

Photochromic Films Prepared by Oxidation Polymerization of a Diarylethene Having Phenol Moieties

Kingo Uchida,* Atsushi Takata, Shinichiro Nakamura,[†] and Masahiro Irie^{††}

Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-2194

[†]MCC-Group Science and Technology Research Center, Mitsubishi Chemical Corporation, 1000 Kamoshida, Yokohama 227-8502

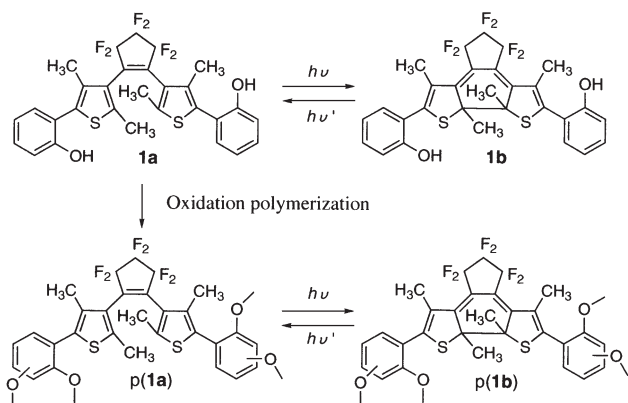
^{††}Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University and CREST, Japan Science and Technology Corporation (JST), 6-10-1 Hakozaiki, Fukuoka 812-8581

(Received January 24, 2002; CL-020083)

Photochromic films containing diarylethene chromophores were prepared by oxidation polymerization of a diarylethene having phenol moieties. Upon alternate irradiation with UV and visible light, the polymer films exhibited coloration/decoloration cycles. The films were amorphous and kept the state after one year storage at room temperature.

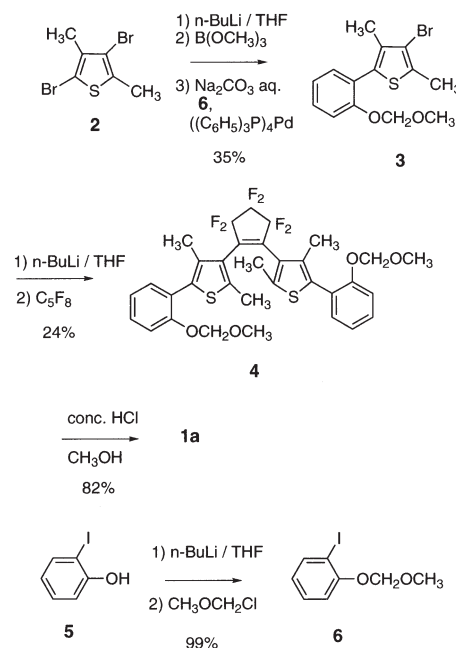
Photochromic molecules attract much attention from both fundamental as well as practical points of view because of their potential for applications to optical devices such as optical memories and switches.¹ Among the photochromic compounds, diarylethenes are regarded as the best candidate, because of the thermal stability of their both isomers and the fatigue resistant property.² For the fabrication of thin photochromic films for the applications, various methods have been employed; for example, the dispersion of the dyes into polymer matrices,³ LB films of diarylethenes having long alkyl chain,⁴ and preparation of crystal⁵ or amorphous films of diarylethenes having bulky substituents.⁶

Dispersing the photochromic molecules into polymer matrices is the most convenient method to prepare the photochromic films.³ Although increment of the dye concentration is strongly desired to enhance the photochromic efficiency, preparation of films containing high concentration of the dyes is not easy because segregation takes place to some extent after long term storage. Bulk amorphous and crystalline photochromic films have been extensively studied for the purpose. We now propose a new method to form thin films by oxidation polymerization.



