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ORIGINAL PAPER

Mechanisms of photo-induced degradation of polythiophene derivatives: re-examination of the role of singlet oxygen

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Abstract Roles of singlet oxygen ($^1O_2$) in photo-induced degradation of poly(3-hexylthiophene) (P3HT) and poly(3-hexyloxythiophene) (P3HOT) were examined. The results indicate that $^1O_2$ has a considerable role in the degradation of P3HT and P3HOT. Photo-irradiation of P3HT in air resulted in the reduction of the π-conjugation. The photo-induced reduction also occurred for P3HOT, and it was much faster than that of P3HT. Manceau et al. have reported that $^1O_2$ was generated by photo-irradiation of P3HT in the presence of oxygen and, nevertheless, $^1O_2$ is not the principal photo-oxidative degradation intermediate of P3HT (Manceau et al., Macromol Rapid Commun 29:1823–1827, 2008). However, exposures of solid P3HT and P3HOT to chemically generated $^1O_2$ provided decreases in the ππ*absorption in our study. The decrease for P3HOT was much larger than that for P3HT. The exposure of P3HOT showed the formation of polarons. The difference in P3HT and P3HOT for the effects of the photo-irradiation and of $^1O_2$ will be ascribed to the difference in their ionization potentials.

Introduction

Conducting polymers have potentials for various applications in electronics, such as organic field effect transistor (OFET) [1], organic solar cells (OSC) [2], organic light emitting diode [3], and actuators [4]. In particular, soluble conducting polymers are key materials to enable flexible, large area, and low-cost products by printing processes [5].

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Poly(3-alkylthiophene)s (P3AT) are one of the most common polymers in researches on OFET [6] and OSC [7]. For applications exposed to light, such as OSC, it is important to understand the mechanisms of their photo-induced degradations [8]. Photo-induced chemical reactions of P3AT have been studied from the early 1990s [9–13]. The reports are, however, relatively sparse, and the mechanisms of the photo-induced degradation are still ambiguous [14–16].

Two major mechanisms have been proposed: reactions of singlet oxygen ($^1O_2$) generated by photo-sensitization with P3AT [9–12, 17] and of photolytically or thermally generated hydroxyl radicals [14–16]. The latter mechanism seems to be presently accepted as a principal photo-degradation process of P3AT [18, 19].

Holdcroft and Abdou investigated the mechanism with $^1O_2$ [9–12]. They examined the degradations of poly(3-hexylthiophene) (P3HT) in solutions by photolysis and by reactions with chemically generated singlet oxygen ($^1O_2$) [10–12], and photo-degradations of solid P3HT [9]. They concluded that the photo-degradations in the presence of oxygen involve photo-sensitized generation and reactions of $^1O_2$. Photolysis of poly(3-hexylthiophene) (P3HT) in O_2-saturated solutions [11, 12] resulted in reduction of the π-conjugation and chain scissions, while those of solid P3HT provided the reduction and cross-linkings. They explained that 1,4-Diels–Alder addition of $^1O_2$ to a thienyl ring followed by rearrangements yielding a sulfine or a trans-diketone caused the reduction as shown in Fig. 1. The chain scissions and cross-linkings were ascribed to formation of P3HT radicals initiated by photolysis of residual iron (III).

Caronna et al. have also suggested that addition of $^1O_2$ to the conjugated double bonds for the mechanism of photo-degradation of poly(3-butythiophene) in the solid state [17]. They analyzed low molecular weight species produced by the photo-irradiation.

Manceau et al. have proposed the mechanism with hydroxyl radicals. They investigated the role of $^1O_2$ in the photolysis of solid P3HT [15] and concluded that $^1O_2$ was not the principal photo-oxidative degradation intermediate of P3HT. They have confirmed that $^1O_2$ could be generated by the photolysis of P3HT in the presence of oxygen. They have reported that P3HT, however, did not decompose by reactions with chemically generated $^1O_2$. They also investigated the photo-degradation of P3HT based on infrared spectra [14] and X-ray photoelectron spectra [16], and proposed a mechanism of the degradation through reactions of radicals as shown in Fig. 2: generation of OH radicals through photo or thermal C–H bond scissions at the α-position of hexyl groups and reactions with oxygen (a), addition of the OH radicals to a sulfur of thienyl rings forming sulfone (b), and ring opening of the sulfone (c).

