Photoinduced Refractive Index Change of a Photochromic Diarylethene Polymer

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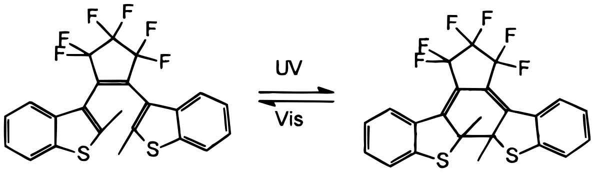
ABSTRACT: The effect of photoirradiation on the refractive index of a diarylethene polymer was investigated. Diarylethene polymer was prepared by a radical polymerization using 1-[6′-(methacryoyloxyethyloxycarbonyl)-2′-methylbenzo[*b*]thiophen-3′-yl]-2-(2″-methylbenzo[*b*]thiophen-3″-yl) hexafluorocyclopentene (BTF6MA), styrene, and butyl methacrylate. A colorless film prepared from the diarylethene polymer turned a deep red hue upon exposure to UV light. The red color was immediately bleached by visible light, and such coloration and bleaching of the polymer film could be switched reversibly by using two light source of UV and visible light. The refractive index (n_{TE}) of the polymer film, with 5.3 mol % of BTF6MA, was determined as 1.5555 and 1.5459 by a prism coupler using TE polarized light of 633 and 830 nm, respectively. Upon irradiation with light of 365 nm, the refractive index was increased, resulting in a photoinduced refractive index change (Δn_{TE}) of 8×10^{-4} as monitored by light of 830 nm. Δn_{TE} was dependent on the wavelength of the monitoring light. The dispersion of light in the diarylethene polymer film could be simulated by the Sellmeier equation, $n_\lambda^2 = n_\infty^2 + D\lambda_0^2/(\lambda^2 - \lambda_0^2)$, in which the refractive index at longest wavelength limit (n_∞) and the oscillator strength (D) for the colorless polymer film were determined as 1.5356 and 0.18, respectively. Similarly, n_∞ and D values for the red polymer film, prepared by UV irradiation, were determined as 1.5368 and 0.042, respectively.

Introduction

Photoinduced refractive index changes in photochromic polymer films are of great importance for opto-controlled waveguiding.[1] Large refractive index changes on the order of 10^{-3} can be induced by a light from photochromophores (photochromic dyes) dispersed in polymer matrices.[2] Such a refractive index change could be attributed largely to reversible structural change of photochromophores in the polymers and applicable to opto-controlled optical switches. Among the photochromophores, bis(thiophen-3-yl)ethene (BTE) derivatives have attracted interest for their high photochromic efficiency and thermal stablility.[3] The photochromic properties of BTE arise from photoinduced ring closure/opening process as depicted below for 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl) hexafluorocyclopentene (BTF6, **1**).



(1)

1, Colorless **2**, Red

Such a photoinduced refractive index change could be attained from a photochromic polymer, in which photochromophores are attached to polymer chains by covalent bonding. Particularly, such a modification of polymer network by a low molecular weight photochromophore is important for the development of stable photochromic polymers for practical application in optical switches and recording devices. There are several reports on the dye molecules dispersed in a polymer matrix such as PMMA, polystyrene, and polyethylene; however, reports on diarylethene bound polymers are rare in the literature.[4] Chromophore bound polymers have the advantage that a high chromophore concentration can be incorporated into the polymer system without crystallization, phase separation, or the formation of concentration gradients.[5] In addition, the bound system is expected to be more stable over time than the doped system, because of the motional hindrance introduced by chemical bonding.[6] Therefore, we embarked on the examination of a diarylethene bound polymer system, since the photochromic diarylethene side chain may confer photoinduced refractive index change to the polymer segments with higher transparency and stability than the doped system. To synthesize a diarylethene-substituted polymer, we use 1-[6′-(methacryoyloxyethyloxycarbonyl)-2′-methylbenzo[*b*]thiophen-3′-yl]-2-(2″-methylbenzo[*b*]thiophen-3″-yl) hexafluorocyclopentene (**8**) as a monomer with comonomers of styrene and butyl methacrylate, to endow self-supportive mechanical properties with some flexibility onto the photochromic polymer network.

We report here the preparation and photoinduced refractive index change of BTF6 substituted polymer.

