Polymer Reactions

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Parallel Polymer Reactions of a Polyfluorene Derivative by Electrochemical Oxidation and Reduction**

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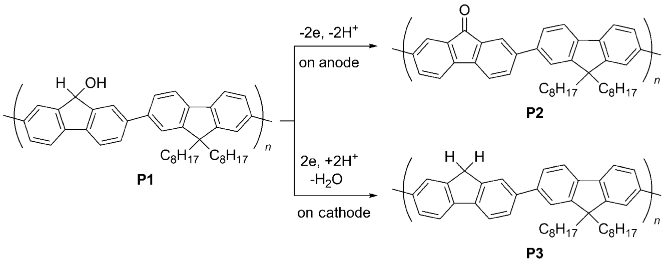
"Paired" electrochemical synthesis can be utilized for anodic oxidation and cathodic reduction of substrates simultaneously within a single circuit (one pot).[1] The physical isolation of both electrode surfaces (reaction sites) can offer multiple reaction fields for opposing oxidation and reduction reactions. Among them, the divergent mode, in which two different products, one from anodic oxidation and another from cathodic reduction, are obtained from one substrate molecule, is of importance with respect to high productivity and high current efficiency. Unfortunately, the products once obtained may be re-electrolyzed at a counter electrode to give a complex mixture.

In solid-phase reactions of conducting polymers on electrodes, first electrochemical doping of the polymers occurs, followed by a chemical reaction of the generated active species, as we reported previously.[2] As the entire reaction is completed on the electrode surface without diffusion of substrate or product, the product polymers can be easily separated from the electrolytic solution and purified by washing with solvents. The important challenge in this study is to achieve paired electrochemical polymer reactions on the anode and cathode simultaneously, in a single cell with high current efficiency. Thus, realizing a parallel polymer reaction that provides various functional polymers with the products completely isolated from each other.

As a model precursor polymer, we used an alternating copolymer of 9-fluorenol and 9,9-dioctylfluorene (**P1**), the electrochemical oxidation of which gives a 9-fluorenone moiety (**P2**), whereas electrochemical reduction results in a fluorene moiety (**P3**; Scheme 1). These fluorene-based polymers are expected to exhibit a variety of optical and electrochemical properties depending on the functional groups at the 9-position of the fluorene moiety.



Scheme 1. Anodic and cathodic reactions of **P1**.

First, the oxidation and reduction of **P1** were independently investigated to optimize the reaction conditions according to the conventional constant-current method of electrochemical polymer reactions (see the Supporting Information, Tables S1 and S2). The anodic oxidation of **P1** on a platinum anode (2×2 cm^2) with a bare Pt cathode (2×2 cm^2) in 0.1 M tetraethylammonium *p*-toluenesulfonate (Et_4NOTs)/isopropyl alcohol (*i*PrOH) afforded the corresponding **P2**, having a 9-fluorenone moiety, with a high reaction ratio, as determined by NMR and IR spectroscopy (see the Supporting Information, Figure S1).[3] The optimized method for the reduction of **P1** involved the use of a zinc cathode (2×2 cm^2), a bare Pt anode (2×2 cm^2), and the same electrolyte (0.1 M Et_4NOTs/*i*PrOH) as for the anodic oxidation. The use of Zn cathode could effectively suppress hydrogen evolution from the reduction of protons.[2c] Under the optimized conditions almost a quantitative reaction ratio of **P1** to **P3**, having a fluorene moiety, was obtained.

With the optimized conditions established, the parallel electrochemical reactions of **P1** on a Pt anode and a Zn cathode in 0.1 M Et_4NOTs/*i*PrOH were investigated. A passage of constant current between **P1**-coated electrodes for 16 F mol^{-1} of charge resulted in almost quantitative conversion of **P1** into **P2** and **P3** on the anode and cathode, respectively (Table 1). The electrons and protons released from **P1** by the anodic reaction were effectively used for the cathodic reaction of **P1**. The parallel reactions of **P1** were successful with the product polymers already isolated on separate electrodes and easily purified by washing with methanol. The total current efficiency of the parallel reactions was almost doubled compared to the current efficiency of the individual reactions, although it was still low owing to the characteristics of electrochemical polymer reactions.[2,4] When the theoretical charge (2 F mol^{-1}) was passed through the circuit, the total current efficiency was remarkably improved in the parallel-reaction system.