A diarylethene derivative 1,2-bis[2,4-dimethyl-5-(*o*-hydroxyphenyl)-3-thienyl]hexafluorocyclopentene (**1a**)⁷ was synthesized from 2,4-dibromo-3,5-dimethylthiophene **2**⁸ as shown in Scheme 1. Figure 1 illustrates the absorption spectral changes of

the hexane solution of **1a** (3.8×10^{-5} mol/l). Upon UV light (280 nm) irradiation, the solution turned to blue and absorption bands appeared at 545 (ϵ : 1.1×10^4 dm³ mol⁻¹ cm⁻¹) and 347 nm (ϵ : 1.1×10^4 dm³ mol⁻¹ cm⁻¹) attributable to **1b**, and the peak of **1a** at 254 nm (ϵ : 2.1×10^4 dm³ mol⁻¹ cm⁻¹) was suppressed. Upon visible light (λ > 500 nm) irradiation, the blue color was bleached and regenerated the open-ring isomer **1a**. The quantum yields of cyclization and cycloreversion of **1** were 0.19 (measured by 280 nm light irradiation) and 0.03 (measured by 492 nm light irradiation), respectively.



Scheme 1. Synthetic route of **1a**.

The diarylethene **1a** was polymerized according to Hay's method.⁹ To the *o*-dichlorobenzene solution (10 ml) containing 0.8 mg of N,N,N',N'-tetramethylethylenediamine and 10 mg of copper (I) bromide, oxygen gas (300 ml/min) was introduced at 85 °C. Diarylethene **1a** (2.5 g, 4.3×10^{-3} mol) in 10 ml of *o*-dichlorobenzene was slowly added to the mixture and stirred for 1.5 h at the temperature. The reaction mixture was poured into a methanol solution (2.5 l) containing 25 ml of hydrochloric acid and 25 ml of phosphinic acid. The precipitate was isolated by centrifuge (3500 rpm, 5 min) and dissolved into a small amount of chloroform. The pre-polymer solution was casted on a quartz plate. After the solvent was evaporated at room temperature a thin film was prepared. The film was insoluble to any solvents. The

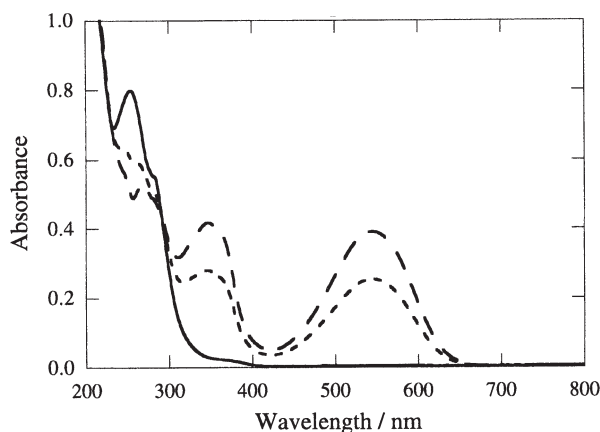


Figure 1. Absorption spectra of hexane solutions of **1a** (3.8×10^{-5} mol/l, solid line), **1b** (broken line), and photo-stationary state (dotted line) under irradiation with 280 nm light.

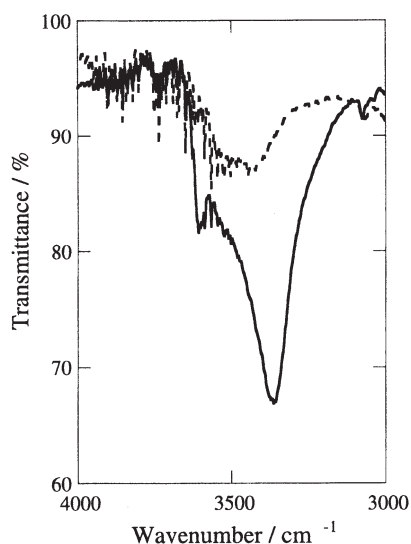


Figure 2. IR spectral changes of the diarylethene **1a** before (solid line) and after polymerization (broken line).

absorption band attributable OH group disappeared in the FT IR spectrum of the polymer film as shown in Figure 2.

