ORIGINAL ARTICLE

Initial photooxidation mechanism leading to reactive radical formation of polythiophene derivatives

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We investigated the initial photooxidation mechanism leading to reactive radical formation of polythiophene derivatives by focusing on the differences in the photochemical behaviors of photounstable poly(3-hexylthiophene) (P3HT) and photostable poly(3-octyloxythiophene) (P3OOT). Electron spin resonance measurements revealed that the [P3HT]$^{+\bullet}$ (formed by oxygen doping) decayed, whereas no change was observed in the photostable [P3OOT]$^{+\bullet}$ after light irradiation. Furthermore, the absorption decrease of the [P3HT]$^{+\bullet}$ (P3HT) was suppressed by superoxide dismutase. Therefore, the oxygen dopant is superoxide, which might also initiate the oxidation of P3HT. The photochemical difference between P3HT and P3OOT can be explained by the reaction of an α-proton with superoxide in the case of P3HT.
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INTRODUCTION

Polymer solar cells (PSCs) have potential advantages in various applications because of their mechanical flexibility, portability, colorful and low fabrication cost. Poly(3-hexylthiophene) (P3HT) is one of the most widely employed p-type materials for the photoactive layer of PSCs.[1–4] Furthermore, it is also known that the use of P3HT degrades PSCs on long-term irradiation of solar light.[5–11] Jørgensen et al.[11,12] recently proposed that the degradation mechanism of PSCs was related to the photooxidation of P3HT. Therefore, the lifetime of PSCs can be increased by preventing the photooxidation of P3HT.

The mechanism for the photooxidation of P3HT has been reported to involve singlet oxygen ($^1O_2$), which directly undergoes a Diels–Alder cycloaddition with the thienyl unit of P3HT.[10,13,14] However, this putative mechanism has come under recent review; for example, Hintz et al.[15] recently reported that the photooxidation of P3HT is initiated by the oxidation of the hexyl side chains. In addition, Manceau et al.[16] also reported that the sulfur atom of the thiophene ring can become oxidized to sulfur oxide by hydroxyl radicals, through hydrogen abstraction from the hexyl side chain at the α-position. These findings imply that the photooxidation mechanism may in fact be different from the previously described direct cycloaddition of singlet oxygen to the thiophene ring, possibly involving another active species that can attack the α-position of the alkyl side chain to form radicals. Furthermore, Manceau et al.[17] also reported that singlet oxygen itself does not react with P3HT.

On the basis of these findings, we have reviewed the photooxidative degradation mechanism of poly(3-alkylthiophenes). Aguirre et al.[18] reported that the [Polym]$^{+\bullet}$ [O$_2$]$^{-\bullet}$ complex is formed by photo-irradiation during the initial stages of photooxidation. Furthermore, Hoke et al.[19] reported that superoxide ([O$_2$]$^{-\bullet}$) is involved in the photooxidation of P3HT and fullerene derivatives by changing the electron affinity of the fullerene. In addition, Seemann et al.[20] suggested that [O$_2$]$^{-\bullet}$ is involved in the photooxidation of P3HT and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), causing irreversible degradation of the P3HT and PCBM in organic solar cells. These reports suggest that [O$_2$]$^{-\bullet}$ is involved in P3HT photo-oxidation; however, the oxidation mechanism of [O$_2$]$^{-\bullet}$ requires further investigation. A recent study in our laboratory using electron spin resonance (ESR) measurements with the spin-trap technique showed that [O$_2$]$^{-\bullet}$ is generated during P3HT photooxidation in solution, causing the degradation of P3HT.[21] In this study, we investigated the photooxidation of a thin film of P3HT.

We previously reported that poly(3-octyloxythiophene) (P3OOT) is highly stable, with hardly any structural change after simulated solar light irradiation (the chemical structure is shown in Figure 1).[22] It was explained by the low reactivity of the oxidation of the sulfur atom in the thiophene ring by the hydroxyl radical.[23] Although the cationic state of photostable P3OOT has been observed by light irradiation in air, the cationic state of P3HT has not yet been observed. It is likely that a stable counter anion exists in P3OOT. The polymer cation and the counter anion would also have an influence on the photooxidation reaction.

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To understand the role of other active species in the photooxidation of polythiophene derivatives and the mechanism of radical formation by such species, P3HT and photostable P3OOT thin films were irradiated by light. Differences in the photochemical behavior between P3HT and P3OOT were observed by light-induced ESR, ultraviolet–visible–near-infrared spectroscopy and density functional theory (DFT) calculations.