Experimental Section

Materials. Dimethylformamide (DMF) was distilled over anhydrous magnesium sulfate under reduced pressure (40 mm) at 78 °C. 2,3-Bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (BTF6) was synthesized from benzothiophene in three steps as described below.[7,8] Other chemicals and solvents were purchased from either Aldrich or Tokyo Kasei and purified according to the literature.

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Synthesis of 2-Methyl-benzo[*b*]thiophene (4). 2-Methylbenzo[*b*]thiophene was synthesized according to the literature.[8] Benzo[*b*]thiophene (**3**, 11.49 g, 31.3 mmol) was dissolved in THF (250 mL) and cooled to −78 °C. To the above solution was slowly added 44.7 mL of *n*-butyllithium (2.0 M, 89.47 mmol). After completion of *n*-butyllithium addition, the cooling bath was removed. The reaction mixture was warmed to room temperature, and then iodomethane (6.58 mL, 105.74 mmol) was added dropwise. After 1 h stirring of the reaction mixture, MeOH was added, followed by addition of water. Organic products were extracted by ethyl acetate and dried with $MgSO_4$. Filtering of $MgSO_4$ followed by removal of solvent afforded pale yellow solids of **4** (12.06 g) with quantitative yield. Mp = 38 °C. ^1H NMR ($CDCl_3$, ppm): δ 2.57 (s, 3 H, CH_3), 6.98 (s, 1 H, aromatic proton), 7.22−7.32 (m, 2 H, aromatic proton), 7.63 (d, 1 H. J = 8.4 Hz, aromatic proton), 7.74 (d, 1 H, J = 7.6 Hz, aromatic proton). Mass spectral data, *m/z* (intensity, %): 147 (M − 1, 100), 135 (10), 115 (16), 103 (9), 71 (7), 57 (28).

Synthesis of 3-Bromo-2-methylbenzo[*b*]thiophene (5).[7] To a solution of **4** (1.01 g, 6.81 mmol) in 20 mL of acetic acid was slowly added 0.38 mL of bromine (7.49 mmol) at room temperature. After 5 h of stirring at room temperature, brine was added. The product mixture was extracted by chloroform and washed with aqueous sodium carbonate solution, water, and aqueous sodium thiosulfate. After removal of residual water with $MgSO_4$, solvent was removed by evaporation. Flash chromatography on a silica gel using hexane as an eluting solvent gave pale yellow crystals of **5** (1.52 g) with 98% yield. Mp = 42 °C. ^1H NMR ($CDCl_3$, ppm): δ 2.55 (s, 3 H, CH_3), 7.32 (t, 1 H, J = 7.5 Hz, aromatic proton), 7.41 (t, 1 H, J = 8.1 Hz, aromatic proton), 7.67−7.72 (m, 2 H, aromatic proton). Mass spectral data, *m/z* (intensity, %): 228 (M + 1, 84), 147 (100), 102 (10), 74 (11).

Synthesis of 1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl) Hexafluorocyclopentene (BTF6, 1).[7] To a solution of **5** (10 g, 44.03 mmol) in THF (150 mL) at −78 °C was added dropwise 21.13 mL of *n*-butyllithium (2.5 M, 52.83 mmol). The mixture was slowly warmed to −30 °C and stirred for 1 h at −30 °C.The mixture was then cooled to −78 °C, and 2.90 mL of octafluorocyclopentene (21.6 mmol) was slowly added at −78 °C. After stirring for 30 min, the mixture was warmed to room temperature and quenched with MeOH. The product mixture was extracted with chloroform and dried with $MgSO_4$. $MgSO_4$ was filtered off, and solvent was removed by evaporation to afford BTF6 as pale yellow solids. BTF6 (5.38 g) was isolated from flash chromatography and then recrystallized from a mixture of chloroform and hexane. Yield of BTF6 was 53% yield. BTF6 (**1**) consists of two configurational isomers of parallel (p) and antiparallel (ap) as reported before.[7] Mp = 49 °C. ^1H NMR ($CDCl_3$, ppm): δ 2.19 (s, 3 H, ap CH_3), 2.48 (s, 3 H, p CH_3), 7.15−7.68 (m, 8 H, aromatic proton). ^{13}C NMR: δ 15.5, 119.5, 122.2, 122.5, 124.8, 124.9, 125.0, 138.6, 138.7, 142.6, 143.0. Mass spectral data, *m/z* (intensity, %): 468 (M+, 100), 453 (8), 438 (20), 419 (38), 401 (11). High-resolution MS; Calculated for $C_{23}H_{14}F_6S_2$: 468.0441. Experimental: 468.0447.

