Macromolecules
COMMUNICATION TO THE EDITOR

Macromolecules **2009**, *42*, 3881–3883 **3881**
DOI: 10.1021/ma900561f

Facile Functionalization of a Thiophene−Fluorene Alternating Copolymer via Electrochemical Polymer Reaction

Shinsuke Inagi, Shotaro Hayashi, Kenta Hosaka, and Toshio Fuchigami*

Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

Received March 16, 2009
Revised Manuscript Received April 27, 2009

In recent years, functional conjugated polymers have been in demand in various fields of materials science, including that of optoelectronic devices. Postfunctionalization of conjugated polymers is a relatively easy but powerful method for designing and constructing highly tuned polymers with desirable properties.[1−4] Successive halogenations of poly(3-alkylthiophene)s at the 4-position using the postfunctionalization method[2,4] and subsequent further substitution of aryl groups[3] have been reported previously, although electrophilic substitution prompted by *N*-chlorosuccinimide (NCS) resulted in an undesirable side reaction.[2] Although electrochemical substitution is a selective and environmentally benign system, characterization of the product has been somewhat indeterminate thus far.[4] We recently developed an electrochemical polymer reaction consisting of the following steps: (i) synthesis of a soluble poly(fluorene) derivative containing an electroactive moiety; (ii) constant current electrolysis of the polymer cast-coated on an electrode; (iii) confirmation of the reaction and characterization of products. This novel approach allowed us to monitor the reactions and characterize the products in detail.[5]

Thiophene−fluorene copolymers have potential as materials for optoelectronic devices[6] because poly(fluorene) shows efficient fluorescence[7] while poly(thiophene) has tunable electronic properties and is highly stable.[8] Therefore, there have been several attempts to tune the optical properties of thiophene−fluorene alternating copolymers by introducing functional groups at the 3-position of the thiophene unit.[9] However, there have been no previous reports of postfunctionalization of thiophene−fluorene copolymers. In this Communication, we report a detailed study of anodic halogenation of a thiophene−fluorene alternating copolymer and the optoelectronic properties of the resulting polymer.

The initial reaction was Suzuki−Miyaura coupling polymerization of 9,9-dioctylfluorene-2,7-diboronic acid ester with 2,5-dibromothiophene (Scheme 1). The crude polymer was purified by reprecipitation into methanol to remove low molecular weight oligomers. The purified alternating copolymer **PTF1** was soluble in common organic solvents such as $CHCl_3$ and showed good film-forming properties. Gel permeation chromatography (GPC) analysis of polymer **PTF1** gave a unimodal profile (M_n = 8700, M_w = 18 100, M_w/M_n = 2.1, where M_n and M_w are the number- and weight-average molecular weight, respectively).

A 2 cm × 2 cm platinum plate cast-coated with **PTF1** was used as the anode for an electrolytic system with a bare 2 cm × 2 cm platinum cathode in acetonitrile containing tetraethylammonium chloride as a supporting electrolyte and chlorine source. The film thickness was estimated as ca. 30−40 μm using a laser focus displacement meter. Constant current electrolysis (10 mA/cm^2) was conducted at room temperature (Scheme 2) to give the product **PTF2**. The polymer film was purified by washing with acetonitrile and dried in vacuo; the product was then redissolved in a good solvent for spectroscopic analysis. ^{1}H NMR spectroscopy showed that the characteristic signal of the protons on the thiophene ring in **PTF1** decreased during electrolysis, while other peaks remained constant (Figure 1). The chlorination ratio (i.e., the ratio of the number of substituted chlorines per repeating thiophene unit) was thus estimated by comparing the signal intensities of the protons on the thiophene ring and the methylene protons of the octyl groups.