EXPERIMENTAL PROCEDURE

Preparation of polythiophene derivatives

Two polythiophene derivatives with different side chains were employed: $-C_6H_{13}$ (P3HT) and $-OC_8H_{17}$ (P3OOT). P3HT (regioregularity: >95%) was purchased from Merck. The weight-averaged molecular weight (M_w) and polydispersity (M_w/M_n) of P3HT were determined by gel permeation chromatography (GPC; Nihon Waters K. K., Tokyo, Japan) to be 18 000 and 1.60, respectively. P3OOT was prepared by polymerization using the Grignard metathesis method.[23] The 3-octyloxythiophene was synthesized from 3-methoxythiophene and 1-octanol in the presence of catalytic sodium hydrogen sulfate. After dibromination, P3OOT was synthesized from 2,5-dibromo-3-octyloxythiophene by a Kumada coupling reaction with 0.5 mol% $NiCl_2(dppp)$, dppp = 1,3-bis(diphenylphosphino)propane. A bright blue powder was obtained with an ~20% yield. The M_w and M_w/M_n values of the polymer were determined to be 12 000 and 1.72, respectively. The ^{1}H NMR spectra of P3OOT at 400 MHz ($CDCl_3$): δ (p.p.m.) displayed peaks at 0.95 (t, 3H), 1.40 (broad, 10H), 1.80 (q, 2H), 4.00 (t, 2H) and 6.80 (s, 1H), with a regioregularity >95%.

Sample preparation and measurement

Polymer films were fabricated by spin coating on CaF_2 substrates. The thickness of each polymer film was 120 ± 10 nm, which was measured by a stylus-type film thickness meter (ULVAC E. S., Inc., Tokyo, Japan, Dektak). Solar-simulated

Figure 1 The chemical structure of poly(3-octyloxy)thiophene (P3OOT).

light (AM 1.5 G) was used to irradiate the polymer films with an intensity of 100 mW cm^{-2}. The device was calibrated using a standard cell for a-Si solar cells (Bunkoh-Keiki Co., Ltd, Ibaraki, Japan). To investigate the temporal changes in the polymer cation upon light irradiation, the light-induced ESR spectra of the films were measured using an X-band ESR spectrometer (JEOL. Ltd, Tokyo, Japan, JES-FA200) with solar-simulated light (AM 1.5 G) irradiation (100 mW cm^{-2}) in ambient air. The sample was inserted into an ESR quartz tube with an inner diameter of 3.5 mm and mounted into a cavity, where the ESR spectrum was measured with light irradiation.[24] To confirm the influence of the superoxide, the samples were dipped in a copper–zinc superoxide dismutase (CuZnSOD, herein denoted by SOD; Wako Pure Chemical Industries, Ltd., Osaka, Japan; activity: 2500 U mg^{-1}) aqueous solution (1.44 mg ml^{-1}). The samples were then rinsed with distilled water. Spectral measurements were performed using a ultraviolet–visible–near-infrared spectrophotometer (Shimadzu Co., Ltd., Kyoto, Japan; UV-3600).

DFT calculations

For the DFT calculations, 3′-hexyl-2,2′:5′,2″-terthiophene was chosen as the model compound for P3HT. First, the geometries of neutral P3HT were calculated by the DFT method using the Becke 3-parameter (exchange) Lee–Yang–Parr (correlation; B3LYP) functional with the 6-311G(d,p) basis set. The geometries of the cation radicals of P3HT (denoted as [P3HT]$^{+\bullet}$) were then optimized from the neutral structures. In addition, we optimized the polymers for proton or hydrogen abstraction by superoxide. The proton or hydrogen atom was abstracted from the α-position of the side chain of the model compounds. An energy diagram was developed from these energy values. The structures were fully optimized using the energy gradient method without symmetry restriction. For the open-shell doublet states, unrestricted B3LYP (denoted as UB3LYP) was used. The calculations were performed using a Gaussian program package (Gaussian09). The Cartesian coordinates for the molecules at the stationary points are provided in the Supplementary Files.

