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Photocatalytic properties of poly(3-octylthiophene-2,5-diyl) film blended with sensitizer for the degradation of iprobenfos fungicide

C. Wen[a], K. Hasegawa[a,*], T. Kanbara[a], S. Kagaya[a], T. Yamamoto[b]

[a] *Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930-8555, Japan*

[b] *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

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Abstract

The fluorescence behaviors of poly(3-octylthiophene-2,5-diyl) (POTh) containing photosensitizers such as perylene (Per) and 9-cyano-anthracence (CNA) and the degradation of iprobenfos fungicide by the POTh film blended with Per were investigated. The fluorescence intensity of POTh was enhanced by the addition of Per whereas it was not apparently exhibited when using CNA. The degradation rate of iprobenfos was examined under the conditions of bubbling O_2 and visible light irradiation. The rate was accelerated by blending Per and/or *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB) which is a cation scavenger with the POTh film. A photosensitizing process involving energy and/or electron transfer from excited Per to POTh and efficient charge separation gave an appropriate explanation for the accelerated degradation of iprobenfos, together with the process that we have previously reported for the degradation of iprobenfos by OH radical formed on the POTh film. The POTh film blended with Per and TMB was stable even after 100 h irradiation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polythiophene film; Photosensitizer; Fluorescence; Energy and/or electron transfer; Cation scavenger; Photocatalytic degradation; Visible light; Fungicide

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1. Introduction

Over the past few decades, a considerable number of studies have been made on the photocatalytic reduction of water, ketones, alkenes and CO_2 in the presence of triethylamine using π-conjugated polymers such as poly (*p*-pheny-lene), poly(pyridine-2,5-diyl) and poly(2,2′-bipyridine-5,5′-diyl) [1–3]. Furthermore, a photocatalytic CO_2 fixation reaction on phenol has been studied with poly(3-hexylthiophene-2,5-diyl) film [4]. The reasons for the high concern about π-conjugated polymers are their electrical and optical properties [5], ease of processability and fabrication, the possibility of large area coatings, and the possibility to design the materials through molecular engineering. Many attempts based on the π-conjugated polymers have also been extended by the addition of photosensitizers to give better energy and/or electron injection and transport properties for potential use [6–12].

Since energy migration and excimer formation are well known processes in polymeric systems, these processes might be expected to affect the photoinduced electron transfer depending on the structure of the polymer [13,14]. The characterization of the primary processes involved in the photoinduced production of charged species has been investigated by several researchers [15–18]. Washio et al. [16] studied the stabilization of poly(*N*-vinylcarbazole) cation ($PVCZ^+$) and showed that the $PVCZ^+$ was only scavenged by certain compounds of appreciably low ionization potential and this reaction could be contributed to electron transfer from the scavengers to cation radical.

Our previous research has focused on the photocatalytic degradation of four agrochemicals containing iprobenfos (IBP) with poly(3-octylthiophene-2,5-diyl) (POTh) and poly(2,5-dihexoxy-*p*-phenylene) (PHPP) films under UV-visible light irradiation [19]. We have recently studied the visible light-induced photocatalytic degradation of IBP using the POTh film and indicated the formation process of OH radical produced on the POTh film, the degradation paths of IBP by OH radical, and the acceleration of the degradation by the addition of Fe^{2+} [20].

To further develop the photocatalytic ability of the POTh film, first, we report the photosensitization of POTh by the fluorescence measurement of POTh containing the sensitizers and/or the cation scavengers in $CHCl_3$. Second, we report the acceleration of the degradation of IBP by the POTh

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[*] Corresponding author. Tel.: +81-76-445-6864; fax: +81-76-445-6703
E-mail address: hasegawa@eng.toyama-u.ac.jp (K. Hasegawa).