Figure 2a shows the chlorination ratio (in other words, the amount of deprotonation of the thiophene ring) versus the amount of charge passed. The number of protons eliminated increased with the charge passed, which indicated that the reaction ratio could be electrically controlled. After a charge of 30 F/mol had been passed, the NMR-based chlorination ratio reached 1.74. Energy dispersive X-ray (EDX) analysis of the polymer provided further information on the level of chlorine substitution (Figure 2b). The measured Cl/S ratio (1.70) indicated that 1.70 chlorine atoms were introduced per thiophene unit, which is in good agreement with the value estimated by ^{1}H NMR. GPC data on **PTF2** (M_n = 9000, M_w = 20 400, M_w/M_n = 2.3) suggested that neither decomposition nor propagation of the polymer occurred even after the passage of excess charge. The foregoing analysis indicated that electrochemical chlorination of the **PTF1** film proceeded efficiently and selectively at the thiophene ring not only at the surface but also within the mass of the polymer.

Next, other electrochemical halogenation reactions of **PTF1** were carried out by constant current electrolysis (Table 1). In contrast to chlorination (entry 1), the level of bromination became saturated around 1.1, as shown by NMR and EDX analysis (entry 2). Anodic iodination did not proceed even after the passage of 70 F/mol (entry 3). These results can be explained by the sequence of nucleophilicity of the halide anions. Anodic fluorination using the neat ionic liquid hydrogen fluoride salt $Et_4NF \cdot 4HF$ did not afford any fluorinated products because the nucleophilicity of the fluoride ion in HF salts is relatively low (entry 4).[10]

A voltammetric study of **PTF1** in Et_4NClO_4/acetonitrile showed oxidation peaks at 1.2 and 1.7 V vs SCE. During anodic halogenation, oxidation of the polymer may compete with oxidation of the halide ions during macro-electrolysis. We demonstrated potentiostatic electrolysis (2.0 V vs SCE, 70 F/mol) of the Et_4NBr/acetonitrile solution using a bare Pt anode and Pt cathode and dipping the polymer film. At that voltage, bromide is oxidized to generate molecular bromine or cationic species in the cell; however, only a trace of bromination (deprotonation) of the polymer was detected. Therefore, anodic halogenation proceeds via oxidation of the polymer film, followed by nucleophilic attack by the halide ion.

Figure 3a shows the UV−vis absorption spectra of **PTF1** and **PTF2** in $CHCl_3$. The absorption maximum was blue-shifted after chlorination. This is thought to be because the introduction of chlorine atoms at the 3- and 4-positions of the thiophene ring in the polymer caused steric repulsion[3a] between adjacent thiophene

---

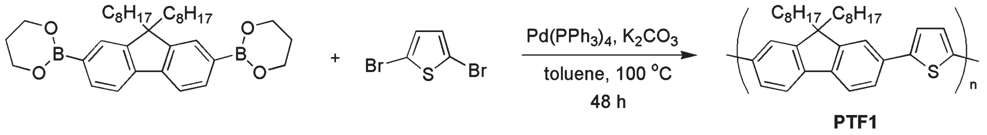
*Corresponding author: Tel +81-45-924-5406, Fax +81-45-924-5406, e-mail fuchi@echem.titech.ac.jp.

and fluorene, which resulted in shortening of the effective conjugation length. Density functional theory (DFT) calculations[11] of **PTF1** and **PTF2** models supported the idea of distortion of the polymer main chain after dichlorination (see Supporting Information, Figure S1). The calculated dihedral angles between the thiophene and fluorene moieties were 20° in **PTF1** and 45° in **PTF2**.