RESULTS AND DISCUSSION

Stability of the polymer cation formed by oxygen doping

To further investigate the polymer cation with light irradiation,[22] the light-induced ESR spectra of P3HT and P3OOT were measured in air and in vacuum (Figure 2). A single, relatively stable signal was observed in the ESR spectra for both P3HT and P3OOT after 1 h of light irradiation in air. The g factors of P3HT and P3OOT were 2.00218 (321.33 mT) and 2.00369 (321.16 mT), respectively. These ESR characteristics are in good agreement with those of P3HT and P3OOT after iodine doping.[25,26] Therefore, the ESR signals upon light irradiation can be ascribed to the polymer cation traps. In addition, the ESR intensities of P3HT and P3OOT in air were markedly higher than in a vacuum, indicating that the ESR signals were derived from doping by oxygen in air. (The ESR signals of the oxygen radical anion
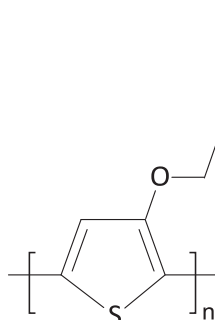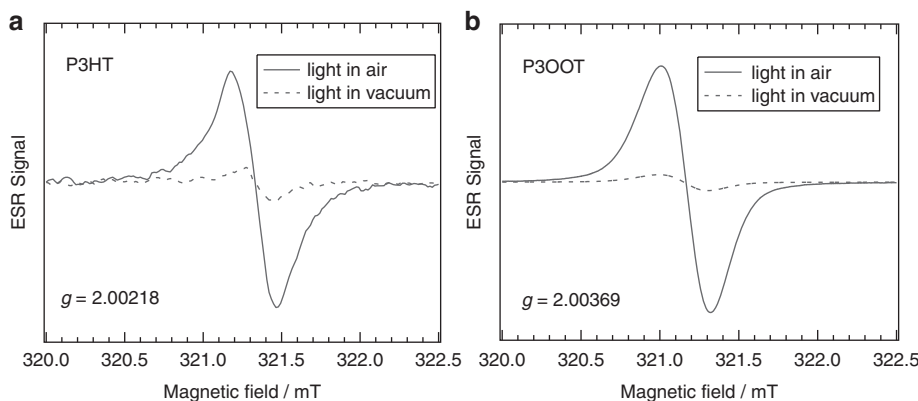

Figure 2 ESR spectra of (**a**) P3HT and (**b**) P3OOT films after 1-h light irradiation in air (—) and in vacuum (---). A full color version of this figure is available at the *Polymer Journal* online.

cannot be detected directly because of the broad signal at room temperature.) Therefore, the ESR signals upon light irradiation cannot be ascribed to the P· radical, which quickly disappears by reacting with oxygen, but rather to the polymer cation (polaron) traps formed by oxygen doping.

The temporal changes in the ESR peak intensities (Figure 2) of the P3HT and P3OOT thin films in air and under vacuum are shown in Figure 3. These data were measured over 20 h of continuous light illumination. Additional data were obtained over 20–27 h after turning off the light. The spin concentrations hardly increased under vacuum ($<10^{-4}$ Pa), compared with the concentrations in air, because oxygen, which accepts the π-electrons from the polymers, was scarce in the vacuum. In contrast, the spin concentrations of P3HT and P3OOT increased in air during light irradiation, which suggests that the [Polym]$^{+•}$ concentration continuously increased during light exposure due to oxygen doping. In the dark conditions (20–27 h), which followed the 20 h of light illumination, the spin concentration of P3HT decayed (~0.01 spins nm^{-3} h^{-1}), whereas the spin concentrations of P3OOT were stable. The changes in the ESR spectra of P3HT and P3OOT after 4 h in the dark are shown in Supplementary Figure S1. These results indicated that the [P3HT]$^{+•}$ formed by oxygen doping was unstable, whereas the [P3OOT]$^{+•}$ was

stable. Regarding the ESR intensity of pristine P3OOT, the P3OOT was easily doped by oxygen after exposure to the atmosphere because the highest occupied molecular orbital (HOMO) level of P3OOT (−4.95 eV) was shallower than that of P3HT (−5.10 eV) by 0.15 eV (Supplementary Table S1).

