CHEMISTRY LETTERS, pp. 585-588, 1993.

Ionic Conductivity Induced by Photooxidation of Ferrocene in Polymer Film Containing Organotin Compound

Tatsuo FUJINAMI,* Nobuo KAWAHARA, Shizuyoshi SAKAI, and Masami OGITA†
Department of Materials Science, Faculty of Engineering,
Shizuoka University, Hamamatsu 432
† College of Engineering, Shizuoka University, Hamamatsu 432

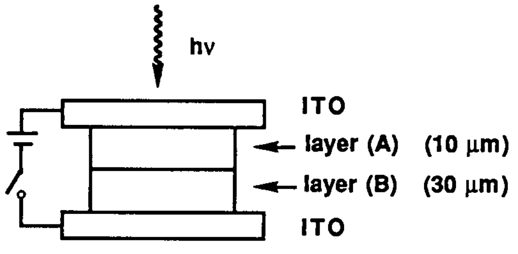
Ionic conductivity of poly(ethyl methacrylate) film containing photooxidizable dibutylferrocene and bromotributylstannane was induced by UV light irradiation in contact with the anion-conducting polymer film containing a cobaltocenium salt. The enhanced ionic conductivity decreased in the dark.

Recently, some attempts have been made to get a photoinduced or a photo-controlled ionic conductivity of polymer films. Kimura et al. reported the photochemical control of ionic conduction by crowned spiropyran which suppressed the Li^+ conductivity due to the enhanced Li^+ complexation of the photoisomerized merocyanine form.1) They also reported the photosensitive ionic conductivity of poly(vinyl chloride) film containing azobenzene liquid crystal and lithium perchlorate - crown complex,2) and it's application to the image storage.3) Hirohashi et al. reported the ionic conductivity induced by the photodissociation of triphenylmethanol4) and the control of the ionic conductivity based on the decrease of the ion mobility in the photo-crosslinked polymer by UV light irradiation.5,6)

We found that the addition of organotin compound enhanced remarkably the anionic conductivity of poly(vinyl chloride) film containing quarternary ammonium salt.7) We report here the photoinduced anionic conductivity of the composite film consisting of poly(ethyl methacrylate) (PEMA), bromotributylstannane and a photooxidizable ferrocene derivative8) under UV light irradiation in contact with the anion-conducting polymer film containing a cobaltocenium salt.

The cell was constructed of bilayer films between transparent ITO electrodes as shown in Fig. 1. Layer (A) consisted of PEMA, bromotributylstannane, and a ferrocene derivative. Layer (B) consisted of PEMA, bromotributylstannane, 1,1'-bis(octylaminocarbonyl)cobaltocenium bromide,[9] and tetrabutylammonium bromide. Each film was prepared by the casting from tetrahydrofuran - methanol solution on ITO glass plate, then they were pressed together to make bilayer films. The photoinduced current of the cell at DC 1.0 V increased under UV light irradiation and decreased in the dark. The change of the photocurrent was dependent on the substituent of ferrocene (Fig. 2). It has been known that electron-donating substituents promote the photooxidation of ferrocene.[10] More oxidizable dibutyl ferrocene **1** was more photoresponsive than ferrocene **3**, **4** having electron-withdrawing butylyl group.

Redox reactions of ferrocene derivatives in the layer (A) and the cobaltocenium salt in the layer (B) under UV light irradiation and in the dark are represented by Scheme 1. In the experiments using an opaque anion-conducting polymer layer between the layer (A) and the layer (B), the irradiation on the layer (A) induced the photocurrent but the irradiation on the layer (B) did not affect. These results show that ferrocene derivatives are photoexcited but the



A : $Fc\text{-}R_2$ (0.5 mmol), Bu_3SnBr(2.0 mmol), PEMA(1.0 g).

B : $Co(C_5H_4CONHC_8H_{17})_2Br$ (0.5 mmol), Bu_4NBr(0.5 mmol), Bu_3SnBr(2.0 mmol), PEMA(1.0 g).

Fig. 1. Cell configuration.