Synthesis of 1-(6′-Acetyl-2′-methylbenzo[*b*]thiophen-3′-yl)-2-(2′′-methylbenzo[*b*]thiophen-3′′-yl) Hexafluorocyclopentene (6). To a solution of **1** (2.67 g, 5.70 mmol) and acetyl chloride (0.8 mL, 11.40 mmol) in nitrobenzene (40 mL) was slowly added 2.28 g of $AlCl_3$ (17.10 mmol) at room temperature. After 5 h of stirring at room temperature, water was added to the reaction mixture. Extraction with chloroform, drying with $MgSO_4$, filtration, and removal of solvent, followed by flash chromatography using a mixture of 20% ethyl acetate in hexane (v/v), gave **6** as white solids in 84% yield. Mp = 62 °C. IR (KBr, cm^{-1}): 1684(−CO of $COCH_3$ group). ^1H NMR ($CDCl_3$, ppm): δ 2.20 (s, 3 H, ap CH_3), 2.24 (s, 3 H, p $COCH_3$), 2.50 (s, 3 H, p CH_3) 2.63 (s, 3 H, ap $COCH_3$), 7.17−8.29 (m, 7 H, aromatic proton). ^{13}C NMR: δ 15.6, 15.9, 27.1, 119.3, 119.7, 122.3, 122.4, 122.6, 123.2, 123.5, 124.7, 124.9, 125.1, 133.7, 138.5, 138.6, 142.0, 143.1, 147.9, 197.6. Mass spectral data, *m/z* (intensity, %): 510 (M+, 100), 495 (67), 452 (10), 419 (13), 84 (71). High-resolution MS; Calculated for $C_{25}H_{16}OF_6S_2$: 510.0547. Experimental: 510.0529.

Synthesis of 1-(6′-Carboxy-2′-methylbenzo[*b*]thiophen-3′-yl)-2-(2′′-methylbenzo[*b*]thiophen-3′′-yl) Hexafluorocyclopentene (7). To a stirred solution of **6** (0.11 g, 0.196 mmol) in dioxane (0.7 mL) was added dropwise a solution of sodium hypochlorite (2.8 mL, 10% solution) in dioxane (0.4 mL) at 50 °C. The mixture was stirred for 2 h at 80 °C and then quenched with saturated sodium carbonate solution. Extraction with chloroform and drying with $MgSO_4$ followed by removal of solvent afforded 0.10 g of **7** as white solids in 99% yield. Mp = 98 °C. IR (KBr, cm^{-1}): 1692(−COOH group). ^1H NMR ($CDCl_3$, ppm): δ 2.24 (s, 3 H, ap CH_3), 2.50 (s, 3 H, p CH_3), 7.19−8.46 (m, 7 H, aromatic proton). ^{13}C NMR: δ 15.6, 15.9, 119.3, 119.8, 122.3, 122.6, 124.9, 125.1, 125.4, 125.7, 126.3, 126.4, 138.3, 138.5, 138.7, 142.7, 143.2, 148.2, 172.5. Mass spectral data, *m/z* (intensity, %): 512 (M+, 100), 482 (11), 464 (5), 445 (11), 419 (24). High-resolution MS; Calculated for $C_{24}H_{14}O_2F_6S_2$: 512.0339. Experimental: 512.0352.