Aoyama et al. examined the photo-degradation of polythiophene derivatives with no α-hydrogen at the side chains: poly(3-octyloxythiophene) (P3OOT), poly(3-phenylthiophene), and poly (3-(1,1-dimethylpropyl)thiophene) [20]. P3OOT was converted to polarons by photo-irradiation in air, and this could be reverted to the pristine one by reduction with hydrazine. The other polythiophene derivatives degraded in the same way as P3HT.

Although the mechanism in Fig. 2 seems to be presently accepted as a principal photo-degradation process of P3AT [18, 19], we have questions about it. P3HT and

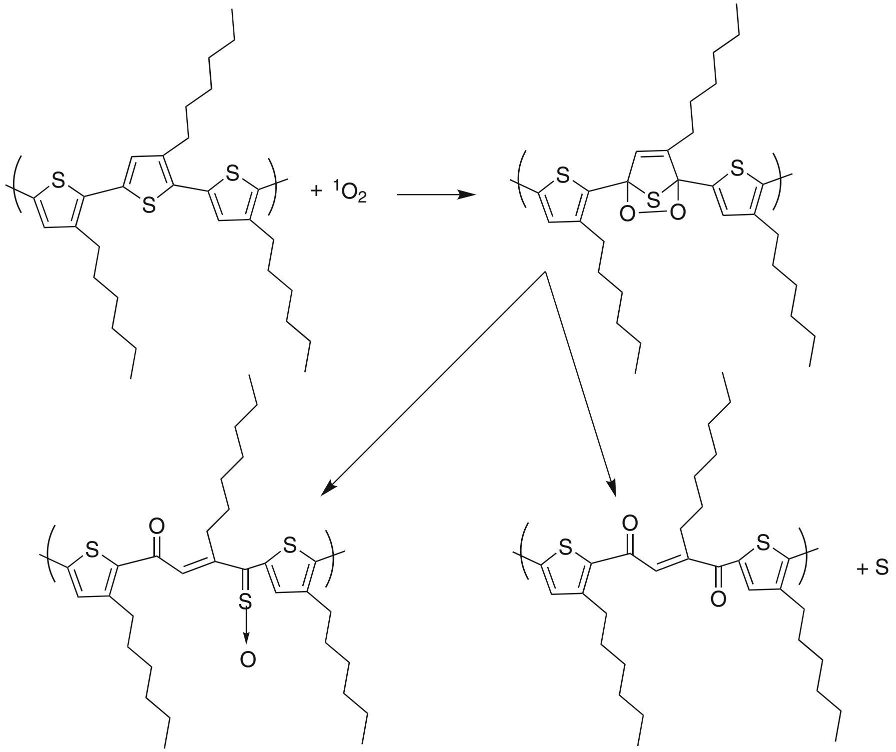

Fig. 1 Ring opening of thienyl rings through Diels–Alder addition of singlet oxygen [11]

OH radial formation may proceed through reactions (a) in Fig. 2. However, a theoretical study suggested that an attack of OH radial on sulfur in P3HT (b) was thermodynamically unfavorable [21]. Furthermore, the ring opening of the sulfone (c) is questionable. To our knowledge, no experimental evidence for the ring opening of thienyl-1,1-dioxide moiety has been reported. In addition, reactions in the mechanism are initiated by C–H bond rapture and addition of oxygen to the α-position of the alkyl side chains. The photo-degradation of polythiophene derivatives with no α-hydrogen, however, occurs in the same way as P3HT [20]. It is inconsistent with the mechanism.

This paper re-examines the role of $^1O_2$ in the photo-degradation of P3AT. Reactions of $^1O_2$ with low molecular unsaturated compounds are well established [22–25]. The Diels–Alder addition followed by ring opening seems to be more plausible than that of the thienyl-1,1-dioxide moiety.

Experimental

Regioregular P3HT was purchased from Aldrich. The weight-averaged molecular weight (M_w) and polydispersivity (M_w/M_n) determined by gel permeation chromatography against polystyrene standards were 55,800 and 1.94, respectively.