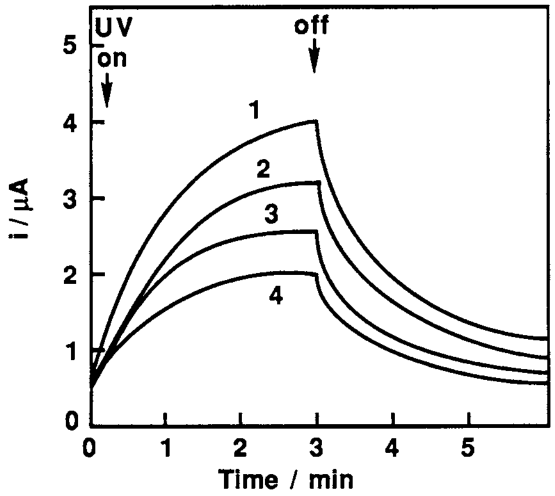
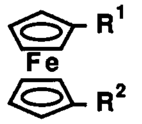


Fig. 2. Photoinduced current of bilayer films.



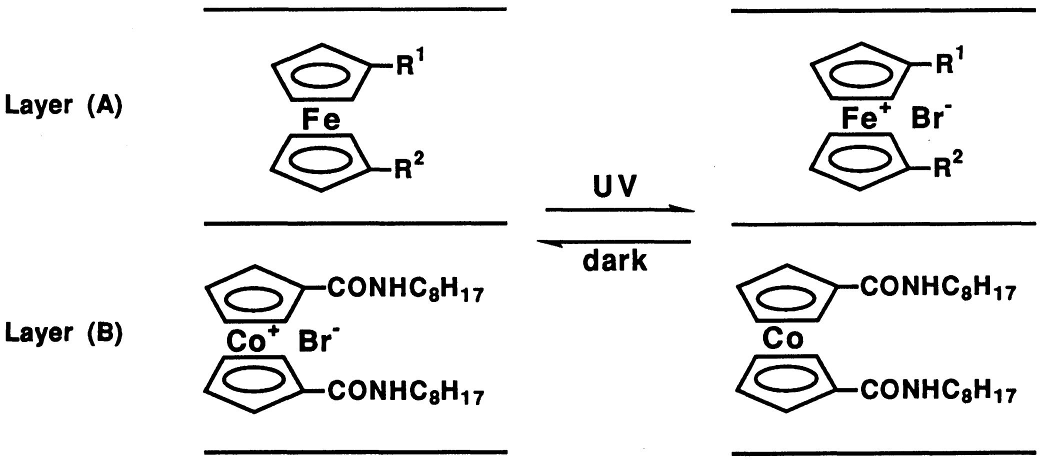
1: $R^1=R^2=C_4H_9$

2: $R^1=C_4H_9$, $R^2=H$

3: $R^1=(CO)C_3H_7$, $R^2=H$

4: $R^1=R^2=(CO)C_3H_7$

cobaltocenium salt is not photosensitive. The photooxidation of dibutylferrocene in the cell was supported by the appearance of the absorbance (λ_{max} 618 nm) of the ferrocenium ion (Fig. 3). The reduction of the cobaltocenium salt was suggested by the decrease of the cobaltocenium band (λ_{max} 363 nm) and the appearance of the cobaltocene band (λ_{max} 440 nm) in the spectrum of the layer (B) after irradiation. No photocurrent was observed without the cobaltocenium salt in the layer (B). Electronic conductivity of the cell was low (3.7×10^{-8} S cm^{-1}) but necessary for the electron transfer accompanied by the photoredox reactions between the layer (A) and the layer (B).



Scheme 1.

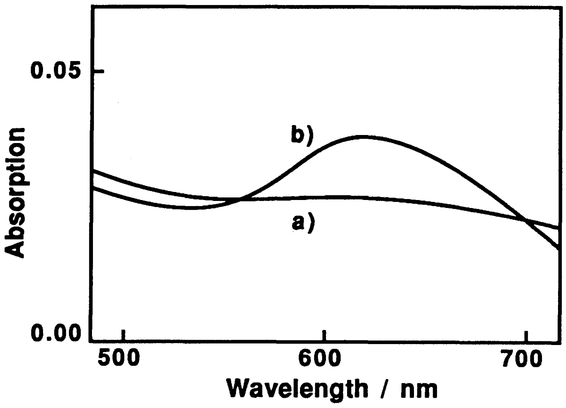


Fig. 3. Absorption spectra of bilayer films. a) under dark condition, b) after UV light irradiation for 5 min.