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Table 1
Electrochemical and photophysical properties of selected photosensitizers and cation scavengers[a]

Compound	E^0 ($D^{\bullet +}/D$) (V)[a]	E^0 ($A/A^{\bullet -}$) (V)[a]	E_s (eV)	Excitation λ_{ex} (nm in $CHCl_3$)	Emission λ_{em} (nm in $CHCl_3$)	Absorption λ_{max} (nm (ε, cm^2 mol^{-1}) in $CHCl_3$)
POTh	1.27	−0.73	2.00	444	569	440 (1.18×10^4)
Per	1.09	−1.76	2.85	389, 410, 437	445, 473, 505	439 (3.27×10^4)
CNA	1.70	−1.34	3.04	365, 382, 402	420, 442	384 (0.85×10^4)
TMB	0.56					
TMP	0.40					
TEA	1.20					

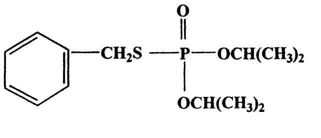
[a] Redox potentials are reported vs. NHE in CH_3CN [21,22], POTh was measured vs. NHE in $CHCl_3$ [20]. POTh: poly(3-octylthiophene-2,5-diyl). Photosensitizers: Per: perylene; CNA: 9-cyanoanthracene. Cation scavenger: TMB: *N*,*N*,*N*′,*N*′-tetramethylbenzidine; TMP: *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine; TEA: triethylamine.

films blended with the sensitizer and/or cation scavenger under the conditions of bubbling O_2 and visible light irradiation. Third, a photosensitizing process of the blended POTh film was suggested.

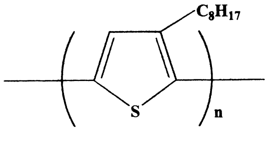
2. Experimental details

2.1. Materials

The IBP, perylene (Per), 9-cyanoanthracence (CNA), *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB), *N*,*N*,*N*′, *N*′-tetramethyl-*p*-phenylenediamine (TMP) and triethylamine (TEA) were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. The POTh was obtained from Aldrich Chemical Co., Inc. Some electrochemical and photophysical properties for these compounds are listed in Table 1. The structures of IBP and POTh are shown below.



Iprobenfos (IBP)



POTh

2.2. Preparation of the POTh films blended with the sensitizer and/or cation scavenger

The POTh film blended with Per (POTh:Per = 1:1 in the molar ratio) was prepared as follows. POTh (20 mg, 1.03×10^{-4} mol of monomer unit) and Per (26 mg, 1.03×10^{-4} mol) were dissolved in $CHCl_3$ (6 cm^3). The solution (0.30 cm^3) was painted onto a Pyrex test tube (18.4 mm i.d., 200 mm in length) and $CHCl_3$ was subsequently evaporated under ambient temperature and atmospheric pressure to produce the blended film (50 mm in height of the film). It was further dried up in vacuo. The surface area of the blended film was about 32 cm^2 and the areal density of Per was about 0.041 mg cm^{-2}. The POTh films blended with Per and TMB (POTh:Per:TMB = 1:1:x in the molar ratios, $x = 0$, 3.0×10^{-3}, 6.0×10^{-3}, 3.0×10^{-2}, 6.0×10^{-2}, 0.15) were also obtained by adding the corresponding amount of TMB to the $CHCl_3$ (6 cm^3) and by evaporating $CHCl_3$ as described above. To examine the photocatalytic effect of Per or TMB, the polystyrene (Ps) film blended with Per or TMB (Ps:Per or TMB = 1:1 in the molar ratio) was prepared by the same manner as that described for the preparation of the POTh film blended with Per.

According to microscopic observation of the POTh films blended with equimolar amount of Per or TMB, Per and TMB were considered to be dispersed in a molecular state among POTh chains because the violet films were very transparent. However, when the molar amount of added Per or TMB was doubled, the fine particles appeared on the surface of the POTh film which became opaque, this implies that Per or TMB should be dispersed in an aggregate state among POTh chains.

2.3. Procedure

A total of 10 cm^3 of the IBP aqueous solution (10 mg dm^{-3}) was put into the test tube coated with the blended POTh film and O_2 was bubbled at a flow rate of 60 cm^3 min^{-1} through the solution in the dark for 30 min at 30°C. After the adsorption of IBP on the blended film was reached to the equilibrium, the solution was irradiated at $\lambda > 380$ nm with a 400 W high-pressure mercury lamp ($\lambda =$ 405, 436, 546, and 577 nm) while circulating a mixed solution of 0.25 mol dm^{-3} $NaNO_3$ and 0.10 mol dm^{-3} $NaNO_2$. The quantity of light (I_0) entered the IBP solution (10 cm^3) was measured with potassium tris(oxalato)ferrate(III) actinometry and corrected for the quantum yields of Fe^{2+} formation. The I_0 was estimated to be 1.5×10^{17} photons s^{-1} for 380–500 nm.