The polymer film p(**1a**) showed a reversible photochromic reaction by alternate irradiation with UV and visible light. The spectral change of the film is shown in Figure 3. X-ray diffraction measurement showed no peaks even after 1 year storage at room temperature. This indicates that the polymer film is in the amorphous phase. The new amorphous photochromic film will be applicable for wave-guide and novel recording media.

This work was supported by Sumitomo Foundation, a Grant-in-Aid for Scientific Research (C) No. 12640567 from the

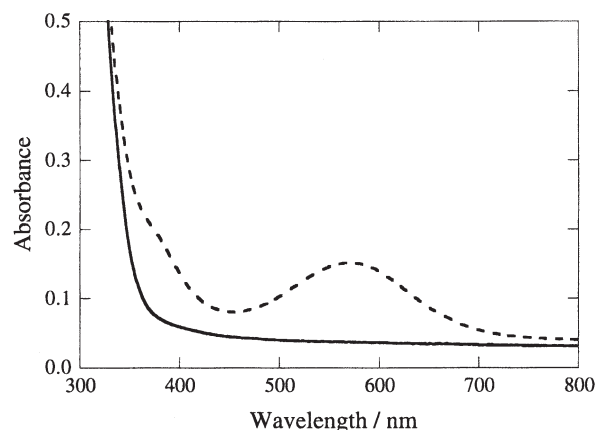


Figure 3. Absorption spectral changes of the amorphous film (3 μ m thickness) prepared by oxidation polymerization of **1a**; solid line: before UV irradiation, broken line: after UV irradiation.

Ministry of Education, Science, Sports, and Culture, and by CREST and ACT of Japan Science and Technology Cooperation (JST).

References and Notes

- 1 H. Duerr and H. Bouas-Laurent, "Photochromism: Molecules and Systems," Elsevir, Amsterdam (1990).
- 2 M. Irie, *Chem. Rev.*, **100**, 1685 (2000); M. Irie and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988); M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **73**, 985 (1998); S. H. Kawai, S. L. Gilat, and J.-M. Lehn, *Chem. Eur. J.*, **1**, 285 (1995); G. M. Tsivgoulis and J.-M. Lehn, *Chem. Eur. J.*, **2**, 1399 (1996).
- 3 N. Tanio and M. Irie, *Jpn. J. Appl. Phys.*, **33**, 1914 (1994); T. Tsujioka, F. Tatzono, T. Harada, K. Kuroki, and M. Irie, *Jpn. J. Appl. Phys.*, **33**, 5788 (1994).
- 4 S. Abe, K. Uchida, I. Yamazaki, and M. Irie, *Langmuir*, **13**, 5504 (1997).
- 5 S. Kobatake, K. Shibata, K. Uchida, and M. Irie, *J. Am. Chem. Soc.*, **122**, 12135 (2000); M. Irie, T. Lifka, S. Kobatake, and N. Kato, *J. Am. Chem. Soc.*, **122**, 4871 (2000); T. Yamada, S. Kobatake, K. Muto, and M. Irie, *J. Am. Chem. Soc.*, **122**, 1589 (2000); M. Irie, K. Uchida, T. Eriguchi, and H. Tsuzuki, *Chem. Lett.*, **1995**, 899.
- 6 T. Kawai, N. Fukuda, D. Groeschl, S. Kobatake, and M. Irie, *Jpn. J. Appl. Phys.*, **38**, L1194 (1999); H. Utsumi, D. Nagahama, H. Nakano, and Y. Shiota, *J. Mater. Chem.*, **10**, 2436 (2000).
- 7 **1a**: colorless needles; mp 93.5–94.9 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) = 1.82 (s, 3H, ap 2-Me), 1.88 (s, 3H, p 2-Me), 2.36 (s, 3H, ap 4-Me), 2.42 (s, 3H, p 4-Me), 6.93–7.00 ppm (m, 8H, aromatic protons); (the ratio of ap: p isomers = 1 : 1).
- 8 M. Irie, K. Sakemura, M. Okinaka, and K. Uchida, *J. Org. Chem.*, **60**, 8305 (1995).
- 9 A. S. Hay, *Polym. Eng. Sci.*, **16**, 1 (1976).