

# Photochromic Recording Medium Using A Diarylethene Polymer

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## Abstract

Effect of photo irradiation on the color change of a diarylethene polymer film was investigated. Diarylethene polymer was prepared by a radical polymerization using 1-[6'-(methacryloyloxyethyloxycarbonyl)-2'-methylbenzo[b]thiophen-3'-yl]-2-(2''-methylbenzo[b]thiophen-3''-yl) hexafluorocyclopentene (BTF6MA), styrene, and butylmethacrylate. A colorless film prepared from the diarylethene polymer turned deep red hue upon exposure to UV light. The red color was immediately bleached by a visible light. Such coloration and bleaching of the polymer film could be utilized to erasable grating patterning using a phase mask, by photoprinting with two light sources of 365 nm and 633 nm. Refractive index change of the polymer film accompanied by the photochromic absorbance change was examined. Thus reversible photo-induced refractive index change ( $\Delta n_{TE}$ ) of 0.0008 was determined from the photochromic conversion, with monitoring light of 830 nm.

## Introduction

Photo-induced absorbance changes in photochromic polymer films are of great importance for opto-controlled imaging.<sup>1</sup> The basis of the photochromic data recording is to utilize absorbance change induced by the structural change from A isomer to B isomer. For recording, isomer A is irradiated with wavelength 1, corresponding to the absorption band of A isomer, and the material transforms from A into B. New absorption at wavelength 2 can be observed. Usually the difference in absorption between the recorded and unrecorded area is used for readout of bit information. But illumination with wavelength 2 stimulate the reverse reaction toward isomer A. Therefore, this type of readout erases any recorded information. To overcome this problem, it is necessary to investigate non-destructive reading method by using a wavelength that the photochromic material does not absorb for reading.<sup>2</sup> In this case no reverse reaction is stimulated and any differences in the optical properties of the isomer can be used for reading.

In this paper we report photochromic recording property and refractive index change in diarylethene polymer film. Among the diarylethene photochromophores,

we have studied 1,2-bis(2-methylbenzo[b]thiophen-3-yl)hexafluorocyclopentene (BTF6) since BTF6 showed high photochromic efficiency and thermal stability.<sup>3</sup>

## Experimental Section

### Materials

2,3-Bis(2-methylbenzo[b]thiophen-3-yl)hexafluorocyclopentene (BTF6) was synthesized from benzothiophene in three steps.<sup>4,6</sup> 1-[6'-(Methacryloyloxyethyloxycarbonyl)-2'-methylbenzo[b]thiophen-3'-yl]-2-(2''-methylbenzo[b]thiophen-3''-yl) hexafluorocyclopentene (BTF6MA) was synthesized from BTF6 in three steps.<sup>6</sup> Other chemicals and solvents were purchased from either Aldrich or Tokyo Kasei and purified according to the literature.

### Synthesis of Diarylethene Polymers

A mixture containing BTF6MA (0.93 g, 1.49 mmol), styrene (1.07 mL, 9.39 mmol), *n*-butyl methacrylate (0.64 mL, 4.02 mmol), and 24.8 mg of AIBN in 22 mL of THF was refluxed under a nitrogen atmosphere for 72 h. After cooling of the reaction mixture to room temperature, solvent and volatile reactants were removed by evaporation. Reprecipitation from a mixture of diethyl ether and hexane afforded white solids with an isolated yield of 50%. Sulfur content was determined as 2.01% by elemental analysis, indicating that 22 % of BTF6MA was incorporated in the polymer. In addition, carbon, hydrogen, and oxygen content determined by elemental analysis as 76.71, 8.26, and 9.61%, respectively, indicated that the molar ratio BTF6MA:styrene:butyl methacrylate is 0.053:0.54:0.406.  $T_g = 77^\circ\text{C}$ ;  $M_w = 10500$ ;  $M_n = 7000$  (polydispersity = 1.49).

A similar reaction with a mixture containing different content of BTF6MA, styrene, *n*-butyl methacrylate, and AIBN in THF afforded diarylethene polymer with different degree of BTF6 substitution in the polymer. For increased absorbance change we have prepared BTF6 bound polymer with 37 % of BTF6 substitution.

### Preparation of Polymer Films

BTF6 bound polymer was dissolved in *p*-xylene at 60°C. The solution was filtered using membranes of 0.45  $\mu\text{m}$  pore size attached to a Teflon syringe, and the solution

was coated on a substrate (silicon wafer, fused silica, or slide glass) by a spin-coater with a spin rate of 1000-2000 rpm. The coated film was dried at 100 °C for 12 h in a vacuum oven to give transparent and homogeneous film with surface roughness less than 0.01  $\mu\text{m}$ . To compare the homogeneity of a doped film, BTF6 (40 mg) and poly(styrene-co-butylmethacrylate) (160 mg) were dissolved in 1 mL of  $\text{CHCl}_3$ . The solution was filtered, casted on a slide glass, and dried at 80 °C for 12 h in a vacuum oven. The surface roughness of the resultant film was 0.05 - 0.1  $\mu\text{m}$ , indicating that the BTF6 bound polymer film gave more homogeneous film.