2.4. Measurements

About 30 mm^3 of the irradiated solution was withdrawn in certain intervals and the concentration of IBP was measured by HPLC. The apparatus and the conditions used were the same as those reported previously [20].

Excitation and fluorescence spectra of POTh, Per, CNA, and POTh containing Per or CNA (1:1 and 1:2 in the molar ratios) in $CHCl_3$ were measured with Hitachi F-2500 fluorescence spectrophotometer after bubbling N_2. Each concentration of them was adjusted to 6.1×10^{-7} mol dm^{-3}. The ratio of the fluorescence intensity (F_c/F_0) of POTh (6.1×10^{-7} mol dm^{-3} monomer unit) or Per (6.1×10^{-7} mol dm^{-3}) was separately measured by changing the concentration of the cation scavengers from 0 to 1.50×10^{-3} mol dm^{-3} under bubbling N_2 where F_c and F_0 are the fluorescence intensities with and without the cation scavenger, respectively.

3. Results and discussion

3.1. Change in the excitation and fluorescence spectra of POTh by the addition of photosensitizers

The Per and CNA were chosen as photosensitizers because these compounds absorb light at >380 nm and exhibit strong fluorescence in $CHCl_3$. They have possibilities of interacting with the excited POTh molecules because the reduction potentials E^0 ($A/A^{\bullet -}$) of Per (−1.76 V) and CNA (−1.34 V) are lower than that of POTh (−0.73 V) as listed in Table 1. Strong fluorescence of Per is observed at 445 and 473 nm by the excited λ_{ex} at 410 nm, and that of CNA is found at 420 and 442 nm by the excited λ_{ex} at 402 nm.

Fig. 1A shows the excitation spectra of POTh on the addition of Per. The POTh has a peak maximum at 444 nm while for the 1:1 and 1:2 molar mixtures of POTh and Per, three new peaks appear at 389, 410 and 437 nm which are in good agreement with the excitation wavelengths of Per, and the peak intensities increase with increasing the concentration of Per. Fig. 1B indicates the fluorescence spectra of POTh on the addition of Per by the excited λ_{ex} at 470 nm which cannot be absorbed by Per. The spectra were distinguished while in the mixed solutions the shoulder broad bands revealed at 500–540 nm by comparing the spectrum of only POTh, and the positive enhancements in the fluorescence of POTh were simultaneously observed. The results led us to assume the formation of excited complex (exciplex) between POTh* and Per. However, the determination of the exciplex is a difficult procedure under our experimental conditions.

Fig. 2 displays the fluorescence spectra of Per on the addition of POTh by the excited λ_{ex} at 410 nm which can be absorbed by both POTh and Per. The fluorescence of Per in the 1:1 molar mixture of POTh and Per was quenched by comparing with that of only Per whereas that of POTh in this mixture showed small increment which closely corresponded to that obtained from Fig. 1B.

We also carried out the fluorescence measurement of POTh with another sensitizer, CNA to account for the photosensitizing effect. Fig. 3A and B illustrate the excitation and fluorescence spectra of POTh on the addition of CNA, respectively. In the excitation spectra of POTh (Fig. 3A), three peaks exhibit at 365, 382 and 402 nm which are assigned to the excitation wavelengths of CNA while the fluorescence spectra (Fig. 3B) are hardly changed when POTh is excited by λ_{ex} at 470 nm which cannot be absorbed by CNA. Fig. 3C illustrates the fluorescence spectra of CNA in the 1:1 molar mixture of POTh and CNA by the excited λ_{ex} at 402 nm which can be absorbed by both POTh and CNA. Nevertheless, the quenching of CNA was verified to be very small, and the fluorescence of POTh in the mixture (1:1) showed no increment which was in agreement with the one observed in Fig. 3B. Because the excitation condition of POTh is the same compared to the results obtained from Fig. 1B and Fig. 3B, the difference in the fluorescence spectra should mean energy and/or electron transfer between POTh and Per owing to the increase in the fluorescence of POTh. On the contrary, energy and/or electron transfer between POTh and CNA seems to be very difficult because that there are not the enhancement in fluorescence of POTh.