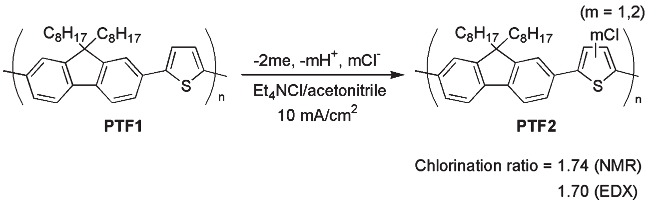
PTF2 showed a blue emission in dilute $CHCl_3$ solution, with a maximum at 467 nm, while **PTF1** showed a green emission (Figure 3b). The quantum yields of fluorescence for the polymers (10^{-6}M) were determined by excitation of the polymers at $\lambda_{max,abs}$ and comparison with the emission of quinine sulfate dehydrate/0.1 M sulfuric acid solution ($\Phi_{fl} = 0.55$) as a standard. The estimated quantum yield of fluorescence of **PTF2** was relatively high (0.73) compared to that of **PTF1** (0.78) despite the introduction of heavy chlorine atoms.

When we employed a transparent indium tin oxide (ITO) electrode instead of platinum for the electrochemical chlorination

Scheme 1. Preparation of PTF1 by Suzuki−Miyaura Coupling Polymerization



Scheme 2. Anodic Chlorination of PTF1 by Constant Current Electrolysis



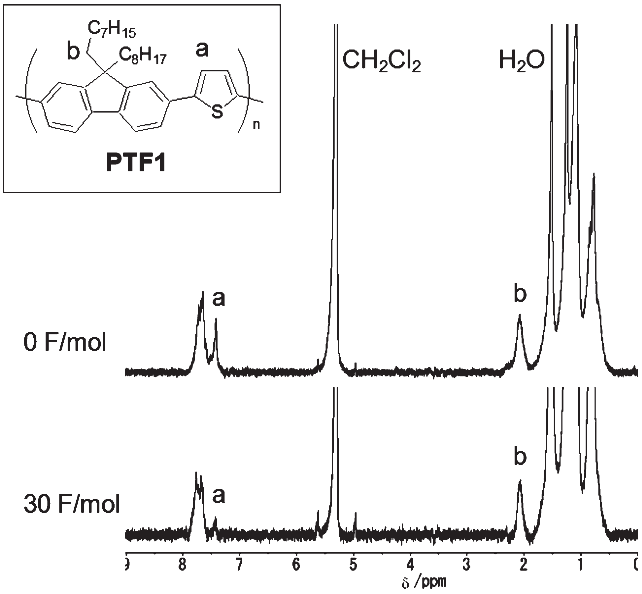
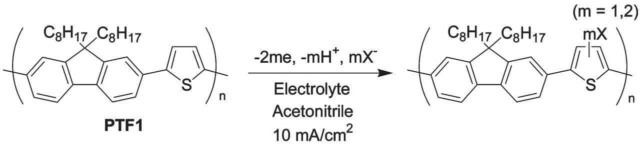


Figure 1. ^{1}H NMR spectra of **PTF1** in CD_2Cl_2 after passage of 0 and 30 F/mol charge.

Table 1. Anodic Halogenations of PTF1 by Constant Current Electrolysis (10 mA/cm^2)



entry	electrolyte	X$^-$	charge (F/mol)	halogenation ratio[a]
1	Et_4NCl	Cl^-	30	1.74 (1.70)[b]
2	Et_4NBr	Br^-	70	1.08 (1.12)[b]
3	Et_4NI	I^-	70	trace
4	$Et_4NF{\cdot}4HF$ (neat)	F^-	30	−

[a] Estimated by ^{1}H NMR. [b] Determined by EDX.

