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Photochemical reactions of poly(3-butoxythiophene-2,5-diyl) with chloroform

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Abstract: Photochemical reactions of poly(3-butoxythiophene-2,5-diyl) with chloroform under irradiation with light were studied. The reactions were separately carried out under air, oxygen, and nitrogen. The obtained results showed that this reaction belongs to the pseudo-first-order reaction with a rate constant k_{obs} of 1.4×10^{-5} s^{-1} at room temperature. The presence or absence of air, oxygen, and nitrogen did not have obvious effects on the reaction rate under irradiation with light.

Key words: Poly(3-butoxythiophene-2,5-diyl), Photochemical reaction, Kinetics
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INTRODUCTION

π-conjugated polymers have received a great deal of attention because of their unique chemical and physical properties, including electrochromism, electrically conducting properties, chemical sensing ability, and electroluminescent properties. Their structures, synthetic methodologies, and physical and chemical properties were intensely studied in the past two decades (Friend *et al.*, 1999; Heeger, 2001; Yamamoto, 2002). Especially, processable derivatives of polythiophene have many attractive characteristics for application to electronic and optical devices such as polymer light emitting diodes (PLEDs), and they show unique electrical and electro-optical properties. In addition, the polymers possess good environmental stability and structural versatility (Friend *et al.*, 1999; Heeger, 2001; Yamamoto *et al.*, 2003; Ikenoue *et al.*, 1990; 1991; Chen and Hua, 1993).

Although, photochemical reactions of some π-conjugated polymers and other organic compounds with $CHCl_3$ had been studied by several research groups (Petrushenko *et al.*, 2001; Kong *et al.*, 2003), to our best knowledge, photochemical reaction of poly(3-butoxythiophene-2,5-diyl) (P3OBuTh) with $CHCl_3$ has not been reported. Herein, we report results of the study on the photochemical reactions of P3OBuTh under air, oxygen, and nitrogen, focusing on the kinetic aspects of the photochemical reaction.

EXPERIMENTAL DETAILS

Poly(3-butoxythiophene-2,5-diyl) was synthesized according to our previous reports (Miyazaki *et al.*, 1993; Yamamoto *et al.*, 1997). All other reagents were purchased from Fluka and Aldrich chemical companies and were used as received.

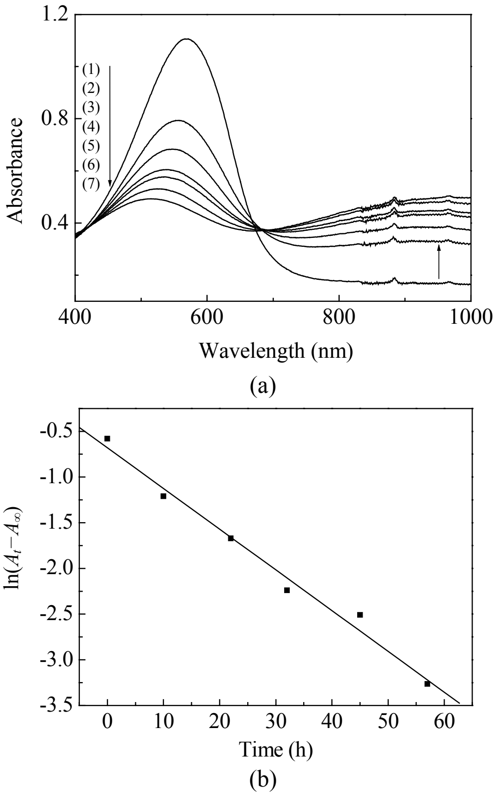
A Schlenk-tube type UV-Vis cell was used to control the atmosphere under which the measurements were carried out. The cell had sufficient space for gases to determine their effects on the reaction of the polymer with chloroform, and the concentration of gases in the space was considered almost unchanged during the reaction. Changes in the UV-Vis spectrum of the polymer solution were followed with a Shimadzu UV-8000 spectrometer. To determine the effects of oxygen on the photochemical reaction, the experiments were carried out separately under air, O_2, and N_2. All the measurements were performed at room temperature (about 25 °C).

Irradiation of the reaction system with light was carried out by using MITSUBISHI/OSRAM FLR/M/36 fluorescent lamps as the source of light; illuminance of light in the reaction system was approximately 400 lx.

RESULTS AND DISCUSSIONS

An interesting photochemical phenomenon was that the reddish color of a freshly prepared $CHCl_3$ solution of P3OBuTh changed to dark blue upon storage of the solution under ambient room-light from the fluorescent lamps described in the Experimental part. Finally, after several days, formation of a precipitate was observed at the bottom of the UV-Vis cell. Fig.1a shows changes of the UV-Vis spectrum during the photochemical reaction of P3OBuTh with $CHCl_3$ under air; the solution in the UV-Vis cell was left at room temperature under irradiation with ambient room-light.