### Instruments

The surface roughness of a polymer film was measured on an  $\alpha$  step (TENCOR instrument,  $\alpha$  step). UV spectra were obtained from a Guided Wave model 260 (Guided Wave, Inc., USA). The refractive index of the polymer film was determined using a prism coupler<sup>7</sup> with 830 nm diode laser as monitoring probe beam. The photodetector for the prism coupler was silicon type or IR detector. The light source for the characterization of the photochromic property of a polymer film was a Xe lamp (Oriel) attached with a monochromator. The light source for the refractive index change and photochromic recording were UV lamp (365 nm, 8  $\mu\text{W}/\text{cm}^2$ , Spectronics Corp.) and He-Ne laser (10 mW). The image was scanned by a NIR scanner.

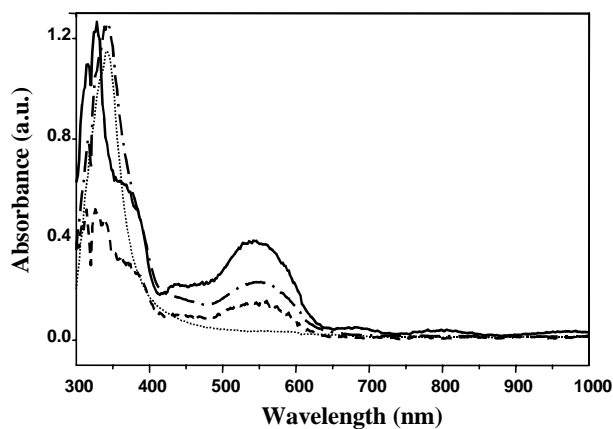


Figure 1. UV spectral change of a glass covered with BTF6 polymer by a light of 320 nm: Before irradiation with 320 nm (.....); After irradiation with 320 nm, degree of BTF6 bound in the polymer film was 5% (-----), 22% (— · — · —), and 37% (——).

### Photochromic Properties of Diarylethene Polymer Film

The solubility of the BTF6 polymer in organic solvent has allowed us to prepare polymer films with high transparency and homogeneity (surface roughness less than 0.01  $\mu\text{m}$ ). On the other hands, the surface roughness of the BTF6 doped poly(styrene-co-butylmethacrylate) film showed average surface roughness of 0.07  $\mu\text{m}$ , indicating that the BTF6

bound polymer film gave more homogeneous film. Inhomogeneity in the doped film could arise from phase separation and concentration gradient. Such inhomogeneity in a film may cause scattering of incident light, lowering resolution in photoprinted images.

Figure 1 shows UV spectral change of diarylethene copolymer film with different degree of BTF6 substitution, by a light of 320 nm. Within a few minutes of irradiation, the film changed its color to red, which bleached completely to an original colorless state upon irradiation with a light of 500–650 nm. Further irradiation of the film for 3 h by light of 320 nm did not change the spectrum or the absorbance at 580 nm (Figure 2). The color was rapidly bleached upon irradiation with light of 633 nm, and the absorbance at 580 nm was decreased to baseline as shown in Figure 2.

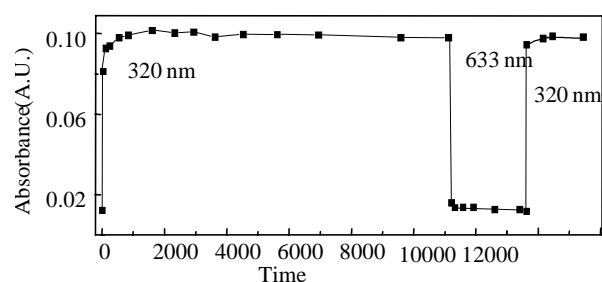
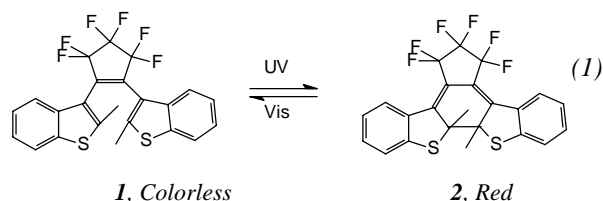


Figure 2. Absorbance change at 580 nm with a light of 320 nm and 633 nm.

Such reversible photochromic properties could be attributed to the photo-induced reversible ring opening/closure process in the BTF6 unit as described in eq 1. Similar coloration of the polymer film was also observed upon exposure to a light of 365 nm (UV lamp), and bleaching of color by 633 nm light (He-Ne laser).