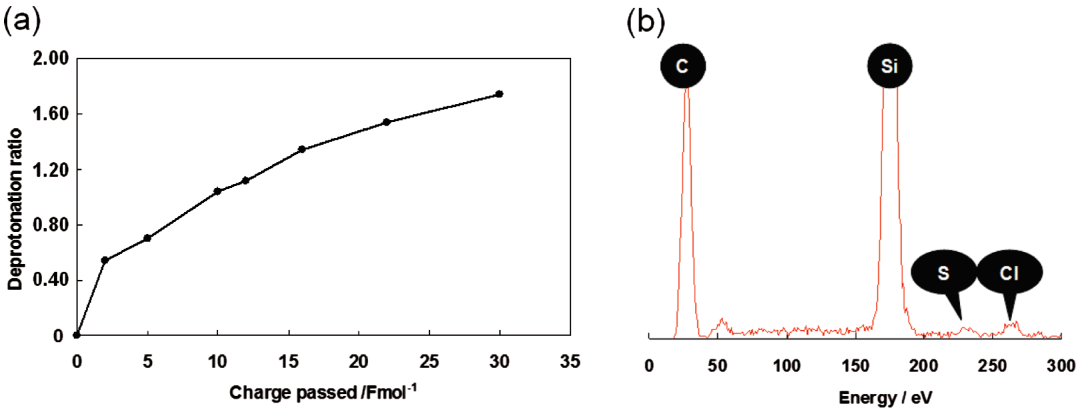


Figure 2. (a) Deprotonation ratio of **PTF1** estimated by ^{1}H NMR. (b) EDX profile of **PTF2** (30 F/mol) with a Si wafer-supported thin film.

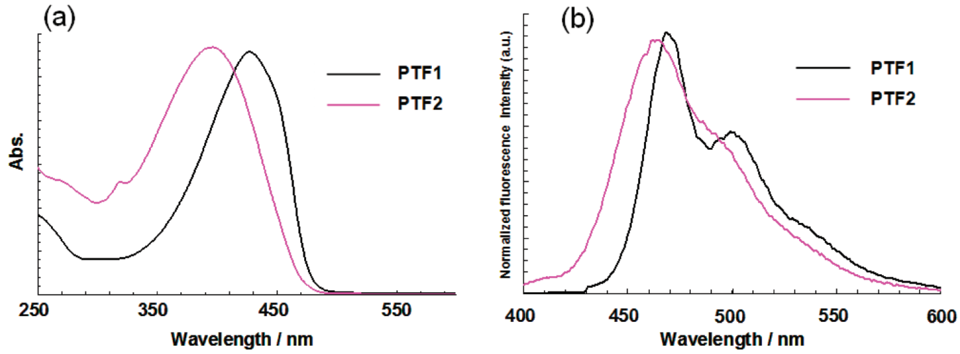


Figure 3. (a) UV−vis absorption and (b) PL spectra of **PTF1** and **PTF2** in chloroform.

of **PTF1**, the reaction also proceeded to a reasonable extent. It is interesting to note that the optoelectronic properties of the resulting polymer film on ITO glass may be directly measured after electrolysis. In fact, the plot of $\lambda_{\mathrm{abs,max}}$ versus charge passed for the film on ITO was almost identical to that of the film after electrolysis on a platinum anode.

In conclusion, we demonstrated the electrochemical halogenation of a thiophene−fluorene alternating copolymer in the presence of tetraethylammonium halide as a supporting electrolyte and halogen source. In the case of the chlorination reaction, a high level of chlorination at the 3- and 4- positions of the thiophene unit was achieved without undesirable side reactions. The simple process of drop-coating of polymers on an ITO electrode followed by electrolytic functionalization is expected to be suitable for fabrication processes for large organic devices. Further investigations and electrochemical analysis, with the aim of clarifying of the reaction mechanism, are now underway.

Acknowledgment. We thank Prof. Mahito Atobe at Tokyo Institute of Technology for EDX analysis and also thank Prof. Ikuyoshi Tomita at Tokyo Institute of Technology for photoluminescence measurement. This study was financially supported by a Grant-in-Aid for Young Scientists (Start-up) (No. 20850015).

