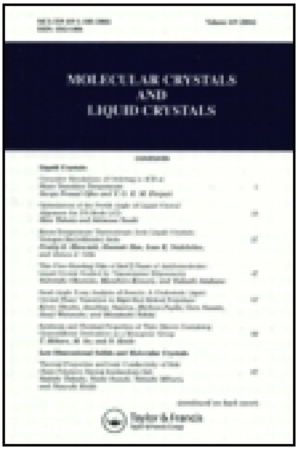

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Photochromic Reactions of the Oxidation Polymer Film of a Diarylethene Derivative

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Photochromic Reactions of the Oxidation Polymer Film of a Diarylethene Derivative

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*Photochromic ring-closure reaction of a network polymer film (**Poly BPOH-C**) obtained by oxidation polymerization of the closed-ring isomer (**BPOH-C**) of 1,2-bis[2-methyl-6-(o-hydroxyphenyl)-1-benzothiophen-3-yl]hexafluorocyclopentene (**BPOH-O**). In the film, diarylethene molecules are densely packed and they are fixed in photoreactive anti-parallel conformation by cross-linking of the polymer networks. The rate of the film was estimated to be less than 30 ps. These values are similar to those of diarylethene monomers obtained in the solutions, in polymer dispersed system, and in crystalline states, indicating that the oxidation polymer film system keeps high response.*

Keywords: diarylethene; network-polymer; photochromism; picosecond transient absorption spectroscopy

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INTRODUCTION

For applications of photochromic systems into optical devices such as optical memories, it is indispensable to fabricate thin films. One of the most convenient methods to prepare the thin films is to disperse the photochromic molecules into polymer matrices [1,2]. Although increment of the dye concentration is absolutely required to enhance the photochromic efficiency, preparation of polymer thin films with high concentration of the dye is not universal because segregation prohibits the reliable data storage in long term. In order to produce the film system with higher reliablity, we have applied an oxidation polymerization to the production of the film (**Poly BPOH-C**) of the closed-ring isomer (**BPOH-C**) of 1,2-bis[2-methyl-6-(*o*-hydroxyphenyl)-1-benzothiophen-3-yl]hexafluorocyclopentene (**BPOH-O**), in which diarylethene molecules are densely packed and they are fixed in photoreactive anti-parallel conformation by cross-linking of the polymer networks [3].

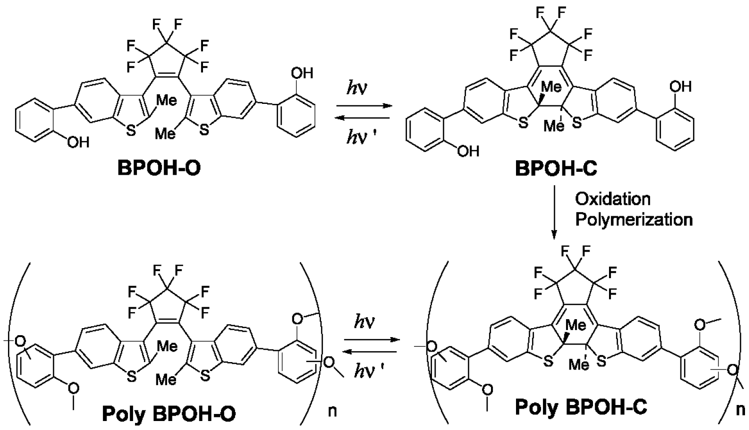
EXPERIMENTAL

The ethyl acetate solution of diarylethene **BPOH-O** was irradiated with UV (313 nm) light and photostationary state mixture was obtained by evaporation of the solvent. The closed-ring isomer **BPOH-C** was separated from the mixture by HPLC and prepolymer of **BPOH-C** was obtained by the oxidation polymerization of **BPOH-C** according to a literature [4]. The prepolymer was dissolved to chloroform, and the solution was spin-courted on the quarts plate (12×12 mm) using a spin quarter MIKASA 1H-D7 to obtain the polymer film (**Poly BPOH-C**). Film thickness of the polymer films was measured by use of micrometer (Mitutoyo Corporation, M110-25) and they were found to be 50–60 μm.

Picosecond laser photolysis system with a repetitive mode-locked Nd^{3+}: YAG laser was used for transient absorption spectral measurements [5–9]. The second harmonic (532 nm) with 15 ps fwhm and 0.5 –1 mJ was used for excitation. The excitation pulse was focused into a spot with a diameter of ca. 1.5 mm. Picosecond white continuums generated by focusing a fundamental pulse into a 10 cm quartz cell containing D_2O and H_2O mixture (3:1) was employed as a monitoring light.

RESULTS AND DISCUSSION

Diarylethene **BPOH** having phenol moieties undergoes cyclization/cycloreversion between open- and closed-ring isomers via the



SCHEME 1

photoexcitation as shown in Scheme 1. The absorption spectral changes of **BPOH** in ethyl acetate solution are shown in Figure 1.

The time-resolved transient absorption spectra obtained by the excitation of the open-ring isomer **BPOH-O** in ethyl acetate solution with a picosecond 355 nm laser pulse showed **BPOH-O** was converted into the closed-ring isomer **BPOH-C** within 20 ps timescale by photoirradiation.