The electrochemical and optical properties of the precursor and product polymers were studied next. To estimate energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **P1**, **P2**, and **P3**, linear sweep voltammetry measurements were carried out on films of the polymers on a glassy carbon (GC) working electrode in 0.1 M tetraethylammonium tetrafluoroborate (Et_4NBF_4)/MeCN (see the

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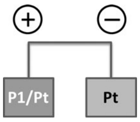
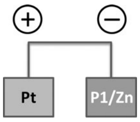
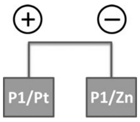
Table 1: Results of independent and parallel polymer reactions of **P1** on electrodes.

Method	Charge passed [F mol^{-1}]		Reaction ratio [%][a]		Current efficiency [%][b]		
	+[c]	−[c]	+[c]	−[c]	+[c]	−[c]	Total[d]
	2	–	50	–	50	–	50
	16	–	92	–	12	–	12
	–	2	–	59	–	59	59
	–	16	–	97	–	12	12
	2	2	45	62	45	62	107
	16	16	94	90	12	11	23

[a] Determined by ^{1}H NMR spectroscopy. [b] Calculated from reaction ratio. [c] +: anodic reaction, −: cathodic reaction. [d] Sum of current efficiency within the circuit.

Supporting Information, Figure S2). The onset potentials of oxidation ($E_{\mathrm{onset}}^{\mathrm{ox}}$) and reduction ($E_{\mathrm{onset}}^{\mathrm{red}}$) are shown in Table 2. The energy levels of the HOMO and LUMO, and thus the electrochemical band gaps, E_g^{el}, could be estimated according to empirical relationships,[5] and these are also listed in Table 2. These results indicated that the parallel polymer reactions provided a variety of poly(fluorene) derivatives with versatile physical properties.

Table 2: Redox onset potentials and energy levels of **P1**–**P3**.

Polymer	$E_{\mathrm{onset}}^{\mathrm{ox}}$ [V vs. SCE]	$E_{\mathrm{onset}}^{\mathrm{red}}$ [V vs. SCE]	HOMO [eV][a]	LUMO [eV][b]	E_g^{el} [eV][c]
P1	1.40	−2.17	−5.8	−2.2	3.6
P2	1.45	−1.67	−5.9	−2.7	3.2
P3	1.58	−2.18	−6.0	−2.2	3.8

[a] HOMO = $-(E_{\mathrm{onset}}^{\mathrm{ox}}+4.4)$. [b] LUMO = $-(E_{\mathrm{onset}}^{\mathrm{red}}+4.4)$. [c] $E_g^{\mathrm{el}} = -(\mathrm{LUMO}-\mathrm{HOMO})$.

Photoluminescence (PL) spectra of polymers in the solid state were different before and after the electrochemical reactions (Figure 1 a). There are bimodal peaks (460 nm and 550 nm) in the spectrum of **P1**, which exhibited light blue-green emission (Figure 1 b). The product from oxidation of **P1**, that is, **P2** exhibited very little emission with a broad emission peak at 550 nm. This low emission of the polymer having the 9-fluoreneone moiety has been discussed previously.[6] In the case of **P3**, obtained by electrochemical reduction of **P1**, the relative intensity of the emission band at 550 nm to that at 460 nm was changed remarkably, relative to the spectrum of **P1**, to afford a bright yellow emission. Previously, we determined that this yellow emission of **P3** in the solid state originated from the interdigitated packing of the conjugated main chain and alkyl substituents at the 9-position of the fluorene moiety.[7] Interestingly, the color of the emissions of the **P2** and **P3** films were drastically different to that of **P1** (Figure 1 b).