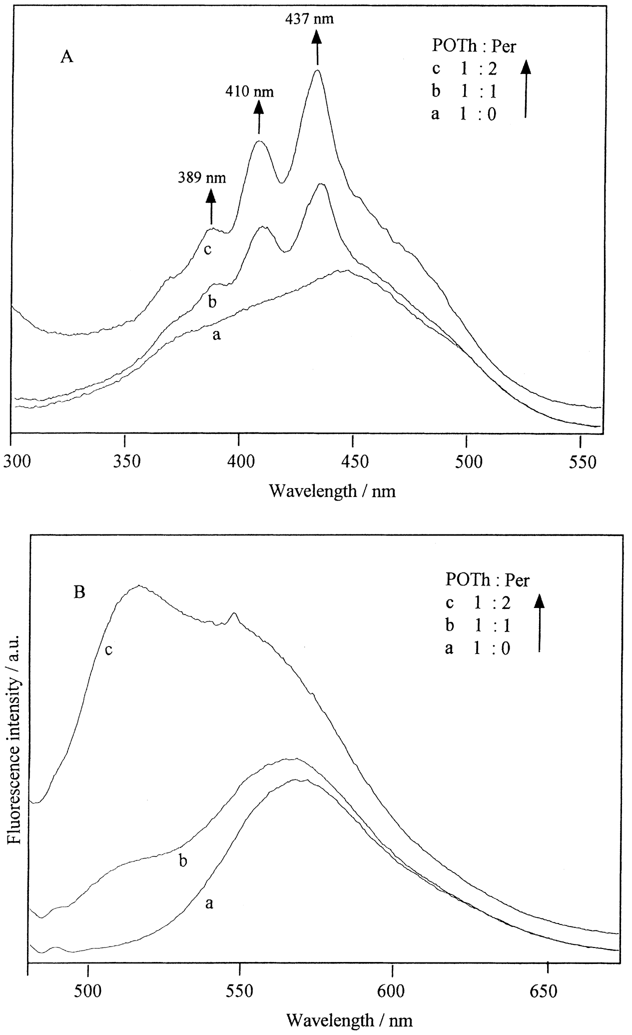


Fig. 1. Changes in (A) the excitation spectra (λ_{em} = 569 nm) and (B) the fluorescence spectra (λ_{ex} = 470 nm) of POTh (6.1×10^{-7} mol dm^{-3}) mixed with Per in $CHCl_3$ under N_2. The molar ratios of POTh and Per are (a) 1:0, (b) 1:1, and (c) 1:2.

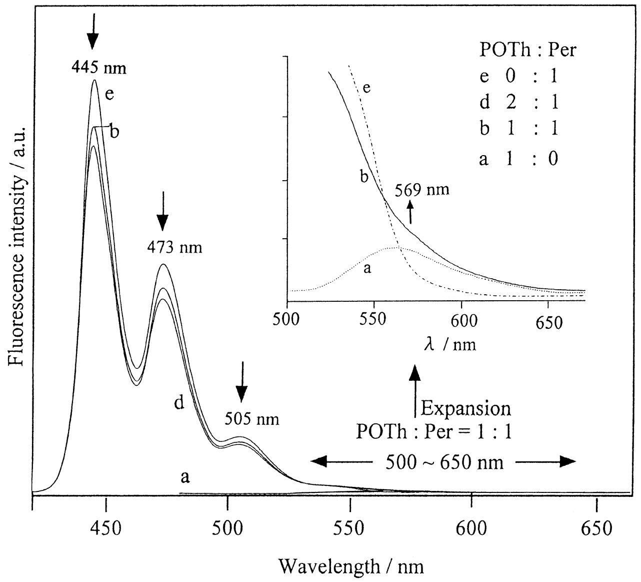


Fig. 2. Changes in the fluorescence spectra (λ_{ex} = 410 nm) of Per (6.1×10^{-7} mol dm^{-3}) mixed with POTh in $CHCl_3$ under N_2. The molar ratios of POTh and Per are (a) 1:0, (b) 1:1, (d) 2:1, and (e) 0:1.