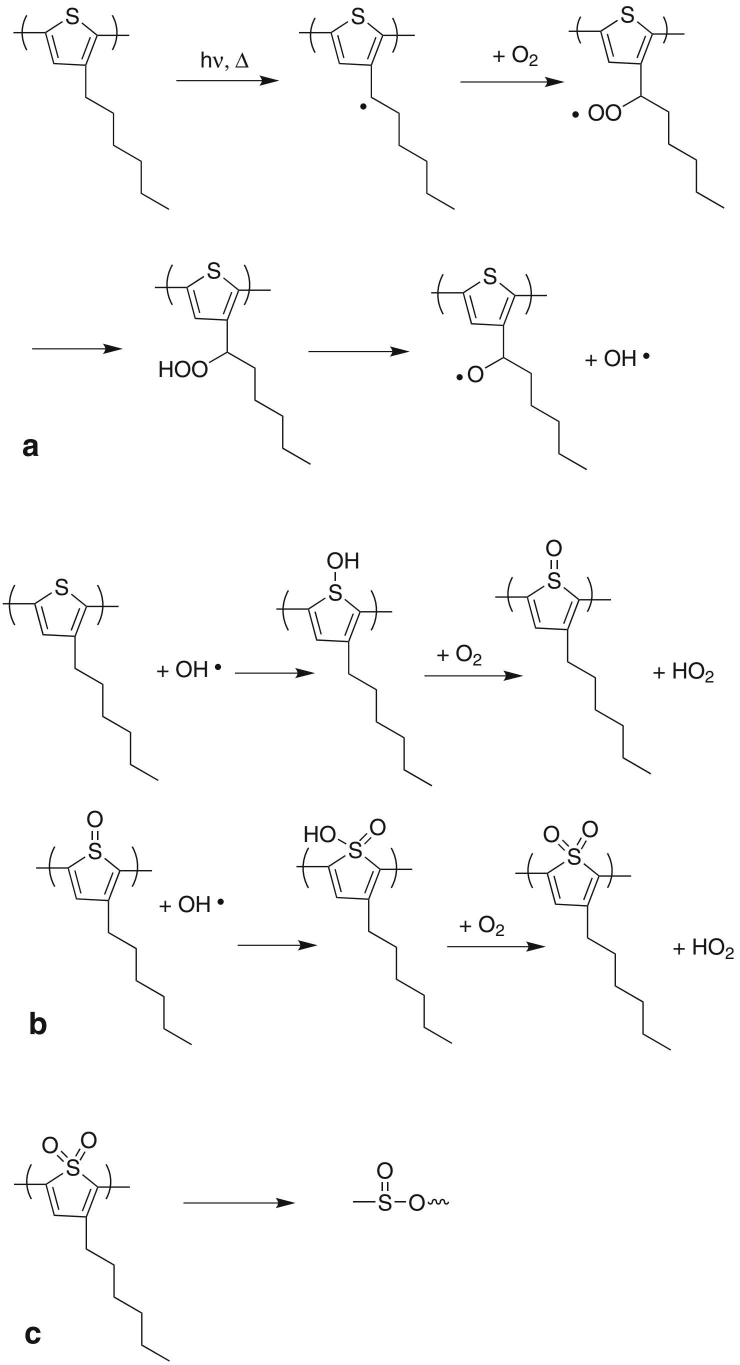

Fig. 2 Ring opening of thienyl rings through **a** generation of hydroxy radicals, **b** formation of sulfoxide (thienyl-1-oxide) and sulfone (thienyl-1,1-dioxide) by reaction with hydroxy radicals, and **c** ring opening of thienyl-1,1-dioxide [14]

P3HT was also obtained by oxidative polymerization of 3-hexylthiophene with $FeCl_3$ [26]. The values of M_w and M_w/M_n were 8300 and 1.60, respectively.

Poly(3-hexyloxythiophene) (P3HOT) was obtained by polymerization of 3-hexyloxythiophene with the Grignard metathesis(GRIM) method [27]. 3-Hexyloxythiophene was synthesized from 3-methoxythiophene and hexanol with sodium hydrogen sulfate ($NaHSO_4$) as a catalyst [28, 29]. The monomer was dibrominated with *N*-bromosuccinimide (NBS) to afford 2,5-dibromo-3-hexyloxythiophene, which was subsequently transformed into the Grignard derivative with methyl magnesium bromide and polymerized with a Kumada coupling reaction, catalyzed by [1,3-bis(diphenylphosphino)propane]nickel(II) dichloride [$NiCl_2$(dppp)]. The values of M_w and M_w/M_n for P3HOT were 7900 and 1.15, respectively.