Supporting Information Available: Experimental section, figures giving the optimized structures of the model compounds for **PTF1** and **PTF2**, and EDX profiles of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Besbes, M.; Trippé, G.; Levillain, E.; Mazari, M.; Le Derf, F.; Perepichka, I. F.; Gorgues, A.; Sallé, M.; Roncali, J. *Adv. Mater.* **2001**, *13*, 1249–1252. (b) Zhai, L.; McCullough, R. D. *Adv. Mater.* **2002**, *14*, 901–905. (c) Buga, K.; Pokrop, R.; Majkowska, A.; Zagorska, M.; Planes, J.; Genoud, F.; Pron, A. *J. Mater. Chem.* **2006**, *16*, 2150–2164. (d) Bu, H.-B.; Gotz, G.; Reinold, E.; Vogt, A.; Schmid, S.; Blanco, R.; Segura, J. L.; Bauerle, P. *Chem. Commun.* **2008**, 1320–1322. (e) Li, H.; Sundararaman, A.; Venkatasubbaiah, K.; Jakle, F. *J. Am. Chem. Soc.* **2007**, *129*, 5792–5793.

(2) (a) Li, Y.; Vamvounis, G.; Holdcroft, S. *Macromolecules* **2001**, *34*, 141–143. (b) Li, Y.; Vamvounis, G.; Yu, J.; Holdcroft, S. *Macromolecules* **2001**, *34*, 3130–3132.

(3) (a) Li, Y.; Vamvounis, G.; Holdcroft, S. *Macromolecules* **2002**, *35*, 6900–6906. (b) Economopoulos, S. P.; Chochos, C. L.; Gregoriou, V. G.; Kallitsis, J. K.; Barrau, S.; Hadziioannou, G. *Macromolecules* **2007**, *40*, 921–927.

(4) (a) Qi, Z.; Rees, N. G.; Pickup, P. G. *Chem. Mater.* **1996**, *8*, 701–707. (b) Soudan, P.; Lucas, P.; Breau, L.; Bélanger, D. *Langmuir* **2000**, *16*, 4362–4366. (c) Fabre, B.; Kanoufi, F.; Simonet, J. *J. Electroanal. Chem.* **1997**, *434*, 225–234.

(5) (a) Inagi, S.; Hayashi, S.; Fuchigami, T. *Chem. Commun.* **2009**, 1718–1720.(b) Hayashi, S.; Inagi, S.; Fuchigami, T. *Macromolecules*, in press .

(6) (a) Tsuie, B.; Reddinger, J. L.; Sotzing, G. A.; Soloducho, J.; Katritzky, A. R.; Reynolds, J. R. *J. Mater. Chem.* **1999**, *9* 2189–2200. (b) Lim, E.; Jung, B.-J.; Shim, H.-K. *Macromolecules* **2003**, *36*, 4288–4293. (c) Liu, X.-M.; Lin, T.; Huang, J.; Hao, X.-T.; Ong, K. S.; He, C. *Macromolecules* **2005**, *38* 4157–4168. (d) Pei, J.; Yu, W.-L.; Ni, J.; Lai, Y.-H.; Huang, W.; Heeger, A. J. *Macromolecules* **2001**, *34*, 7241–7248. (e) Pei, J.; Yu, W.-L.; Huang, W.; Heeger, A. J. *Chem. Commun.* **2000**, 1631–1632.

(7) (a) Le Deit, H.; Rault-Berthelot, J.; Simonet, J. *Synth. Met.* **1992**, *47*, 373–376. (b) Grice, A. W.; Bradley, D. D. C.; Bernius, M. T.; Indasekaran, M.; Wu, W. W.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 629–631. (c) Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007–2009. (d) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453–2455.

(8) Roncali, J. *Chem. Rev.* **1992**, *92*, 711–738.

(9) Pal, B.; Yen, W.-C.; Yang, J.-S.; Su, W.-F. *Macromolecules* **2007**, *40*, 8189–8194.

(10) (a) Inagi, S.; Sawamura, T.; Fuchigami, T. *Electrochem. Commun.* **2008**, *10*, 1158–1160. (b) Sawamura, T.; Inagi, S.; Fuchigami, T. *J. Electrochem. Soc.* **2009**, *156*, E26–E28.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin,K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y. ; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision E.01*; Gaussian, Inc.: Wallingford, CT, **2004**.