On the basis of the experimental results and some pertinent suggestions of other researchers concerning the photosensitization [23–25], we attempted to suggest the photosensitizing process for POTh as follows:

$$\mathrm{POTh}\xrightarrow{h\nu}\mathrm{POTh}^* \quad (1)$$

$$\mathrm{Per}\xrightarrow{h\nu'}\mathrm{Per}^* \quad (2)$$

$$\mathrm{Per}^* + \mathrm{POTh} \rightarrow \mathrm{Per} + \mathrm{POTh}^* \quad (3)$$

$$\mathrm{Per}^* + \mathrm{POTh} \rightarrow \mathrm{Per}^{\bullet +} + \mathrm{POTh}^*(\mathrm{e}^-) \quad (4)$$

$$\mathrm{POTh}^*,\ \mathrm{POTh}^*(\mathrm{e}^-) \rightarrow \mathrm{POTh} + h\nu_{\mathrm{f}} \quad (5)$$

where Eqs. (3) and (4) exhibit that the interaction between POTh and Per occurs, that is, energy and/or electron of activated Per is injected into POTh which is readily quenched by emitting energy and/or electron obtained in the photosensitization, resulting in the increase of the fluorescence (Eq. (5)). The Per is considered to have two functions. It accepts a photogenerated energy and/or electron from its excited states and thus promotes effective transfer into the conduction band of POTh. However, we cannot clarify energy or electron transfer process which mainly occurs in the present system.

3.2. Changes in the fluorescence intensity of POTh by the addition of scavengers

We have reported a photocatalytic degradation of IBP by OH radical formed on the POTh film (Scheme 1) [20]. This mechanism gave a proper explanation for the degradation of IBP. However, it was insufficient to interpret the regeneration process of POTh from POTh$^{\bullet +}$.

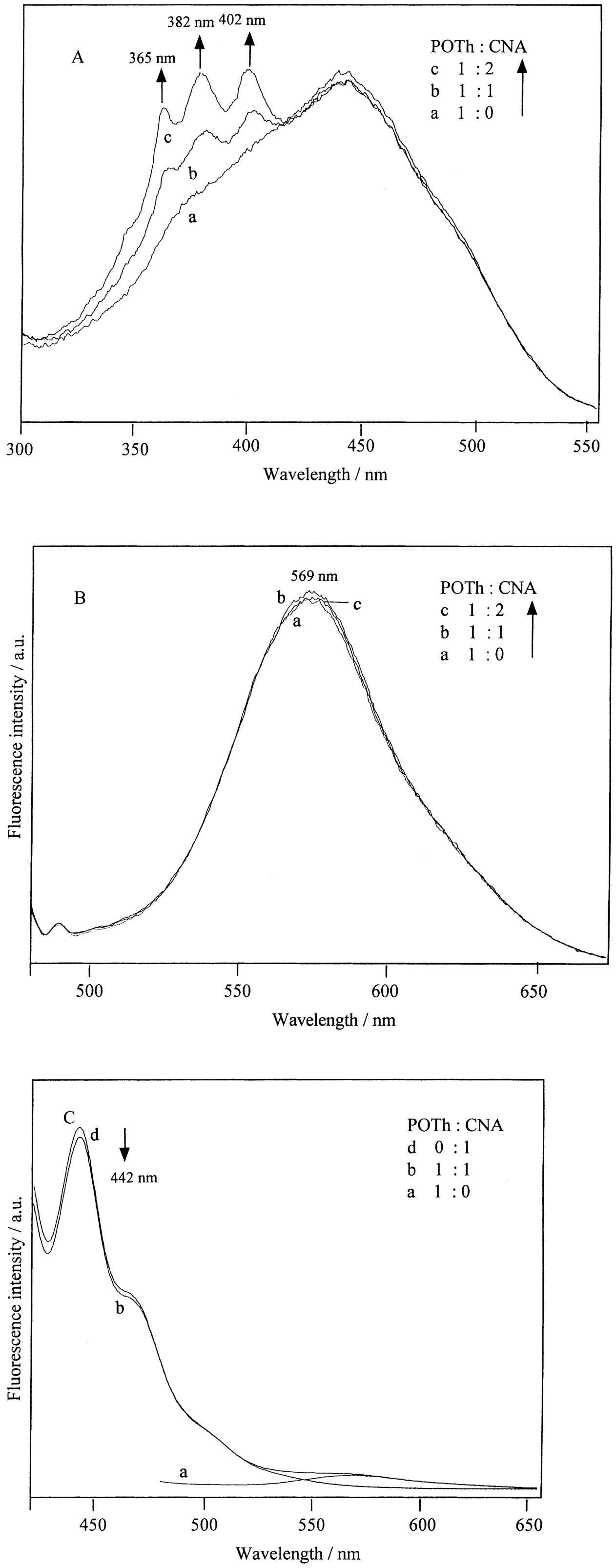
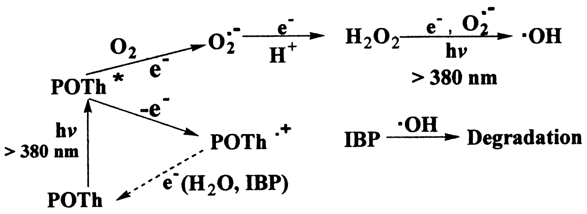