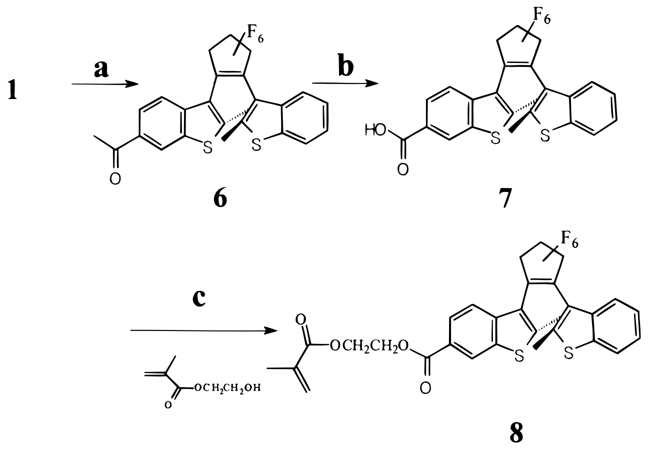
Synthesis of 1-[6′-(Methacryoyloxyethyloxycarbonyl)-2′-methylbenzo[*b*]thiophen-3′-yl]-2-(2′′-methylbenzo[*b*]-thiophen-3′′-yl) Hexafluorocyclopentene (8). To a solution of **7** (2.3 g, 4.491 mmol) in dichloromethane (50 mL) were added methacrylic acid 2-hydroxyethyl ester (0.69 mL, 5.39 mmol), DCC (1.2 g, 5.84 mmol), and DMAP (60 mg). The mixture was stirred at room temperature for 5 h. Addition of dichloromethane followed by aqueous washing, drying, and flash chromatography (10% ethyl acetate−hexane) afforded 2.59 g of **8** as white solids with an yield of 92%. Mp = 52 °C. IR (KBr, cm^{-1}): 1723(−COO− group). ^1H NMR (300 MHz, $CDCl_3$): δ 1.95 (s, 3 H, $CH_2{=}C(CH_3)COO-$), 2.22 (s, 3 H, ap CH_3), 2.49 (s, 3 H, p CH_3), 4.49−4.63 (m, 4 H, $-COOCH_2CH_2$-$OCO-$), 5.59 (s, 1 H, $CH_2{=}C(CH_3)COO-$), 6.15 (s, 1 H, $CH_2{=}C(CH_3)COO-$), 7.17−8.41 (m, 7 H, aromatic proton). ^{13}C NMR: δ 15.6, 15.9, 18.7, 62.8, 63.3, 119.3, 119.7, 122.3, 122.6, 124.8, 124.9, 125.1, 126.0, 126.3, 126.6, 136.3, 138.2, 138.3, 138.6, 142.1, 143.1, 166.4, 167.6. Mass spectral data, *m/z* (intensity, %): 624 (M+, 100), 593 (3), 495 (43), 479 (7), 419 (4), 248 (9), 113 (55), 69 (24). High-resolution MS; Calculated for $C_{30}H_{22}O_4F_6S_2$: 624.0864. Experimental: 624.0862. Anal. Calcd for $C_{30}H_{22}O_4F_6S_2$: C, 57.68; H, 3.52; S, 10.27. Found: C, 58.11; H, 3.47; S, 10.01.

Synthesis of Diarylethene Polymers. A mixture containing **8** (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 by elemental analysis as 2.01%, indicating 5.3 mol % of **8** 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 diarylethene (**8**):styrene:butyl methacrylate is 0.053:0.54:0.406. T_g = 77 °C; M_w = 10 500; M_n = 7000 (polydispersity = 1.49).

A similar reaction with a mixture containing **8** (0.40 g, 0.64 mmol), styrene (0.98 mL, 8.52 mmol), *n*-butyl methacrylate (0.58 mL, 3.65 mmol), and 18 mg of AIBN in 18 mL of THF afforded diarylethene polymer. The content of sulfur, carbon, hydrogen, and oxygen was determined as 1.15 ± 0.013%, 78.98 ± 0.20%, 8.78 ± 0.087%, and 9.26%, respectively, by elemental analysis. From the elemental analysis result, the molar ratio diarylethene (**8**):styrene:butyl methacrylate was determined as 0.031:0.537:0.432. T_g = 66 °C; M_w = 11 500, M_n = 7200 (polydispersity = 1.60). For the study on the photoinduced refractive index change, the polymer substituted with 5.3 mol % (22 wt %) of diarylethene unit (**8**) was investigated.

Preparation of Waveguide Films. BTF6-substituted polymer (100 mg), in which the molar content of **8** was 5.3%, was dissolved in *p*-xylene at 60 °C. The solutions were filtered using membranes of 0.45 μm 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 homoge-

Scheme 1[a]



[a] Conditions employed: (a) **1** (5.70 mmol), acetyl chloride (11.40 mmol), $AlCl_3$ (17.10 mmol), nitrobenzene, rt, 84%; (b) **6** (0.20 mmol)/dioxane, sodium hypochlorite/dioxane, 50−80 °C, 99%; (c) **7** (4.491 mmol)/dichloromethane, methacrylic acid 2-hydroxyethyl ester (5.39 mmol), DCC (5.84 mmol, DMAP (60 mg), rt, 5 h, 92%.

neous film with surface roughness less than 0.01 μm. To compare the homogeneity of a doped film, BTF6 (40 mg) and PMMA (160 mg) were dissolved in 1 mL of $CHCl_3$. 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 μm, indicating that the BTF6 bound polymer film gave more homogeneous film.