Investigation of the decrease in the P3HT polaron formed by oxygen doping

As seen in ESR measurements, the [P3HT]$^{+•}$ formed by oxygen doping after continuous irradiation decreased. This decrease can be explained by two possible mechanisms. First, a reversible reaction may occur in which the [P3HT]$^{+•}$ exposed to the oxygen dopant returns to neutral P3HT and O$_2$.[13,25] Second, the decomposition of [P3HT]$^{+•}$ itself can be accompanied by radical quenching by the oxygen dopant. If the former mechanism is the dominant mode, then the photoabsorption of irradiated P3HT should be partially recovered after turning off the light. Thus, we examined the ultraviolet–visible absorbance changes of P3HT. First, the P3HT film was irradiated for 5 h in air to form [P3HT]$^{+•}$ by oxygen doping. Then, the film was kept in the dark for 20 h. UV measurements were conducted before and after storage in the dark. It was difficult to detect an absorption difference in the near-infrared region for the [P3HT]$^{+•}$ (polaron)
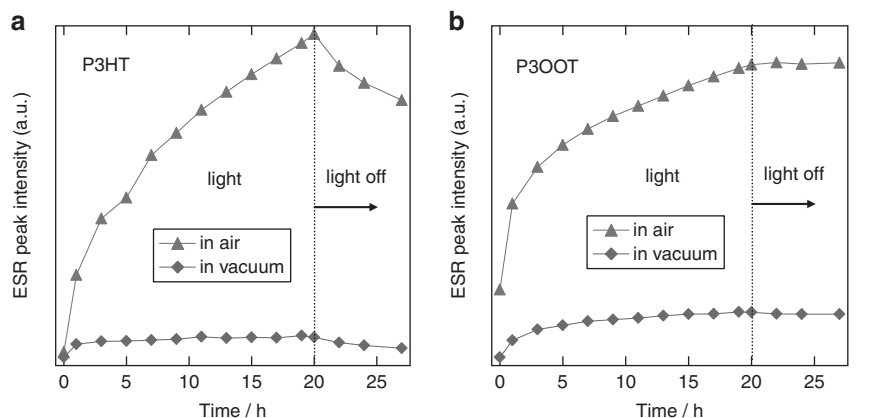

Figure 3 Temporal changes in the ESR peak intensities of the (**a**) P3HT and (**b**) P3OOT films in air (▲) and in vacuum (◆); light conditions: 0–20 h and dark conditions: 20–27 h. A full color version of this figure is available at the *Polymer Journal* online.
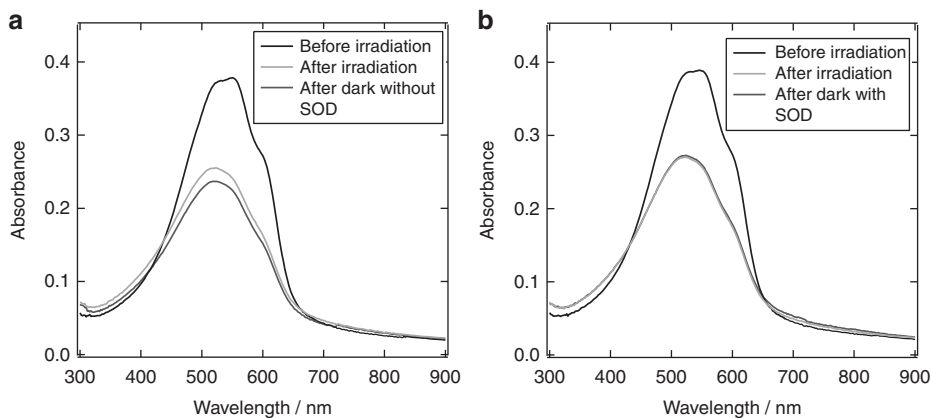

Figure 4 Ultraviolet–visible/near-infrared spectra of P3HT films in the presence/absence of SOD: (**a**) before irradiation (black line), after 12-h irradiation (red line) and 20 h under dark (blue line) conditions in water (without SOD) after 12-h irradiation; and (**b**) before irradiation (black line), after 12-h irradiation (red line) and 20 h under dark (blue line) conditions in SOD aqueous solution (with SOD) after 12-h irradiation. A full color version of this figure is available at the *Polymer Journal* online.

because the oxygen-doped polaron signal was broad and weak;[25] however, a decrease in absorption in the visible region was clearly observed after keeping the irradiated samples in the dark for 20 h.