### Photochromic Recording

Since the film could be colored by UV lamp, UV source could be used as a writing source. Figure 3 shows grating images obtained from photoprinting of the BTF6 bound polymer film (degree of substitution of BTF6 of 22%), using a phase mask. The phase mask with a spacing of 300  $\mu\text{m}$  was replicated by photoprinting using UV light (365 nm) exposure. The grating image was scanned by using a near IR imaging source. It was clearly shown that the photochromic image obtained from the BTF6 bound polymer film was effective for photon mode grating

fabrication. Upon excitation of the film with He-Ne laser (633 nm), the image was completely erased.

Reverse recording was also possible using He-Ne laser as a writing beam. Thus the film was irradiated using UV lamp (365 nm) for 1 min without a mask, to prepare colored film. The red colored film was covered by a mask and irradiated with He-Ne laser (10 mW). The image was obtained as bleached grating mark. Once data was read by near IR imaging, the film was irradiated with UV light to erase the marked area. New recording was accomplished by using a He-Ne laser to mark new data. Such data recording-erasure process was repeatable up to several thousand of cycles.

To utilize such reversible photochromic imaging into micro patterning, it was necessary to detect small change in the film. One of the method could be utilizing refractive index change by photochromic reaction in the film. This type of reading is non-destructive method since the photochromic diarylethene does not absorb for reading light and no reverse reaction is stimulated. Particularly, a small difference in refractive index change between the two isomer in the near IR region can be used for reading bit information without erasing recording data.

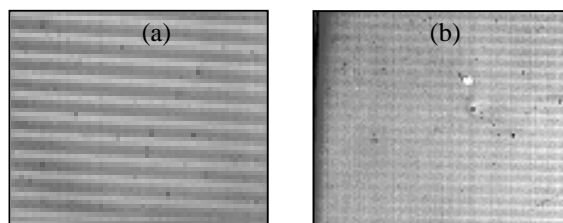


Figure 3. Photochromic grating image obtained from (a) BTF6 bound polymer film by excitation with UV (film thickness of 2.4  $\mu\text{m}$ ) and (b) BTF6 doped poly(styrene-co-butylmethacrylate) film with UV irradiation. The grating line width is 300  $\mu\text{m}$ .

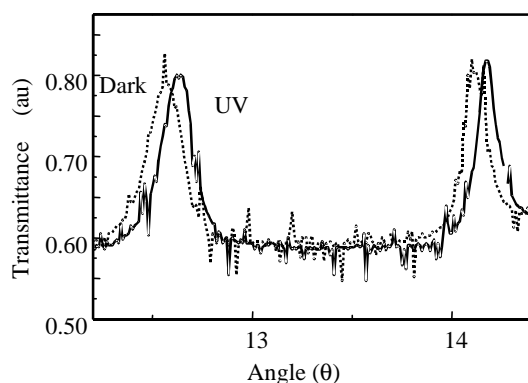


Figure 4. Photo-induced peak shift in the angle spectra for BTF6 bound polymer film with a monitoring light of 830 nm.

The refractive index of an optical waveguide coated with diarylethene polymer film could be evaluated by the prism coupling method.<sup>7</sup> The incident angle dependence of measured reflectance is shown in Figure 4 for the film of

diarylethene polymer (22 wt % of BTF6) using a probe beam of 830 nm. Upon irradiation of the polymer film with a light of 365 nm for 1 min, the peak in the incident angle dependence of measured reflectance was shifted to a higher value. Figure 4 compares the peak shift in the incident angle dependence of reflectance plot with a monitoring light of 830 nm. The refractive index ( $n_{TE}$ ) of the UV-irradiated polymer film was determined as 1.5467 with a monitoring light of 830 nm, resulting in a photo-induced refractive index change of 0.0008.

Interestingly the photochromic refractive index change was increased to 0.0042 in the polymer film of 37 % BTF6 substitution. Such a high refractive index change could be utilized to near IR imaging based on the refractive index detection. We are currently investigating NIR imaging of the BTF6 bound film, to miniaturize grating system.

## Conclusion

BTF6 bound polymer showed improved film property than the BTF6 doped polymer system. Photochromic writing was possible with UV lamp (365 nm) and He-Ne laser. Large photochromic refractive index change up to 0.0042 in the BTF6 bound polymer film brings up possibility of NIR imaging with non-destructive reading system

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## Biography

Eunyoung Kim received her B.S. degree in Chemistry from Yonsei University at Seoul (Korea) in 1982, a master degree in Chemistry from Seoul National University at Seoul (Korea) in 1984, and Ph.D. in Chemistry from University of Houston in 1990. Since 1992 she has been working in the Korea Research Institute of Chemical Technology at Taejeon, Korea. Her work has primarily focused on the development of functional polymers, including photochromic polymers, photoconductive polymers, and charge transport issues. She is a member of the Korean Society for Imaging Science and Technology.