Instruments. ^1H and ^{13}C NMR spectra were determined on a Bruker ARX-300 spectrometer. FT-IR spectra were obtained from a Bio-Rad Digilab Division FTS-80. The molecular weight average of the BTF6 polymer was characterized by gel permeation chromatography (GPC) (model: Waters R-401 ALC/GPC) with THF as an eluent and polystyrene standard for calibration. The surface roughness of a polymer film was measured on an α step (TENCOR instrument, α 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[9] with 633 nm He−Ne laser and 830, 1300, and 1550 nm diode laser as monitoring probe beams. The photodetector for the prism coupler was silicon type or IR detector. Other components for the prism coupler were an amplifier (OP07DP), AD/DA converter (DATA TRANSLATION DT01-EZ; −10 to + 10 V from channel 0, single ended mode), stepping motor and driver (Parker Compumotor SX), and optics (Figure 3). 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 was a UV lamp (365 nm, 8 $\mu W/cm^2$, Spectronics Corp.). Since the coupling intensity and peaks could be changed by different film area and film thickness, the position of the film and coupling spot was not changed during the measurement.

Results and Discussion

Preparation of a Diarylethene Monomer and Its Polymer. Among the diarylethene derivatives, a hexafluorocyclopentene derivative (BTF6) is attractive since synthesis and functionalization are easier than for other derivatives. Substitution of BTF6 with a functional group was accomplished by acetylation, followed by oxidation and condensation reactions, as summarized in Scheme 1.

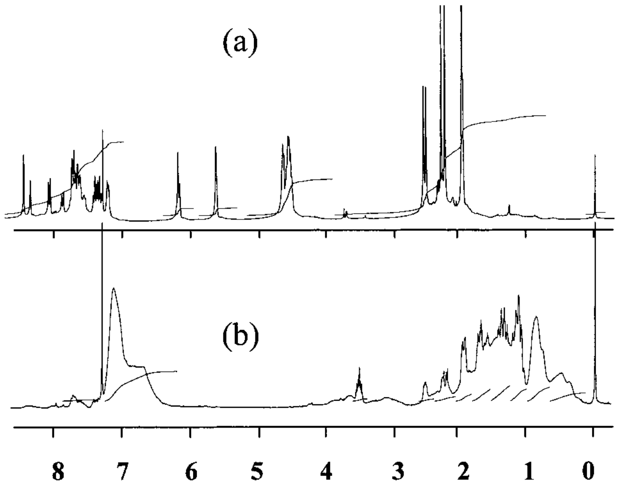
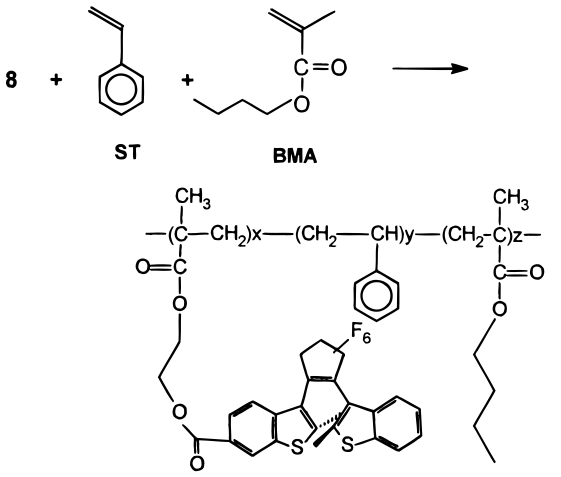


Figure 1. ^1H NMR spectrum of diarylethene polymer (5.3 mol %) dissolved in $CDCl_3$ and compared with that of monomer **8**.

Diarylethene-substituted polymers could be synthesized from **8**, styrene (ST), and butyl methacrylate (BMA) via free radical polymerization as described below.