Fig. 3. Changes in (A) the excitation spectra (λ_{em} = 569 nm) and (B) the fluorescence spectra (λ_{ex} = 470 nm) of POTh (6.1×10^{-7} mol dm^{-3}) mixed with CNA, and (C) the fluorescence spectra (λ_{ex} = 402 nm) of CNA mixed with POTh. The molar ratios of POTh and CNA are (a) 1:0, (b) 1:1, (c) 1:2 and (d) 0:1 and all the spectra were measured in $CHCl_3$ under N_2.



Scheme 1. Outline of the photocatalytic degradation of IBP by the POTh film.

In a pulse radiolysis study on poly(*N*-vinylcarbazole) cation ($PVCZ^+$), TMB as a cation scavenger was employed to increase the rate of disappearance of the cation radical [16]. Considering the fact, three cation scavengers possessing lower redox potentials were selected under our experimental conditions. Fig. 4A and B show the changes in the ratio of fluorescence intensity (F_c/F_0) of POTh and Per against the concentration of each the cation scavenger, respectively. In Fig. 4A, only one TMB caused the increase in F_c/F_0 of POTh and the others gave the decrease or no change. In contrast, when the cation scavengers were added to Per, the integrated decreases or no change in F_c/F_0 of Per were found (Fig. 4B).

North and Treadaway [18] studied the energy or electron transfer process in polymer systems and proposed that the transfer of electronic energy between molecules may be influenced both by the relative diffusive motion of a donor and an acceptor and by radiationless migration of the donor excitation energy. Based on this theory, the increase in F_c/F_0 of POTh is probably due to effective electron transfer from TMB to $POTh^{\bullet+}$ whereas the decreases are difficult to account for electron transfer from the cation scavengers to $Per^{\bullet+}$.

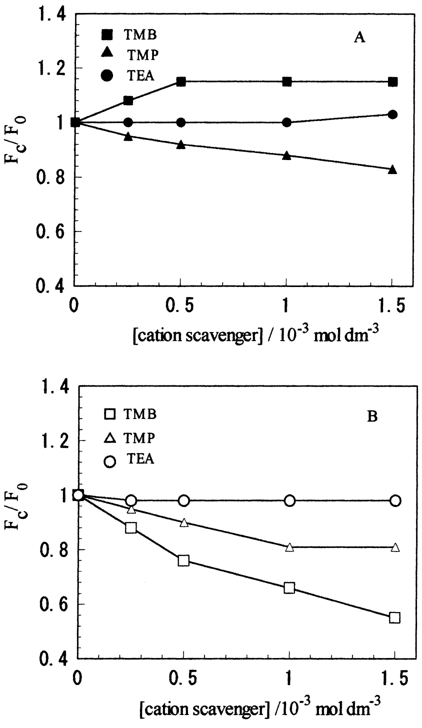


Fig. 4. Plots of the ratios of fluorescence intensity (F_c/F_0) of (A) POTh and (B) Per against the concentration of each cation scavenger in $CHCl_3$ under N_2. [POTh] = [Per]; $6.1\times10^{-7}\,mol\,dm^{-3}$, POTh; $\lambda_{ex} = 444\,nm$ and $\lambda_{em} = 569\,nm$, Per; $\lambda_{ex} = 410\,nm$ and $\lambda_{em} = 473\,nm$.