Films of P3HT and P3HOT were prepared by spin-coating from their solutions in chloroform on glass plates.

$^1O_2$ was generated from the reaction between hydrogen peroxide and sodium hypochlorite [10, 15, 30, 31]. The polymer films were exposed to $^1O_2$ by two methods. One is the same as that by Manceau et al. [15]: 100 μL of 0.6 mol dm^{-3} aqueous solution of hydrogen peroxide was dropped on the films, and then 100 μL of 0.6 mol dm^{-3} aqueous solution of sodium hypochlorite was added. Manceau et al. conducted this operation only once. However, we repeated this operation several times for the same film after rinsing with methanol and drying it. The other one is a similar operation with the same solutions. The mixing was, however, made in a small Petri dish. The polymer-coated plates were put on the dish with the coated side down. The distance between the surface of the solution mixture and the polymer films was about 1 cm.

Light from a xenon lamp (Hamamatsu L2275) was irradiated through an optical filter (Toshiba Glass Co. UV-31) that transmits light longer than 310 nm. The illuminances at the surfaces of the polymer films were measured with an illuminometer (AS ONE LM-332).

Ultraviolet–visible–near-infrared (UV–Vis–NIR) spectra of the polymer films were measured with a Shimadzu UV-3600 spectrophotometer.

3-Hexylthiophene, 3-methoxythiophene, and methyl magnesium bromide were purchased from Aldrich, NBS and $NiCl_2$(dppp) from Tokyo Chemical Industry Co., Ltd., and 1-hexanol, $NaHSO_4$, hydrogen peroxide, sodium hypochlorite, and methanol from, Junsei Chemical Co., Ltd.

Results

Photo-irradiation of poly(3-heyxylthiophene) and poly(3-hexyloxythiophene)

We compared the rates of photo-degradation of P3HT and P3HOT. If photo-degradation of polythiophene derivatives occurs through the radical mechanism in Fig. 2, the rate of the photo-degradation should depend on the chemical structures of the side chains. Since the initial step is C–H bond scission at an α-position of alkyl side chains, the rate for polythiophene derivatives having side chains without α-hydrogens should much decrease.

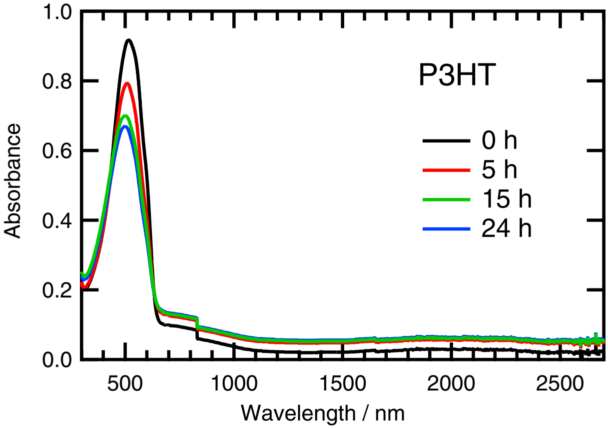

Fig. 3 Photo-absorption spectra of a poly(3-hexylthiophene) film before (*black line*) and after 5 h (*red line*), 15 h (*green line*), and 24 h (*blue line*) irradiation with a xenon lamp (color figure online)

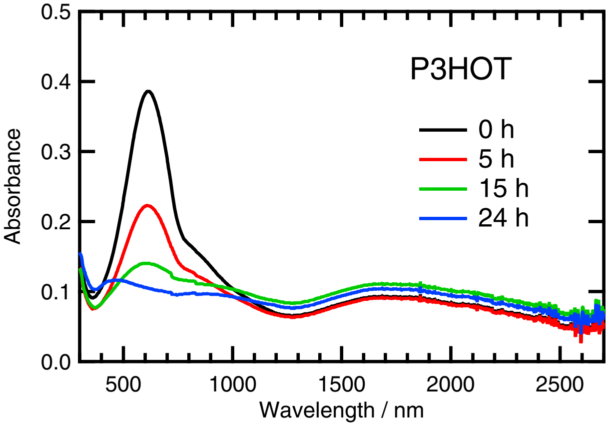

Fig. 4 Photo-absorption spectra of a poly(3-hexyloxythiophene) film before (*black line*) and after 5 h (*red line*), 15 h (*green line*), and 24 h (*blue line*) irradiation with a xenon lamp (color figure online)