(2)

The molar ratio between x:y:z in eq 2 was determined as 0.031:0.537:0.432, by elemental analysis, when the feed ratio **8**:ST:BMA was 0.05:0.67:0.29. To increase the content of BTF6, the feed ratio was changed to 0.1:0.63: 0.27, keeping the ratio between ST to BMA as 7:3. The BTF6 content of the polymer prepared from the latter was increased in the consumption of BMA, and the molar ratio between x:y:z was determined as 0.053:0.54: 0.406, by elemental analysis. The weight-average molecular weight of the polymer (M_w) was 11 500 and 10 500 for 3.1% and 5.3 mol % of BTF6 content, respectively.

The polymers were soluble in a number of organic solvents, such as xylene, $CHCl_3$, THF, and acetone. Figure 1 shows the ^1H NMR spectrum of BTF6 polymer (5.3 mol %) dissolved in $CDCl_3$ and compared with that of monomer **8**. The peaks at δ 2.2−2.6 and 7.2−8.4 are characteristic of BTF6 units originating from the proton resonance of methyl and aromatic groups, respectively. The broad peaks at 6.5−7.0 ppm can be assigned as the aromatic proton resonance of styrene, and broad multiplets below 2 ppm could be assigned as the proton resonance of butyl units. The content of BTF6 could be determined qualitatively as lower than 7 mol %; however, it was difficult to quantify due to the broad peaks and overlapping peaks.

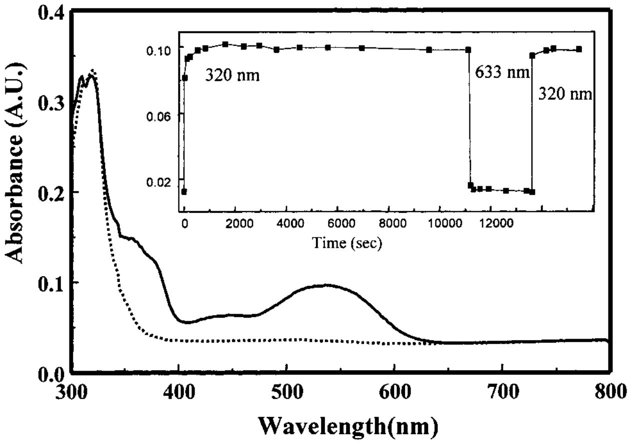


Figure 2. UV spectral change of a glass covered with BTF6 polymer (5.3 mol %) by light of 320 nm. Absorbance change at 540 nm with light of 320 and 633 nm is shown in the inset.

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 μm). On the other hands, the surface roughness of the BTF6-doped PMMA film showed surface roughness of 0.05−0.1 μm, 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, impeding precise determination of the light dispersion property of a film.

Figure 2 shows UV spectral change of a glass covered with BTF6 polymer (5.3 mol %) by 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 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 540 nm (Figure 2, inset). The color was rapidly bleached upon irradiation with light of 633 nm, and the absorbance at 540 nm was decreased to baseline as shown in Figure 2 (inset). Such reversible photochromic properties could be attributed to the photoinduced reversible ring opening/closure process as described in eq 1.

Similar coloration of the polymer film was also observed upon exposure to light of 365 nm (UV lamp), and bleaching of the color was by a He−Ne laser (633 nm). The photochromic conversion by 365 nm UV light was estimated as 70% by comparing the absorbance increase at 538 nm by 320 nm light. To study the effect of the photoinduced reversible ring opening/closure process on the refractive index change, we examine prism coupling angles of a UV (365 nm) irradiated film before and after irradiation with a He−Ne laser. Importantly, the photoinduced ring opening/closure process accompanies refractive index changes as described below.

Photoinduced Refractive Index Change of Diarylethene Polymer Film. The refractive index of an optical waveguide coated with diarylethene polymer film could be evaluated by the prism coupling method.[9] Figure 3 shows a block diagram of a setup for a prism coupler using different probe beams. The coupling of a laser beam by a prism into a planar dielectric light guide is governed by the angle θ of the incident light into the prism base. This angle determines the phase velocity in the x direction, $V(i) = (c/n_p) \sin \theta$, of the incident waves in the prism (index n_p) and in the gap. Strong coupling of light into the film occurs when we choose θ so that $V(i)$ equals the phase velocity V_m of one of the characteristic modes of propagation in the guide ($m = 0, 1, 2, 3, ...$). By determining the synchronous angles θ_m of the strongest coupling, the characteristic propagation constants of the polymer film, relative to the propagation constants, $k_0 = \omega/c$, of free space, could be determined ($N_m = c/V_m = n_p \sin \theta$). From the characteristic propagation constants of the polymer film, prism angle, refractive index of the prism at the monitored wavelength, and film thickness, the refractive index of the film could be determined as described by the following equation:[10]