On the other hand, because the formation of $O_2^{\bullet-}$ is confirmed by the fluorescence quenching of POTh in $CHCl_3$ under O_2 [20], electron transfer between POTh and TMB and the regeneration of TMB are anticipated to proceed via Eqs. (6)–(8) in the presence of O_2.

$$POTh^* + O_2 \rightarrow POTh^{\bullet+} + O_2^{\bullet-} \tag{6}$$

$$POTh^{\bullet+} + TMB \rightarrow POTh + TMB^{\bullet+} \tag{7}$$

$$TMB^{\bullet+} + Per \rightarrow TMB + Per^{\bullet+} \tag{8}$$

Electron was injected from the excited POTh into oxygen to give $POTh^{\bullet+}$ and $O_2^{\bullet+}$ (Eq. (6)) [20], and resultant $POTh^{\bullet+}$ was reduced by TMB to generate POTh and $TMB^{\bullet+}$ (Eq. (7)). Moreover, TMB seems to be reproduced through the reduction of $TMB^{\bullet+}$ by Per (Eq. (8)) because that the fluorescence quenching of Per was observed with increasing the concentration of TMB as shown in Fig. 4B. It is known that $TMB^{\bullet+}$ is formed by electron transfer from TMB to $PVCZ^+$, and the time resolved absorption spectrum of $TMB^{\bullet+}$ has been also reported [16].

3.3. *Effects of photosensitizer and scavenger on the degradation of IBP using POTh film*

To confirm the photocatalytic effect of the POTh films blended with photosensitizer, the degradation of IBP by the POTh film blended with Per was compared with that using the POTh film under the conditions of bubbling O_2 and visible light irradiation. The experimental results are shown in Fig. 5. When the Ps film blended with Per is used, the degradation of IBP is similar to that of photolysis. This fact

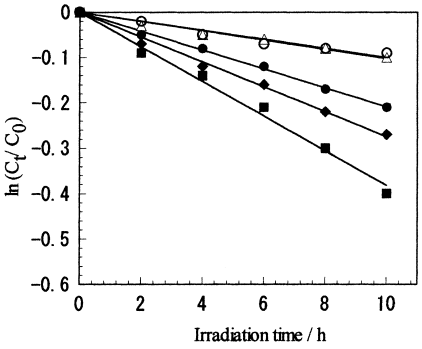


Fig. 5. Effects of the Per blended with the POTh film on the degradation of IBP under the conditions of bubbling O_2 and visible light irradiation. $\lambda > 380\,nm$, $[IBP] = 10\,mg\,dm^{-3}$, (○); photolysis, (△); Ps film blended with Per (1:1), (●); POTh film, (■) and (◆); POTh films blended with Per (POTh:Per = 1:1 (■) and 1:2 (◆)).

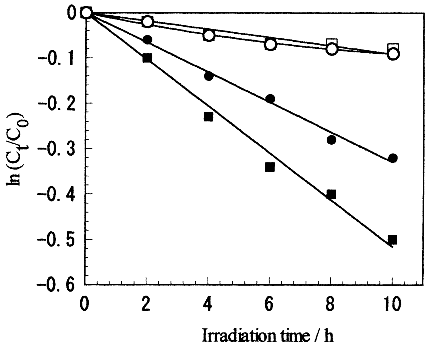
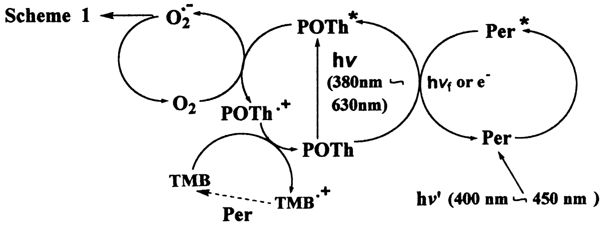


Fig. 6. Effects of the TMB blended with the Per-blended POTh film on the degradation of IBP under the conditions of bubbling O_2 and visible light irradiation. $\lambda > 380\,\mathrm{nm}$, $[\mathrm{IBP}] = 10\,\mathrm{mg\,dm^{-3}}$, (○); photolysis, (□); Ps film blended with TMB, POTh films blended with TMB (●) and Per and TMB (■).

implies that Per never works as a photocatalyst. The degradation rate of IBP using the POTh film blended with Per (1:1) is clearly accelerated according to a first-order kinetics with the concentration of IBP and the rates changed in the following order: POTh film blended with Per (1:1) > POTh film blended with Per (1:2) > POTh film. Thus, the degradation rate decreased when Per was doubled. The reversion may be explained by the turbidity of the POTh film which was caused by the poor dispersion of Per among POTh chains as noted in Section 2.2. The acceleration effects on the degradation of IBP are realized by the POTh film blended with Per.

