerance to oxidation, because it lowers the HOMO energy level. Therefore, the chlorine-gradient PT film has an intrinsic energy gradient across the film. Anodic doping of the chlorine-gradient film (0.1 C) was also performed in 0.1 M Bu_4NPF_6/acetonitrile (Figure 4). When the gradient film was charged at 0.8 V (vs. SCE), only the non-chlorinated area was doped and subsequently exhibited a blue color (Figure 4 b). The interface of the doped and undoped polymer was gradually shifted to a chlorine-rich area during the course of the applied potential. All of the polymer film was doped when charged at 1.4 V (vs. SCE), as indicated by Figure 4 e.

In summary, we have successfully demonstrated novel bipolar patterning by electrochemical doping and electrochemical chlorination across PT films. This method can afford conducting-polymer films with gradient functionality. Furthermore, this bipolar technique is powerful because it does not require attaching of the polymer to an electrical circuit. Hence, this methodology may prompt exploration of new polymer-based soft matter gradients. Efforts to expand the scope of this bipolar patterning methodology and to extend the work to other conducting polymers are currently under way.

Experimental Section

Electrochemical doping of PT film on a bipolar electrode: The PT film on an ITO electrode was placed in a U-type electrolytic cell equipped with a platinum anode ($10 \times 10\ mm^2$) and a platinum cathode ($10 \times 10\ mm^2$) connected to a Hokuto Denko HABF-501A apparatus as illustrated in Figure 1. The distance between the bipolar electrode and the platinum electrodes was kept constant (2.5 cm).

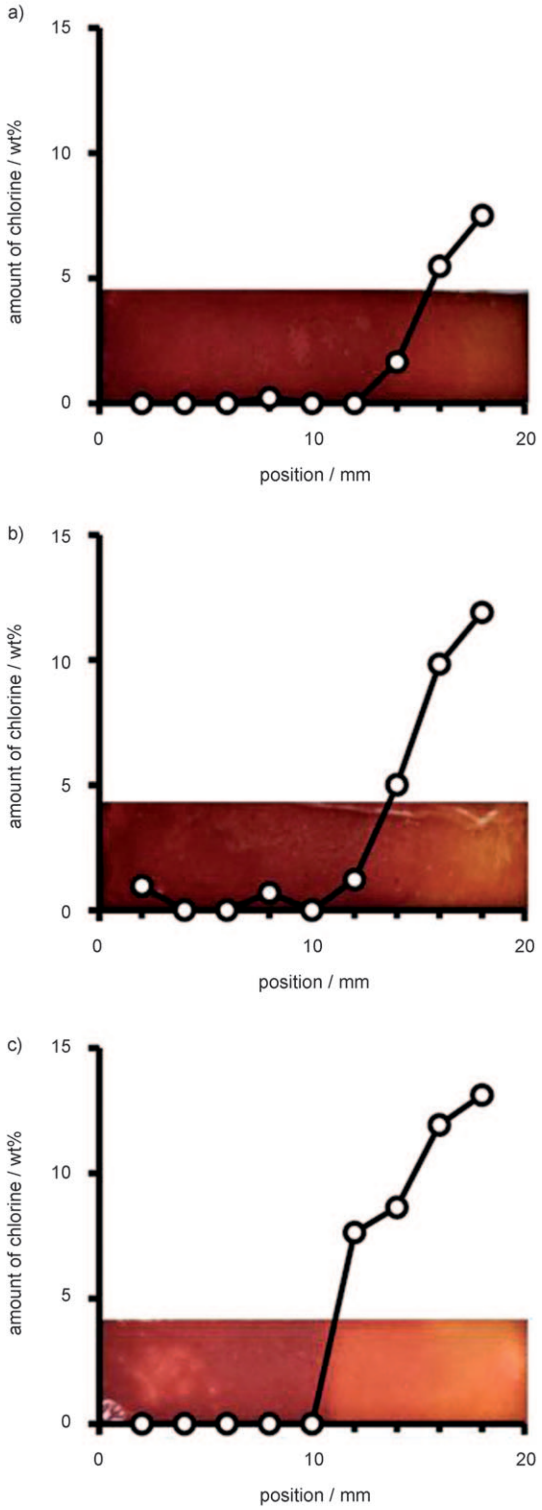

Figure 3. Photographs of the chlorinated film produced by bipolar patterning and the amount of chlorine introduced into the PT film at each distance from the cathodic side after charging with a) 0.05, b) 0.1, and c) 0.2 C in 0.005 M Et_4NCl/acetonitrile.

The electrochemical doping of the PT film was carried out by constant-current (1 mA) electrolysis in 0.005 M Bu_4NPF_6/acetonitrile. After the charge was passed, the film was washed with acetonitrile and dried in vacuo.

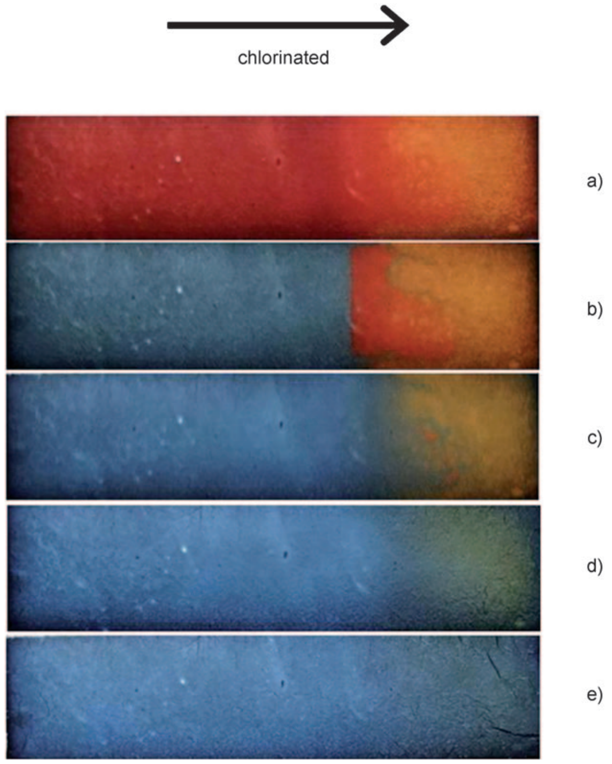

Figure 4. Photographs of the chlorinated PT film (0.1 C) a) before and b–e) after anodic doping at b) 0.8, c) 1.0, d) 1.2, and e) 1.4 V versus SCE in 0.1 M Bu_4NPF_6/acetonitrile.

Electrochemical chlorination of PT film on a bipolar electrode: The PT film on an ITO electrode was placed in a U-type electrolytic cell connected to a Hokuto Denko HABF-501A apparatus as above, and with the same electrode distance. The electrochemical chlorination of the PT film was carried out by constant-current (1 mA) electrolysis in 0.005 M Et_4NCl/acetonitrile. After the charge was passed, the film was washed with acetonitrile. The chlorinated PT film was then dedoped by potentiostatic electrolysis at −0.3 V for 30 min in 0.005 M Bu_4NPF_6/acetonitrile. The film was washed with acetonitrile and dried in vacuo.

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[11] The anodically doped PT film was stable and kept its charged state and the dopant, even when rinsed with acetonitrile under open-circuit conditions. The PT film could also be cathodically doped at the cathodic side on the bipolar electrode; however, no color change was observed during electrolysis. The main reaction at the cathodic side on the bipolar electrode is probably reduction of a trace of contaminating water.