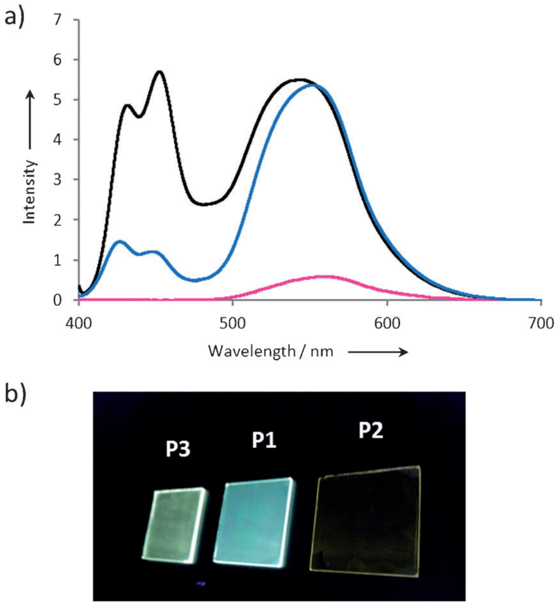


Figure 1. a) Photoluminescence spectra of films of **P1** (black), **P2** (red), and **P3** (blue), excited at their absorption maxima. b) Photographs of spin-coated films of **P1**, **P2**, and **P3** on glass plates under UV irradiation ($\lambda = 365$ nm).

The use of bipolar electrochemistry, involving a wireless electrode driven by an external electric field from feeder electrodes, for these parallel reactions is attractive because electrochemical oxidation and reduction takes place simultaneously on the same surface of the bipolar electrode with a potential slope between both poles.[8] A multicolored gradient film is expected on application of a potential slope to a **P1**-coated bipolar electrode to perform the bipolar polymer reaction we developed,[9] because of the drastically different color of the emissions of the resulting polymers, **P2** and **P3**. However, to achieve this, both anodic and cathodic reactions must be performed on the same electrode material. Boron-doped diamond (BDD) is known to have a wide potential window and thus is useful for electrosynthesis.[10] Indeed, the potential window of BDD in Et_4NOTs/*i*PrOH seemed to be suitable for both the anodic and cathodic reactions of **P1** (see the Supporting Information, Figure S3). We carried out the electrochemical polymer reaction of **P1** on a BDD anode and cathode (1×1 cm^2) independently under the optimized conditions as described previously, and the products were obtained in a sufficient reaction ratio (**P2**: 81 %, **P3**: 80 %; see the Supporting Information, Scheme S1).

Next, a BDD plate (3×3 cm^2) covered with **P1** was placed between driving stainless electrodes (1×4 cm^2) in the setup shown in Figure 2 a and a constant current (0.1 mA cm^{-2}) was passed between them in 5 mM Et_4NOTs/*i*PrOH. After the electrolysis, under UV irradiation the emission of the polymer film was a graduation from yellow→blue→dark orange from the cathodic pole to the anodic pole (Figure 2 b). The gradient polymer film was peeled off from the BDD plate with adhesive tape, and divided into three pieces (**P1**, **P2**, and **P3**) for PL measurements. As shown in Figure S4 (see the Supporting Inofrmation), each PL spectrum corresponded

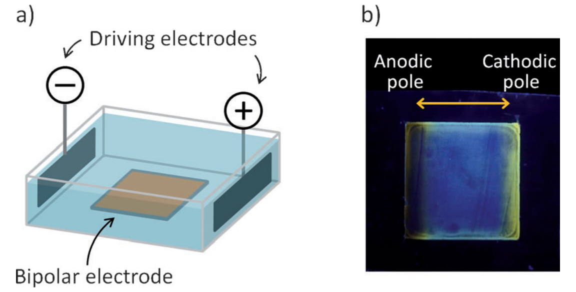


Figure 2. a) Schematic illustration of the setup used for bipolar electrolysis. b) Photograph of the conducting polymer film (after being peeled off from the electrode with adhesive tape) under UV irradiation ($\lambda = 365$ nm) with a gradient composition.

well to those shown in Figure 1. Previous reports on the use of bipolar electrolysis for producing gradient materials focused only on an anodic reaction with a sacrificial cathodic reaction or vice versa.[9] This parallel bipolar electrolysis successfully provided a new of composition-gradient film.