UV–Vis–NIR spectra of P3HT and P3HOT films before and after irradiation with light of the same intensity from a xenon lamp in air are shown in Figs. 3 and 4, respectively. The absorption bands around 500 nm for P3HT and around 550 nm for P3HOT are due to the ππ* transition. These bands decreased by the irradiation, and the rate of the decrease for P3HOT was faster than that for P3HT. It is not explained by the mechanism in Fig. 2; the rate for P3HOT should be slower than that for P3HT according to this mechanism.

The absorbance of bands around 1000 and 1650 nm for P3HOT increased by photo-irradiation. This result agrees with that by Aoyama et al. [20] for poly(3-octyloxythiohene) (P3OOT). These bands can be assigned to polarons [29]. It was confirmed by doping of P3HOT with iodine vapor. The absorption spectra of a

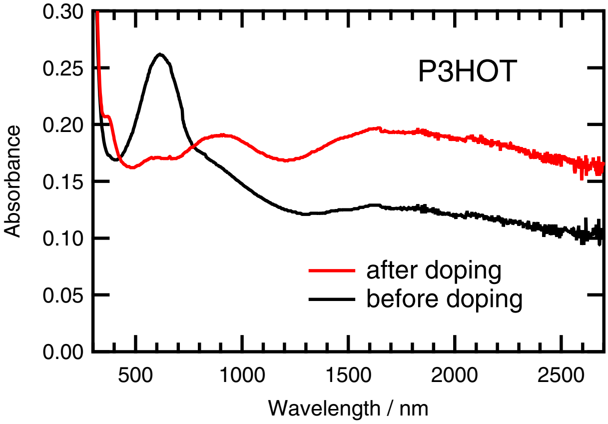

Fig. 5 Photo-absorption spectra of a poly(3-hexyloxythiophene) film before (*black line*) and after (*red line*) doping with iodine vapor (color figure online)

P3HOT film before and after the doping are shown in Fig. 5. The absorbance of these bands increased by the doping. Polarons were generated by the photo-irradiation of P3HOT.

Only a small fraction of the decrement of neutral P3HOT was converted to polarons by the photo-irradiation. The increment at 1650 nm and the decrement at 600 nm in absorbance for a film after the doping in Fig. 5 are 0.068 and 0.094, respectively. The ratio of the increment to the decrement is 0.72. On the other hand, the increment, the decrement, and the ratio for a film after 24 h of the photo-irradiation in Fig. 4 are 0.018, 0.247, and 0.075, respectively. The conversion efficiency from neutral P3HOT to polarons by the photo-irradiation is hence about 1/10 of that by the doping. Most of the neutral P3HOT decomposed through processes other than the conversion to polarons by the photo-irradiation.

Exposure of poly(3-heyxylthiophene) and poly(3-hexyloxythiophene) to singlet oxygen

Exposure of P3HT to $^1O_2$ resulted in considerable decrease in the π-conjugation. When only once $^1O_2$ was generated directly on the P3HT film following the procedure of Manceau et al. [15], UV–Vis–NIR spectra showed little change. However, they showed considerable decrease in the absorbance for the ππ* transition after repeating this procedure several times. Manceau et al. estimated that the reaction between 100 μL of the solutions would produce 60 μmol of $^1O_2$, and this is 900-fold excess [15]. However, we observed that bubbles generated in the solution mixture rose to the solution surface, implying that a large part of $^1O_2$ escaped to the atmosphere and only a small fraction of $^1O_2$ reached the surface of the film.