$$N = \sin \alpha \cos \theta + (n_p^2 - \sin^2 \alpha)^{1/2} \sin \theta \qquad (3)$$

where α is the prism angle (45°) of incidence on the entrance face of the prism. The incident angle dependence of measured transmittance is shown in Figure 4 for the film of diarylethene polymer (5.3 mol % of BTF6) using a probe beam of 1550 nm. The refractive index (n_{TE}) of the film in the dark was determined as 1.5380. The refractive index of the TM mode (n_{TM}) was determined as 1.5389, indicating that the birefringence of the polymer film was small.

The refractive index (n_{TE}) of the film was increased to 1.5395, 1.5459, and 1.5555 with a monitoring wavelength of 1300, 830, and 633 nm, respectively. The increase in the refractive index at higher energy with shorter wavelength could be expected from a dispersion formula of the Sellmeier equation (eq 4)[11,12]

$$n_\lambda^2 = n_\infty^2 + D\lambda_0^2/(\lambda^2 - \lambda_0^2) \qquad (4)$$

where D is related to the oscillator strength, λ is the wavelength of a monitoring light, λ_0 is the absorption maximum, and n_∞ is the refractive index at longest wavelength limit. Indeed, Figure 5 shows a linear relationship between the refractive index (n^2) and the monitoring wavelength ($\lambda_0^2/(\lambda^2 - \lambda_0^2)$), using 320 nm as λ_0. From the intercept and slope of the plot, n_∞ and D were determined as 1.356 and 0.18, respectively. Figure 6 shows a simulated plot of the refractive index against monitoring wavelength, indicating that the refractive index rises in the short wavelength region as the absorbance of the polymer increases.

Upon irradiation of the polymer film with a light of 365 nm for 1 min, the peak in the incident angle dependence of measured transmittance was shifted to a higher value. Figure 7 compares the peak shift in the incident angle dependence of transmittance plot with a monitoring light of 830 and 1550 nm. The refractive index (n_{TE}) of the UV-irradiated polymer film was determined as 1.5467 with monitoring light of 830 nm, resulting in a photoinduced refractive index change of 0.0008. Table 1 lists refractive index values for the film at different wavelengths. The refractive index of the UV-irradiated film with monitoring light of 633 nm could not be determined due to the absorption of the monitoring light by the colored film.

Using the Sellmeier equation (eq 4), the dispersion property in the colored polymer film could be determined, as done for a colorless film described above. From the linear relationship between the refractive index (n^2)