It seems that the decomposition of [P3HT]$^{+\cdot}$ and P3HT itself by oxygen doping occurs in addition to the reversible reaction to the neutral state. If the oxygen dopant is superoxide, as reported by others,[18–20,26] it is probable that the oxidation of [P3HT]$^{+\cdot}$ will proceed. It is known that superoxide is one of the strongest oxidants among oxygen species and that it can trigger hydrogen or proton abstraction.[27–30] Therefore, if superoxide has an effect on the reaction, photooxidation will be suppressed by a superoxide quencher. SOD is a redox enzyme that selectively quenches superoxide.[31,32] Once again, we focused on the irradiated state of P3HT ([P3HT]$^{+\cdot}$ formed by oxygen doping) and examined the changes in ultraviolet–visible absorbance of P3HT using SOD (Figure 4) to confirm the effect of superoxide. First, the P3HT films were irradiated for 12 h. The films were then dipped in either an aqueous SOD solution or distilled water (without SOD) in the dark for 20 h. UV measurements were conducted before and after storage in the dark. In water (Figure 4a), the decrease in visible absorbance was similar to what was observed in

air. However, in the SOD solution (Figure 4b), no change in the absorbance was observed. Therefore, the decrease in P3HT absorbance was suppressed by SOD, confirming that the oxygen dopant is superoxide and that superoxide is involved in P3HT oxidation. In addition, Dr Chen (L Chen, personal communication, 24 January 2014) has reported that the photooxidation of P3HT in chlorobenzene is drastically suppressed by adding 5,5-dimethyl-1-pyrroline N-oxide (DMPO) based on the ESR signal of DMPO-O_2^-. This fact strongly supports the role of superoxide in P3HT oxidation.

The reactivity of superoxide with P3HT as determined by DFT calculations

In the superoxide-mediated oxidation reaction, superoxide participates in an ionic reaction with the proton[27,29,31] and a free-radical reaction with the hydrogen.[27–30] Therefore, we assume that superoxide can trigger an oxidation reaction to abstract either a hydrogen atom or a proton at the reactive α-position of the hexyl side chain of [P3HT]$^{+\cdot}$.[15,16] DFT calculations (see Figure 5) can be used to examine the mechanism by which the abstraction occurs. It was found that the reaction of superoxide with the α-proton of [P3HT]$^{+\cdot}$ is exothermic, producing a heat of reaction of 121.1 kcal mol^{-1}. In contrast, the reaction of superoxide with the α-hydrogen of [P3HT]$^{+\cdot}$ is endothermic, producing a negative heat of reaction of −14.1 kcal mol^{-1}. Therefore, the DFT calculations revealed that superoxide easily abstracts the α-proton of P3HT; however, hydrogen abstraction is less favored. Conversely, superoxide did not react with the proton of the β-position of the octyl side chain of [P3OOT]$^{+\cdot}$ because of the low reactivity of the β-hydrogen.[22] Therefore, the superoxide cannot abstract a proton from [P3OOT]$^{+\cdot}$. Hatakeyama *et al.* reported that the deprotonation (α-proton) reaction of poly(3-alkylthiophene)$^+$ ([P3AT]$^{+\cdot}$) occurs easily at the α-position in the side chain, but that the deprotonation of poly(3-alkoxythiophene)$^+$ [P3OAT]$^{+\cdot}$ does not take place because there are no reactive protons in the alkyl side chain.[33] This fact strongly supports our results. Thus, the photooxidation progresses through deprotonation in the presence of superoxide, resulting in the formation of a radical at the α-position of the alkyl side chain.[15,16] The deprotonation is followed by an electron transfer from the excited polymer to oxygen (oxygen doping). The mechanism of the initial photooxidation of P3HT is shown in Scheme 1.
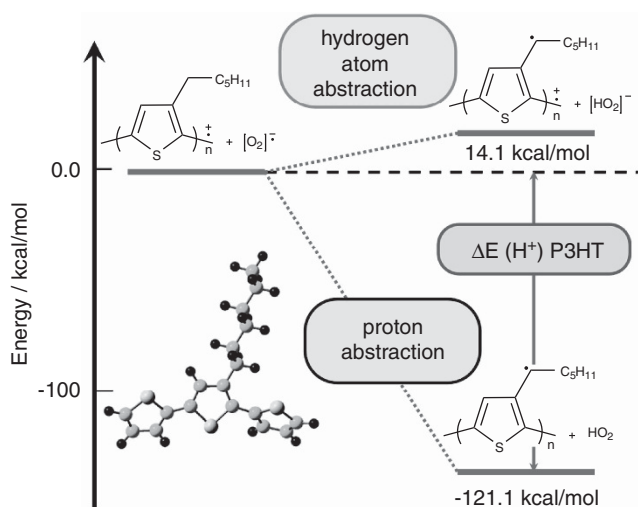
Figure 5 Energy diagram of [P3HT]$^+\cdot$ [O_2]$^-\cdot$, [P3HT·]$^{+\cdot}$ + [HO$_2$]$^-$ and [P3HT·]+ HO$_2$. Superoxide radical [O_2]$^-\cdot$ reacts with the α-hydrogen and α-proton of P3HT. Inset: model compound (3′-hexyl-2,2′:5′,2″-terthiophene) structure of P3HT. A full color version of this figure is available at the *Polymer Journal* online.