The direct contact of the solutions to P3HT films may cause effects other than those of $^1O_2$. We then put a P3HT-coated glass plate on a Petri dish with the coated

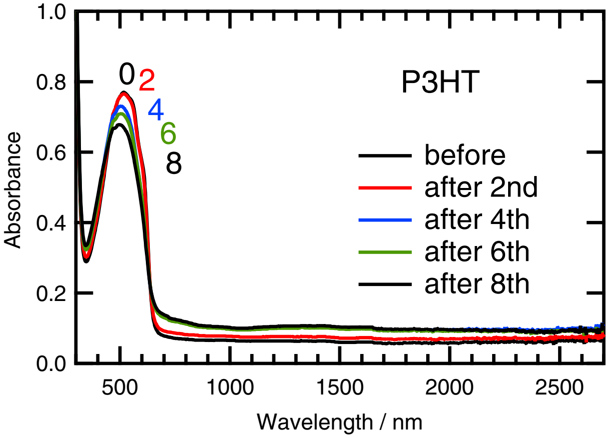

Fig. 6 Photo-absorption spectra of a poly(3-hexylthiophene) film before (*black line*) and after the second (*red line*), fourth (*blue line*), sixth (*green line*), and eighth (*black line*) exposures to singlet oxygen (color figure online)

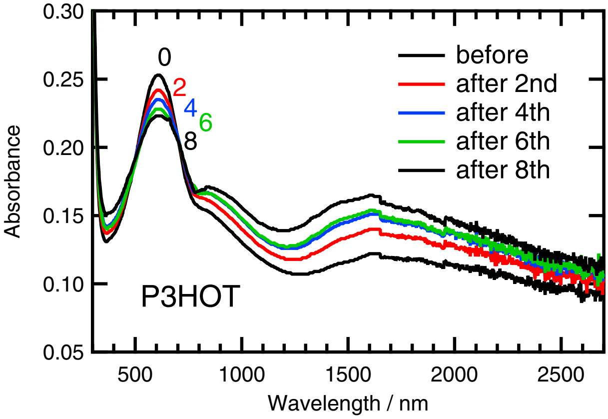

Fig. 7 Photo-absorption spectra of a poly(3-hexyloxythiophene) film before (*black line*) and after the second (*red line*), fourth (*blue line*), sixth (*green line*), and eighth (*black line*) exposures to singlet oxygen (color figure online)

side down and mixed the solutions in the dish without contact with the film. Figure 6 shows the spectra before and after this operation. The absorbance of the $\pi\pi^*$ transition around 500 nm decreased by repeating the exposure. Hence, $^1O_2$ can reduce the π-conjugation.

We also examined the reactivity of P3HOT with $^1O_2$. Figure 7 shows the absorption spectra of P3HOT before and after exposure to $^1O_2$, which was performed by the second method. It showed a significant decrease in the $\pi\pi^*$ absorption and an increase in polarons. It indicated that neutral P3HOT efficiently converted to the polarons by reactions with $^1O_2$. The spectrum after the exposure was stable for at least 1 h.

Discussion

The π-conjugation of P3HOT was reduced faster than that of P3HT by the photo-irradiation in air. This result cannot be explained by the radical mechanism in Fig. 2. The reactions are initiated by C–H bond scission of a side chain in this mechanism, and this step will be a rate-determining one. Since the scission of C–H bonds at the α-position of the hexyl chains is easier than that of C–H bonds of the hexyloxy chains, the degradation of P3HT should be faster than that of P3HOT.

Exposures of P3HT and P3HOT to $^1O_2$ also induced the reduction of the π-conjugation. The reduction for P3HOT was faster than that for P3HT. In addition, the reactions of $^1O_2$ caused increase in polarons only for P3HOT. These results indicate that $^1O_2$ has a role in the photo-induced degradation of P3HT and P3HOT in air.

The difference in the reactions of $^1O_2$ with P3HT and P3HOT will arise from the difference in their oxidation potentials. They are 0.94 V vs. SCE for P3HT and 0.27–0.73 V vs. SCE for P3HOT, respectively [32–34].

Polarons can be generated by reactions of P3HOT with $^1O_2$, but cannot be generated by those of P3HT. This may be evaluated by the following.

The energy associated with excitation of a charge transfer complex of an electron donor and an acceptor is given by

$$E_e = \mathrm{IP_D} - \mathrm{EA_A} - W, \tag{1}$$

where $\mathrm{IP_D}$ and $\mathrm{EA_A}$ are the ionization potential of the donor and the electron affinity of the acceptor, respectively [35]. W is the Coulombic attraction energy of the complex [35].

