



Photo-induced oxidation of polythiophene derivatives: Dependence on side chain structure

Yoshinori Aoyama^a, Toshihiro Yamanari^b, Nagatoshi Koumura^b, Hiroto Tachikawa^c, Masaru Nagai^d, Yuji Yoshida^{a,b,*}

^a Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsutayto, Midori-ku, Yokohama 226-8503, Japan

^b Research Center for Photovoltaic Technologies, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

^c Division of Materials Chemistry, Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060-8628, Hokkaido, Japan

^d Fuji Electric Advanced technology Co., Ltd, 1 Fujimatchi, Hino-city, Tokyo 191-8502, Japan

ARTICLE INFO

Article history:

Received 29 November 2012

Received in revised form

29 December 2012

Accepted 16 January 2013

Available online 31 January 2013

Keywords:

Photooxidation

Poly(3-hexylthiophene)

Side chain

Polymer solar cells

Fourier transform infrared spectroscopy

ABSTRACT

The photooxidation of poly(3-hexylthiophene) (P3HT) has previously been investigated and it is known that the sulfur atom of the thiophene ring is oxidized into sulfur oxides by a hydroxyl radical that arises through hydrogen abstraction at the hexyl side chain at the α -position. In this study, in order to further investigate the photooxidation mechanism of the polymer, the side chain at α -position was varied and three different polythiophene derivatives with phenyl (P3PhT), *tert*-pentyl (P3DMPT), and alkoxy (P3OOT) groups were synthesized with no α -hydrogens. We observed the differences in the photochemical behavior of the polythiophene derivatives by UV–vis–NIR and FT-IR (ATR) spectroscopy during simulated solar light irradiation. It was found that the photooxidation of P3PhT and P3DMPT progressed in the same way as P3HT, whereas the analogous decomposition of P3OOT was not observed.

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1. Introduction

Polymer solar cells (PSCs) have many potential advantages in their mechanical flexibility, portability, and low manufacturing cost. Among the conducting polymers used, poly(3-hexylthiophene) (P3HT) is one of the most commonly employed materials for the photo-active layer because of its high conductivity [1,2]. According to recent studies on PSCs utilizing P3HT, the power conversion efficiency has been drastically improved [3–10] and large-scale production can be expected imminently [11]. On the other hand, it is well known that a PSC based on P3HT degrades with long-term solar light irradiation. Jørgensen et al. recently proposed that photooxidation of the polymer was related to the mechanism of degradation of PSCs [12].

The photooxidation of P3HT has been investigated [13–19]. Hintz et al. reported that the photooxidation of P3HT was initiated by the oxidation of the hexyl side chains [18]. In addition, Manceau et al. reported that the sulfur atom of the thiophene ring was oxidized into sulfur oxide by hydroxyl radicals, which arose through hydrogen

abstraction from the hexyl side chain at the α -position [19]. The photooxidation of poly(3-butylthiophene) and poly(3-octylthiophene) has also been investigated [20–22]. On the other hand, Rivaton et al. reported that polythiophene (PT) had substantial stability, even after long-term light irradiation [16]. In addition, poly(3-carboxydithiophene) (P3CT), which has a carboxyl side chain, was shown to have good stability under light illumination [23,24]. Thus, it is hypothesized that the photooxidation of polythiophene derivatives is dependent on the structures of their side chains.

In this paper, in order to investigate the photooxidation of polyalkylthiophene derivatives, the side chain at the α -position was varied and three different polythiophene derivatives with no α -hydrogen were synthesized (phenyl, alkoxy, and *tert*-pentyl). The differences in photochemical behavior of the derivatives and the previously studied P3HT were investigated by UV–vis–NIR and FT-IR (ATR) spectroscopy during simulated solar light irradiation.

2. Experimental details

2.1. Synthesis of polythiophene derivatives

Three polythiophene derivatives with different side chains were prepared: $-\text{C}_6\text{H}_5$ poly(3-phenyl)thiophene (P3PhT), $-\text{C}(\text{CH}_3)_2\text{C}_2\text{H}_5$

* Corresponding author. Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsutayto, Midori-ku, Yokohama 226-8503, Japan. Tel.: +81 29 861 9423; fax: +81 29 861 6232.

E-mail address: yuji.yoshida@aist.go.jp (Y. Yoshida).

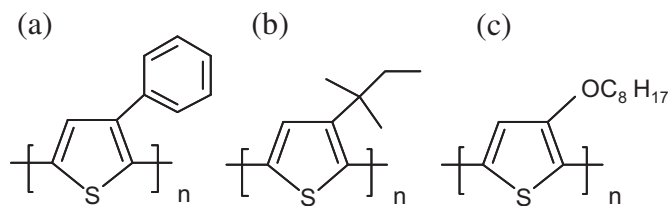


Fig. 1. The chemical structures of (a) poly(3-phenyl)thiophene (P3PhT) (b) poly(3-(1,1-dimethylpropyl)thiophene) (P3DMPT), and (c) poly(3-octyloxy)thiophene (P3OOT).

poly(3-(1,1-dimethylpropyl) thiophene) (P3DMPT), and $-\text{OC}_8\text{H}_{17}$ poly(3-octyloxy)thiophene (P3OOT), as shown in Fig. 1. The P3PhT was prepared by polymerization using the Grignard metathesis method [25]. 3-Phenylthiophene was dibrominated with *N*-bromosuccinimide (NBS) in tetrahydrofuran (THF) to afford 2,5-dibromo-3-phenylthiophene. This was then polymerized using a Kumada coupling reaction catalyzed by $\text{NiCl}_2(\text{dppp})$ [dppp = 1,3-bis(diphenyl phosphino)propane]. A bright red powder was obtained with ca. 20% yield, which was soluble in organic solvents such as chloroform and THF. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.10 ppm (s, 1H), δ 7.36 ppm (t, 1H), δ 7.43 ppm (t, 2H), δ 7.49 ppm (d, 2H). Regio-regularity > 95%. GPC (Waters Co., LTD.): $M_w = 1.59$ kg/mol, $M_w/M_n = 1.39$.