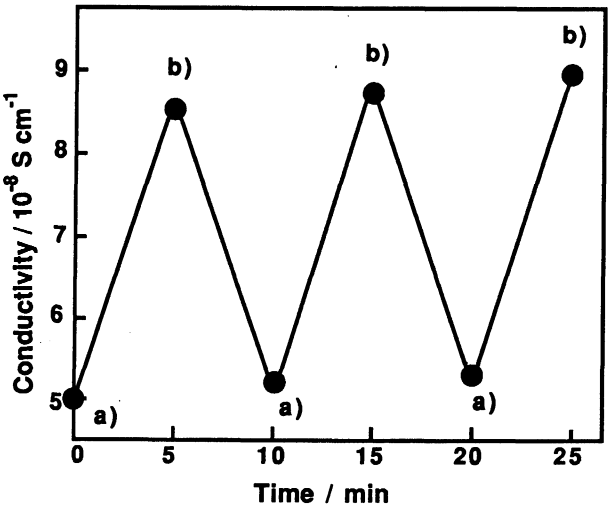


Fig. 4. Ionic conductivity changes of bilayer films on UV light irradiation. a) UV light on, b) UV light off.

Photochemical change of ionic conductivity of the cell containing **1** was measured by the AC impedance method at 25 °C (Fig. 4). The ionic conductivity was induced by UV light irradiation in the open circuit and the enhanced conductivity decreased to the initial level in the dark. This photoinduced change of ionic conductivity was reversible. Before UV light irradiation, the layer (B) was ionically conductive (3.2×10^{-7} S cm^{-1}) but the ferrocene layer (A) had not ionic species. Under UV light irradiation, bromide ion should transfer from the cobaltocenium salt layer (B) to the ferrocene layer (A) in which bromotributylstannane can transport bromide ion in the polymer. In the dark, the reproduction of the stable ferrocene and cobaltocenium complexes should occur to reduce the conductivity due to the decrease of Br$^-$ concentration in the ferrocene layer (A). When DC 1.0 V was applied during irradiation to promote the oxidation of **1** and the reduction of cobaltocenium salt, photoinduced conductivity rised to 1.3×10^{-7} S cm^{-1}.

In conclution, the bilayer system based on the redox couple was able to give the photoinduced ionic conductivity in the polymer film containing organotin compound. Further investigations are now progressing to obtain the fast and large change of ionic conductivity induced by irradiation using other redox systems.

References

1) K. Kimura, T. Yamashita, and M. Yokoyama, *Chem. Lett.*, **1991**, 965.

2) K. Kimura, T. Suzuki, and M. Yokoyama, *Chem. Lett.*, **1989**, 227.

3) K. Kimura, T. Suzuki, and M. Yokoyama, *J. Chem. Soc., Chem. Commun.*, **1989**, 1570.

4) N. Kubo, N. Kobayashi, and R. Hirohashi, *Polym. Bull.*, **28**, 69(1992).

5) K. Kobayashi, N. Kawai, M. Sadakuni, R. Hirohashi, and E. Tsuchida, *New Polym. Mat.*, **2**, 103(1990).

6) N. Kubo, K. Ikeda, and R. Hirohashi, *Nippon Kagaku Kaishi*, **1992**, 1148.

7) T. Fujinami, H. Ishikawa, H. Takaoka, S. Fukuzawa, S. Sakai, and M. Ogita, *Chem. Lett.*, **1990**, 127.

8) T. Akiyama, Y. Hashi, G. Goto, and A. Sugimori, *Bull. Chem. Soc. Jpn.*, **46**, 1851(1973); T. Akiyama, S. Sugimori, and H. Hermann, *Bull. Chem. Soc. Jpn.*, **46**, 1855(1973).

9) 1,1'-Bis(octylaminocarbonyl)cobaltocenium bromide was prepared by the reaction of 1,1'bis(chloro-carbonyl) cobartocenium hexafluorophosphate with octylamine, followed by the exchange of anion. Octyl group was necessary to be soluble in the polymer film composed of PEMA and bromotributylstannane.

10) T. Akiyama, T. Kitamura, T. Kato, and H. Watanabe, *Bull. Chem. Soc. Jpn.*, **50**, 1137(1977).

(Received November 17, 1992)