According to the principle of bipolar electrochemistry, an array consisting of two or more bipolar electrodes can be driven to offer multiple reaction sites at the same time. Finally, parallel bipolar electrolysis was carried out with the configuration as shown in Figure 3 a, in which two BDD plates (1×5 cm^2) partially covered with a film of **P1** on one edge were placed parallel in the bipolar cell. After a passage of constant current (0.5 mA cm^{-2}, cell voltage: 22 V),[11] **P1** on the anodic surface of one bipolar electrode was effectively transformed to **P2** accompanied by the formation of **P3** on the cathodic surface of the other bipolar electrode (Figure 3 b). Thus, revealing that multiple bipolar electrodes worked as reaction sites for conducting polymers.

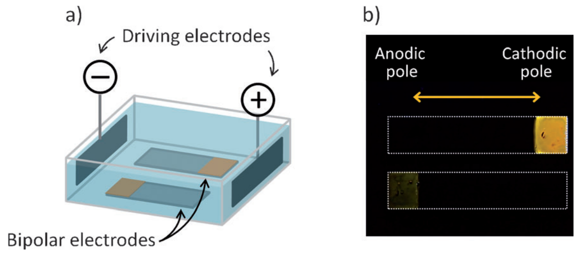


Figure 3. a) Schematic illustration of the setup used for the parallel reaction using bipolar electrodes. Orange: polymer film. b) Photograph of the conducting polymer films on BDD plates (indicated with dotted lines; upper: after cathodic reduction; lower: after anodic oxidation) under UV irradiation ($\lambda = 365$ nm).

In conclusion, we have demonstrated electrochemical polymer reactions of a single parent polymer **P1** to provide **P2** by anodic oxidation and **P3** by cathodic reduction. Parallel reactions in the same cell were successfully carried out with high current efficiency and without interference between the reactions. This parallel polymer reaction composed of oxidation and reduction simultaneously in one pot is unlike conventional polymer reactions. The integration of reaction sites at the electrode surfaces, which are physically separated from one another, enabled these parallel polymer reactions. The optical properties, in particular the photoluminescence of the polymers, were totally different in the solid state. Parallel reactions of **P1** on a BDD bipolar electrode gave a multi-colored gradient film. Furthermore, the bipolar electrodes provided a flexible platform for manipulating multiple electrochemical reactions for conducting polymers.

Experimental Section

Parallel electrochemical reactions of **P1**: A chloroform solution of **P1** was cast on a Pt plate electrode (2×2 cm^2) and on a Zn plate (2×2 cm^2), and dried under reduced pressure. An electrolytic solution of 0.1 M Et$_4$NOTs/isopropyl alcohol (10 mL) was added to an undivided cell, and deaerated by bubbling argon through it. A constant current (10 mA cm^{-2}) was passed for 16 F mol^{-1}, after which the polymer films (**P2** and **P3**) were purified separately by washing with methanol. Then the product polymers were redissolved in chloroform (or [D]chloroform) and analyzed by spectroscopy.

Gradient polymer reaction of **P1** on bipolar electrode: A **P1** film on boron-doped diamond (BDD) plate (3×3 cm^2) was placed in between driving electrodes (stainless steel, 1×4 cm^2) in an undivided cell containing 5 mM Et$_4$NOTs/isopropyl alcohol (15 mL) as shown in Figure 2 a. A constant current (0.1 mA cm^{-2}) was passed for 0.078 C to give a gradient polymer film.

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[3] The reaction ratios for **P2** and **P3** were estimated from ^{1}H NMR spectra by comparing the intensities of the signals corresponding to the benzyl proton in the fluorene moiety and the α-methylene protons of the octyl groups.

[4] The electrochemical reactions of a conducting polymer proceed efficiently at early stage but require a lot of electricity to go to completion. This is because there is less starting material (sites on the polymer for the reaction) and because of the change of the potential of the polymer during electrolysis.

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[11] A passage of 0.1 mA cm^{-2} (cell voltage: 7.3 V) was not for the electrolytic reaction on the bipolar electrodes.