The P3DMPT was prepared by polymerization using the Grignard metathesis method [26]. 2,5-Dibromo-3-(1,1-dimethylpropyl)thiophene was synthesized from 2,5-dibromothiophene and 2-chloro-2-methylbutane by a Friedel–Crafts reaction using AlCl_3 as a catalyst. The final product was synthesized from 2,5-dibromo-3-(1,1-

dimethylpropyl)thiophene by the same reaction as was used for P3PhT. A red brown powder was obtained with ca. 10% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 1.00 ppm (t, 3H), δ 1.35 ppm (q, 2H), δ 1.60 ppm (s, 6H), δ 6.80 ppm (s, 1H). Regio-regularity > 95%. GPC: $M_w = 11.4$ kg/mol, $M_w/M_n = 2.30$.

P3OOT was prepared by polymerization using the Grignard metathesis method [27]. 3-Octyloxythiophene was synthesized from 3-methoxythiophene and octanol with NaHSO_4 as a catalyst. 3-Octyloxythiophene was dibrominated and the final product was synthesized from 2,5-dibromo-3-octyloxythiophene by the same reaction as was used for P3PhT. A bright blue powder was obtained with ca. 20% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.95 ppm (t, 3H), δ 1.40 ppm (broad, 10H), δ 1.80 ppm (q, 2H), δ 4.00 ppm (t, 2H), δ 6.80 ppm (s, 1H). Regio-regularity > 95%. GPC: $M_w = 12.0$ kg/mol, $M_w/M_n = 1.72$.

2.2. Sample preparation and measurement

P3HT ($M_w = 18.0$ kg/mol, $M_w/M_n = 1.60$, Regio-regularity > 95%), which has similar molecular weight, polydispersity, and regio-regularity, was purchased from Merck. We exclude the effect of the regio-regularity with four polymers [28]. Polymer films were fabricated by spin-coating onto CaF_2 substrates. All the thicknesses of polymer films were 120 nm, which were measured by stylus method film thickness meter (ULVAC E. S., Inc.). The effect of the thickness difference with four polymers was excluded [28–30]. These films were irradiated with simulated solar light (AM 1.5 G) of 100 mW/cm^2 intensity for up to 100 h in ambient air. The irradiation intensity was calibrated using a standard cell for a-Si solar cells (Bunkoukeiki Co., LTD.). UV–vis–NIR (Shimadzu Co., LTD.)

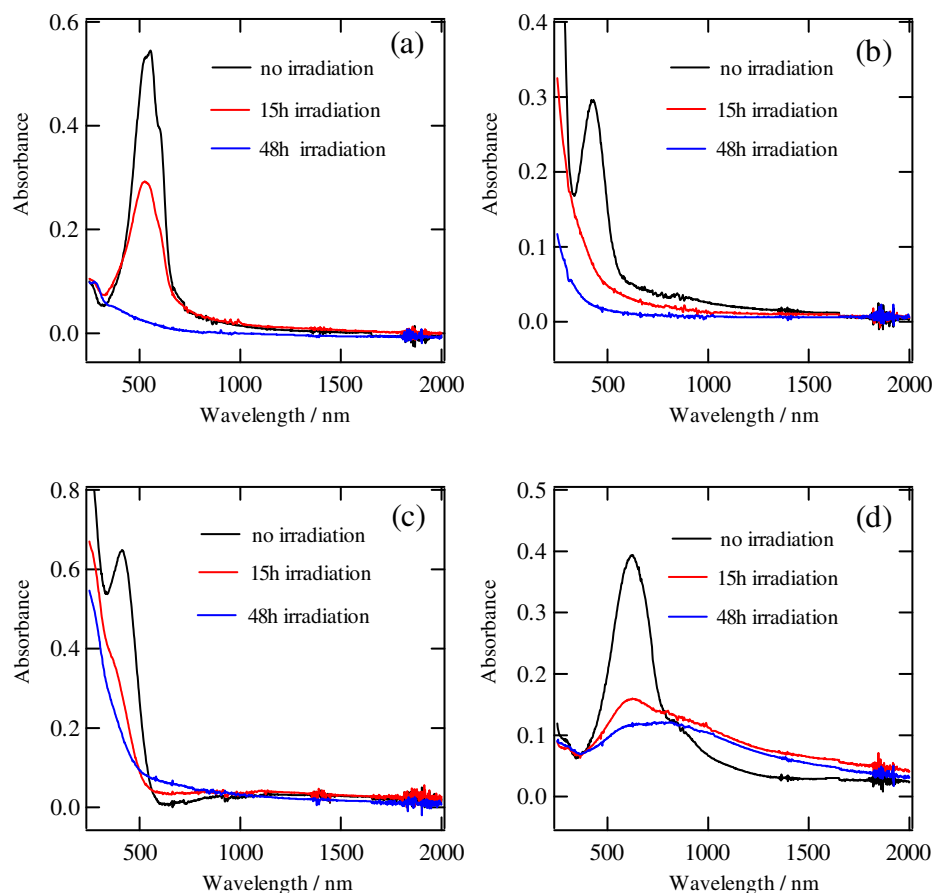


Fig. 2. UV–vis–NIR spectra of (a) P3HT, (b) P3PhT, (c) P3DMPT, and (d) P3OOT films after (—) no-irradiation, (—) 15 h irradiation, and (—) 48 h irradiation. Polymer films were irradiated with simulated solar light (AM 1.5 G) of 100 mW/cm^2 intensity.

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