E_e can be estimated by the following empirical relation [36]:

$$E_e(\mathrm{eV}) = E(\mathrm{D/D^+}) - E(\mathrm{A^-/A}) + 0.15 \pm 0.10, \tag{2}$$

where $E(\mathrm{D/D^+})$ and $E(\mathrm{A^-/A})$ are the oxidation potential of the donor and the reduction potential of the acceptor, respectively. The values of $E(\mathrm{D/D^+})$ for P3HT [35] and P3HOT [32–34] were reported to be 0.94 and 0.27–0.73 V vs. SCE, respectively. $E(\mathrm{A^-/A})$ was −0.82 V vs. SCE [35]. E_e for $\mathrm{P3HT^+ - O_2^-}$ has been estimated to be 1.9 eV above the ground state [35], while E_e for $\mathrm{P3HOT^+ - O_2^-}$ is estimated to be between 1.2 and 1.6 eV with Eq. (2).

The electron affinity of the oxygen molecule is 0.4480 eV [37], and the excitation energies for $^1O_2$ ($^1\Delta_g$) is 0.979 eV [38]. The sum of these energies, which can be used for the formation of the complexes, is 1.43 eV. Hence the formation of $\mathrm{P3HT^+ - O_2^-}$ with E_e of 1.9 eV is difficult, whereas $\mathrm{P3HOT^+ - O_2^-}$ with E_e of 1.2 and 1.6 eV can be generated by the reaction between P3HOT and $^1O_2$.

The formation of polarons by photo-irradiation of P3HOT will be also due to $^1O_2$ generated by photo-sensitization. The difference in the conversion efficiencies to polarons by the photo-irradiation and exposure to $^1O_2$ will be caused by photo-excitation of polarons. Figure 8 shows the probable mechanisms for the photo-degradation of P3HOT: a polaron ($\mathrm{P3HT^+ - O_2^-}$) is converted to a pair of neutral P3HOT and $^1O_2$ by the photo-excitation, and it returns to a polaron or causes the Diels–Alder addition followed by ring opening. The polaron can be photo-excited

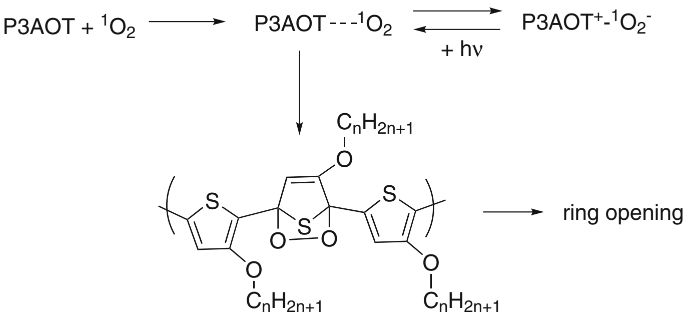

Fig. 8 Reactions between poly(3-alkoxythiophene) (P3AOT) and singlet oxygen under photo-irradiation

again and may convert to the neutral pair, whereas the addition and ring opening is irreversible. The π-conjugation thereby reduces.

Photo-irradiated P3HT will also degrade through the Diels–Alder addition of $^1O_2$. The addition of $^1O_2$ to the thienyl ring is probable for a reaction path to ring opening [39, 40].

The degradation through the complex of $P3HT^+$ and O_2^- has been suggested [40–42]. Aoyama et al. have proposed that O_2^- abstracts a proton at an α-position of hexyl groups of $P3HT^+$, a polyenyl radical of P3HT forms, and this decomposes [42, 43]. However, we believe that ring opening of this radical is improbable. As far as we know, thermal or photolytic reduction of π-conjugation of polyenyl radicals has not been reported. Furthermore, this mechanism cannot explain the degradation of poly(3-phenylthiophene) and poly[3-(1,1-dimethylpropyl)thiophene], which decomposed in the same way as P3HT [43].

Conclusions

$^1O_2$ reacted with P3HT and resulted in the decrease in the π-conjugation, contrary to the results of Manceau et al. [15]. We believe that $^1O_2$ plays a considerable role in the photo-degradation of polythiophene derivatives, and the addition of $^1O_2$ to the thienyl ring followed by ring opening is a most probable mechanism for the degradation.

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