The absorption spectral changes of oxidation polymer film **Poly BPOH** are shown in Figure 2. Broken line is the original absorption

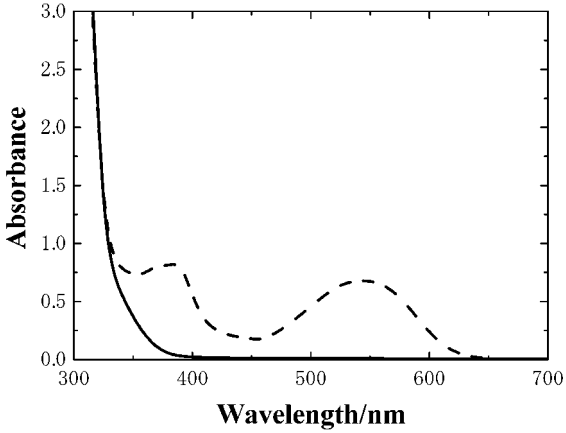


FIGURE 1 Absorption spectra of **BPOH-O** (solid line) and photostationary state (broken line) in ethyl acetate solution.

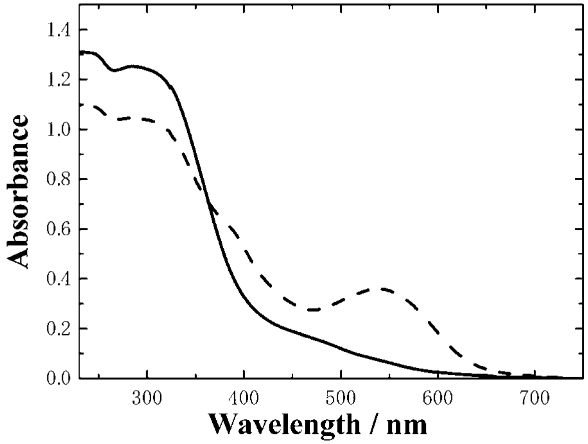


FIGURE 2 Absorption spectra of the open-ring state (**poly BPOH-O**, solid line) and the closed-ring state (**poly BPOH-C**, broken line) of the oxidation polymer film **Poly BPOH**.

spectrum of **Poly BPOH-C** obtained by oxidation polymerization of the closed-ring isomer **BPOH-C**. Upon homogeneous irradiation with visible light, the red-purple color due to the closed-ring structure disappeared and a spectrum as shown solid line (**Poly BPOH-O**) in the figure was obtained.

The polymer film **Poly BPOH-O** was used to observe the cyclization reaction of the polymer film. The time-resolved transient absorption spectral changes of the film **Poly BPOH-O** excited with a 15 picosecond 355 nm laser pulse were shown in Figure 3(a). Upon irradiation the band around 560 nm attributable to the closed-ring structure was gradually increased. In the Figure 3(b) the convolution curves calculated on the basis of different time constant (10 ps; solid line, 20 ps; broken line, and 30 ps; dotted line) of absorbance changes were depicted with the observed values. The S/N ratio was fairly worse compared the ones of obtained in solution. This is due to the low absorption of the thin film.

The present results indicate that the photochromic reactions of the polymer film proceeds very fast even the photochromic parts were fixed in the polymer matrices. The time constants of cyclization reaction of the film were estimated to be less than 10 ps. This rapid response is probably attributable to that the diarylethene molecular parts are fixed in the photo-reactive anti-parallel conformation by oxidation polymerization from the closed-ring isomer **BPOH-C**. The polymer

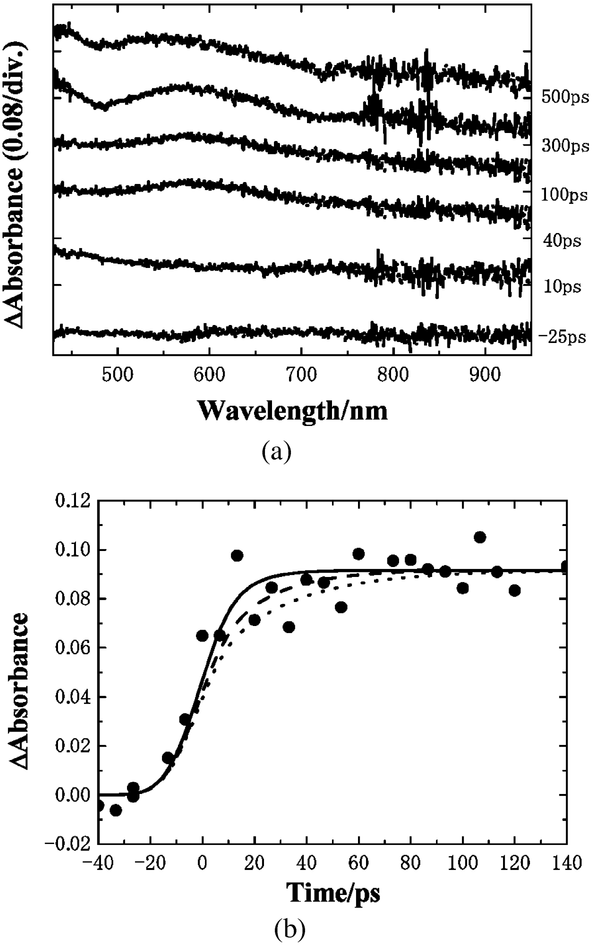


FIGURE 3 Time-resolved transient absorption spectra of **Poly BPOH-O** excited with a 15 picosecond 355 nm laser pulse (a) and time profile of the absorbance at 560 nm (b). Solid, broken, and dotted lines are convolution curves calculated on the time constants of 10, 20, and 30 ps, respectively.

film containing high concentration photochromic dyes showing rapid response will be applicable rewritable optical memory and display.

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