As shown in Fig.1a, the original peak of neutral P3OBuTh at about 570 nm decreases with time, while a new peak around 930 nm gradually increases. Similar changes were not observed with other polythiophenes such as poly(3-alkylthiophene-2,5-diyl); they were very stable in their chloroform solutions even under irradiation with the ultraviolet light. As shown in Fig.2, P3OBuTh was stable without light, especially in the absence of oxygen. On irradiation with light, the photochemical reaction started without an induction period. As shown in Fig.2, the atmosphere does not have significant effect on the photochemical reaction. For a similar photochemical reaction of π-conjugated poly(phenothiazine), Jenekhe (Kong *et al.*, 2003) proposed a reaction process involving generation of phenothiazine radial cation and reaction of the radical cation with $CHCl_3$, on the basis of reported results (Petrushenko *et al.*, 2001). Phenothiazine is a highly electron-donating unit, facilitating formation of the radial cation under irradiation with light. Thiophene is also an electron-donating unit, whose electron-donating ability is enhanced by attachment of the electron-donating butoxy group at the thiophene unit in P3OBuTh.



(a)

(b)

Fig.1 (a) Changes of UV-Vis spectra during the photochemical reactions of P3OBuTh with $CHCl_3$ under air. Time: (1) 0 h, (2) 10 h, (3) 22 h, (4) 32 h, (5) 45 h, (6) 57 h, (7) 70 h; (b) Plots of ln(A_t-A_∞) vs t at 570 nm at room temperature. Illuminance of light was approximately 400 lx (from the fluorescent lamp described in the experimental part)

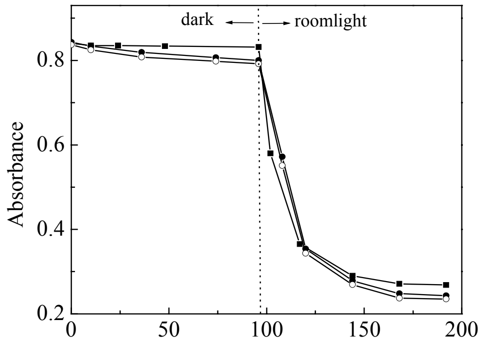


Fig.2 Changes of UV-Vis absorption at 570 nm of P3OBuTh in $CHCl_3$: (■) under N_2; (●) under air; (○) under O_2

Consequently similar formation of radical cation in P3OBuTh under irradiation with light is conceivable. The photochemical reaction of P3OBuTh may proceed through the reaction of the photoexcited

P3OBuTh molecule with $CHCl_3$ to produce the radical cation of P3OBuTh (or p-doped P3OBuTh). The low reactivity of poly(3-alkylthiophene-2,5-diyl) toward the photochemical process is attributed to insufficient electron-donating ability of the polymer compared with that of P3OBuTh; highly electron-donating nature of P3OBuTh has been reported (Miyazaki *et al*., 1993; Yamamoto *et al*., 1997). As depicted in Fig.1b, the photochemical reaction between P3OBuTh and $CHCl_3$ obeys pseudo-first-order rate law and the first-order rate constant was determined. The standard integrated expression below was applied to treat experimental data.

$$\ln(A_t - A_\infty) = -k_{\mathrm{obs}}t + \ln(A_0 - A_\infty) \qquad (1)$$

where A_0, A_t, A_∞ are the absorbance at 570 nm at the beginning, at time t, and at the end of the reaction, respectively. Data plots obtained by using Eq.(1) give a straight line Fig.1b, from whose slope, a pseudo-first-order rate constant of $k_{\mathrm{obs}}=1.38\times10^{-5}\ \mathrm{s}^{-1}$ was calculated. As discussed above, the photochemical reaction is considered to consist of the following elementary reactions based on reported photochemical reactions of electron-donating organic compounds and halogenated compounds (Petrushenko *et al*., 2001; Kong *et al*., 2003; Shimamori *et al*., 1993).

$$\mathrm{P3OBuTh} \xrightarrow{h\gamma} \mathrm{P3OBuTh}^{*}$$

$$\mathrm{P3OBuTh}^{*} + \mathrm{CHCl_3} \rightarrow [(\mathrm{P3OBuTh}^{+\cdot}\mathrm{Cl}^{-})\mathrm{CHCl}_2^{\cdot}]$$

$$[(\mathrm{P3OBuTh}^{+\cdot}\mathrm{Cl}^{-})\mathrm{CHCl}_2^{\cdot}] \rightarrow (\mathrm{P3OBuTh}^{+}\cdot\mathrm{Cl}^{-}) + \cdot\mathrm{CHCl_2}$$

In the above chemical equations, $\mathrm{P3OBuTh}^{*}$ exhibits photoexcited P3OBuTh molecule. In the third equation, the $\cdot CHCl_2$ radical species are considered to be converted into new compounds such as 1,1,2,2-tetrachloroethane. The above shown three step process leads to the first one-electron oxidation (or p-doping) of P3OBuTh, and repeated photochemical reaction is considered to lead to further p-doping of P3OBuTh. Reactions involving radical species are sometimes affected by O_2, although no obvious effect of O_2 was observed for the present oxidation of P3OBuTh. The photoactivated P3OBuTh seems to have much higher reactivity toward chloroform than toward O_2.

As outlined in this work, the photochemical reaction of electron-donative poly(3-butoxythiophene-2,5-diyl) with chloroform under irradiation with light has been followed. The photochemical reaction obeys the pseudo-first-order rate law, and the rate constant k_{obs} of $1.38\times10^{-5}\ \mathrm{s}^{-1}$ has been estimated.

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