CONCLUSIONS

To understand the initial photooxidation mechanism leading to reactive radical formation from polythiophene derivatives, we investigated the differences in the photochemical behaviors
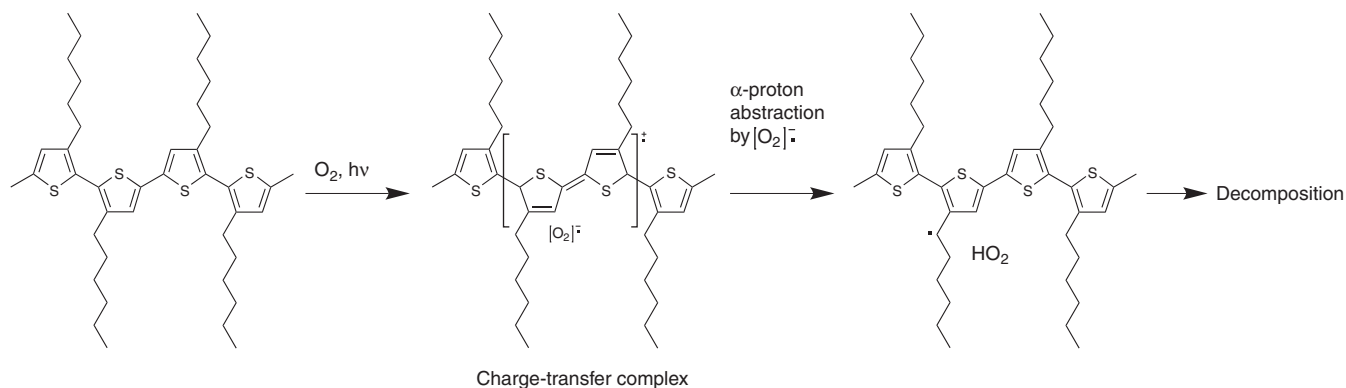
Scheme 1 Initial photooxidation mechanism leading to reactive radical species of P3HT by [O_2]$^-\cdot$, which is formed by electron transfer reaction from P3HT to O_2.

of P3HT and P3OOT by means of light-induced ESR and ultraviolet–visible–near-infrared spectroscopy. In air, both [P3HT]$^{+\bullet}$ and [P3OOT]$^{+\bullet}$ were formed by oxygen doping upon light irradiation. Although [P3HT]$^{+\bullet}$ was unstable, [P3OOT]$^{+\bullet}$ was found to be stable. The decomposition of [P3HT]$^{+\bullet}$ and P3HT itself were triggered by the oxygen dopant because of the suppression of the decay by SOD. Therefore, the oxygen dopant is superoxide, and thus, the oxidation of P3HT is likely initiated by superoxide. Furthermore, the DFT calculation revealed that the reaction of superoxide with the α-proton of [P3HT]$^{+\bullet}$ is exothermic, which indicates that superoxide can more easily abstract the α-proton from [P3HT]$^{+\bullet}$ by ionic reaction than the α-hydrogen in [P3HT]$^{+\bullet}$ by radical reaction. The photochemical differences between P3HT and P3OOT can be explained by the reaction of the α-proton with superoxide, indicating that the photooxidation of P3HT progresses through deprotonation in the presence of superoxide, resulting in the formation of a reactive radical at the α-position of the alkyl side chain.

HIGHLIGHTS

We investigated the differences in the photochemical behaviors of P3HT and photostable P3OOT by LESR, UV–Vis spectroscopy and DFT calculations.

The [P3HT]$^{+\bullet}$ formed by oxygen doping was unstable, but the [P3OOT]$^{+}$ was stable.

The decay of [P3HT]$^{+\bullet}$ was suppressed by superoxide dismutase.

The photochemical difference between P3HT and P3OOT can be explained by the reactive α-proton on the P3HT.

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Supplementary Information accompanies the paper on Polymer Journal website (http://www.nature.com/pj)