Optimum amount of TMB added into the POTh film blended with Per (1:1) was examined to obtain a maximum degradation rate of IBP. The degradation rate was measured by varying the amount of TMB under bubbling O_2 and visible light irradiation for 2 h. The plots of $\ln(C_t/C_0)$ against the amount of blended TMB revealed an increase-decrease curve with a maximum at the areal density of about $0.0011\,\mathrm{mg\,cm^{-2}}$ (POTh:Per:TMB $= 1{:}1{:}3.0 \times 10^{-2}$ in molar ratio). Fig. 6 depicts the results of the degradation of IBP photocatalyzed by the POTh film blended with Per and the optimum amount of TMB. By comparing the results shown in Fig. 5, it is apparent that the degradation of IBP by the POTh film blended with TMB is further enhanced whereas the Ps film blended with TMB has no effect on the degradation rate. These results suggest that TMB is not a photocatalyst but a real cation scavenger that causes a probable cycle reaction within the POTh films. This also means that effective energy and/or electron transfer between the sensitizer (Per), the cation scavenger (TMB) and POTh can improve significantly the photocatalytic ability of the POTh film.

In our previous study [19], the degradation of IBP deviated from the first-order kinetics after about 5 h irradiation because of the partial photodegradation and/or peeling of the POTh film under the conditions of bubbling O_2 and irradiation at $\lambda > 290\,\mathrm{nm}$. In contrast when the POTh film blended with Per or TMB was used, the film became stable for the photodegradation and/or peeling, especially peeling of the POTh film blended with Per and TMB was not observed after 100 h irradiation under the conditions of bubbling O_2 and irradiation at $\lambda > 380\,\mathrm{nm}$. The reason is probably accounted by the cooperative action of the photosensitization and regeneration of POTh using both Per and TMB.



Scheme 2. Postulated photosensitizing process of the POTh film blended with Per and TMB under O_2.

3.4. Postulated photosensitizing process of the POTh film blended with Per and TMB

We have already reported a photocatalytic process of the POTh film [20] and the degradation paths of IBP caused by OH radical which was generated on the photoexcited POTh film through $O_2{}^{\bullet -}$ and H_2O_2 [20]. As a precursor of OH radical, the crucial role of $O_2{}^{\bullet -}$ was discussed in earlier studies [26,27]. The POTh film blended with Per and TMB has been found to be most effective for the degradation of IBP as shown in Fig. 6. Based on the results, postulated photosensitizing process is suggested in Scheme 2.

POTh and Per were excited after visible light irradiation (Eqs. (1) and (2)). The POTh was further sensitized by injecting energy and/or electron from Per* to POTh (Eqs. (3) and (4)). When TMB was added to POTh, TMB caused the increase in the ratio of fluorescence intensity of POTh (Fig. 4A) as contrasted with the result obtained from Fig. 4B. This shows that electron transfer from TMB to $\mathrm{POTh}^{\bullet +}$ is effective as compared with that from TMB to $\mathrm{Per}^{\bullet +}$. Therefore, it is easy to understand the reduction of $\mathrm{POTh}^{\bullet +}$ by adding TMB under the conditions of bubbling O_2 and visible light (Eq. (7)). Since the Ps films blended with Per or TMB did not cause the degradation of IBP, both Per and TMB could not act as photocatalysts which transfer the excited electrons to O_2 to give $O_2{}^{\bullet -}$. The POTh film blended with Per and TMB accelerated the degradation of IBP because that a new feed of $O_2{}^{\bullet -}$ could be formed during the photosensitizing process.

4. Conclusion

We have explored the photosensitization of POTh by employing Per and TMB as a sensitizer and a cation scavenger and succeeded in accelerating the visible light-induced catalytic degradation of IBP. When Per or TMB was added to POTh, the fluorescence intensity of POTh was enhanced in $CHCl_3$, mainly due to the effective energy and/or electron transfer. The POTh film blended with Per and TMB accelerated the degradation of IBP and the effect could be ascribed to the enhancement in $O_2^{\bullet -}$ production.

Considering these facts, a postulated photosensitizing process (Scheme 2) was suggested, and the combination of the Schemes 1 and 2 offered proper interpretations for the high photocatalytic properties of the blended POTh film. Thus, the degradation of IBP was found to proceed through the photosensitizing degradation in addition to the degradation initiated by the excitation of the POTh film.

It should also be mentioned that the blended POTh film was very stable because that the photosensitization of POTh happened under condition blended with Per and TMB.

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