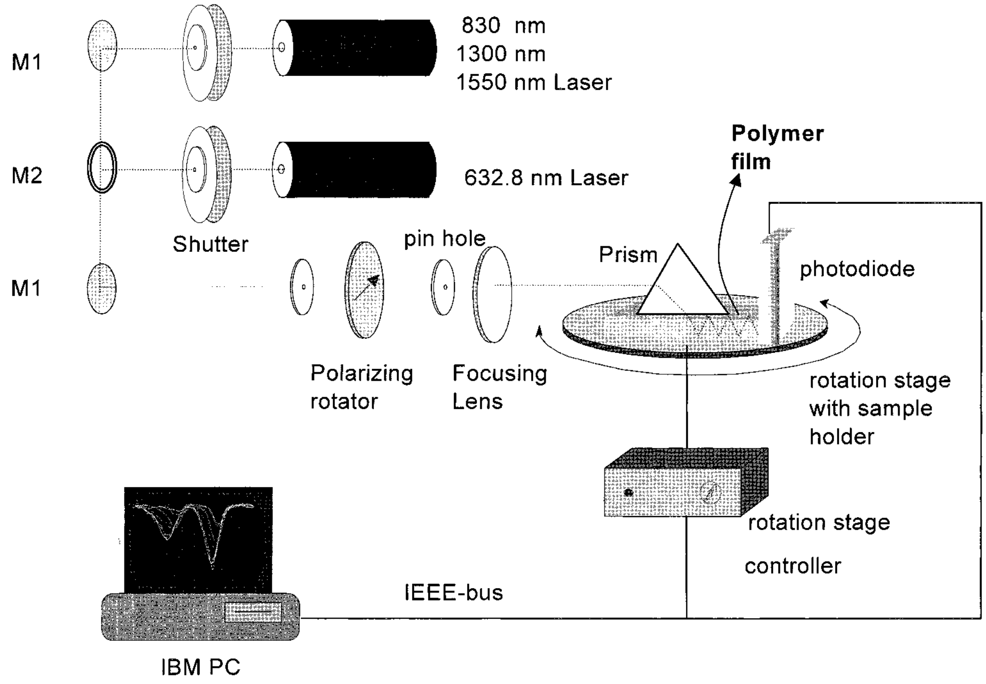


Figure 3. Block diagram of a setup for a prism coupler using different probe beams. M1 is a mirror and M2 is a dichroic mirror.

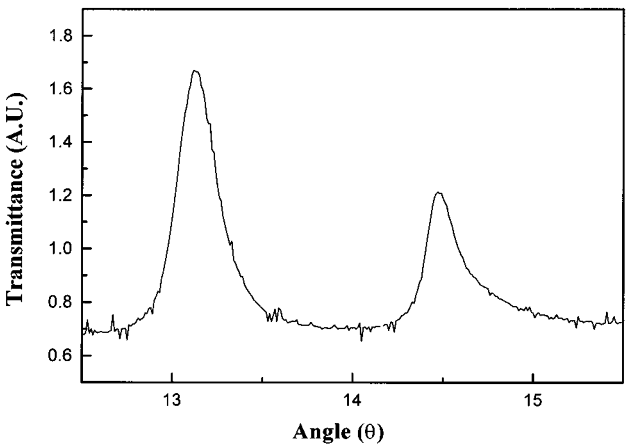


Figure 4. Incident angle dependence of measured transmittance for the film of diarylethene polymer (5.3 mol % of BTF6) using a probe beam of 1550 nm.

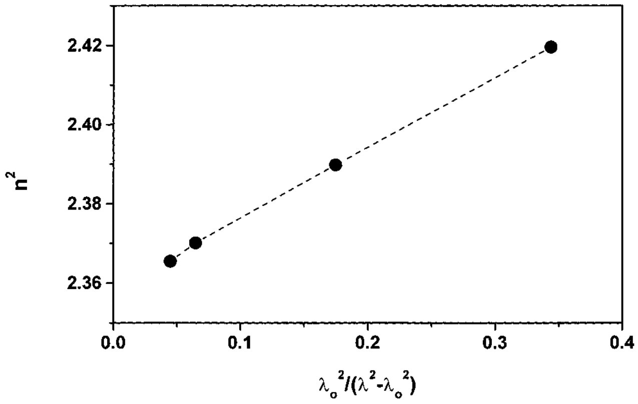


Figure 5. Plot of the refractive index (n^2) against monitoring wavelength ($\lambda_0{}^2/(\lambda^2 - \lambda_0{}^2)$), using 320 nm as λ_0.

of the polymer film and the monitoring wavelength ($\lambda_0{}^2/(\lambda^2 - \lambda_0{}^2)$), using 538 nm as λ_0, n_∞ and D were determined as 1.5368 and 0.042, respectively. The result shows that the refractive index of the colored film is

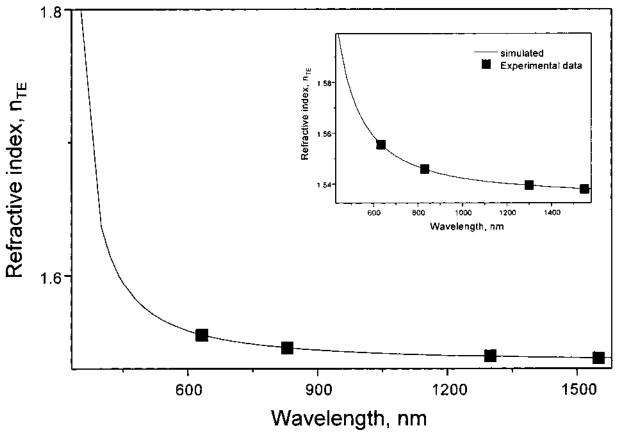


Figure 6. Simulated plot of the refractive index for colorless BTF6 polymer film against monitoring wavelength.

increased, but the oscillator strength is decreased. Such a change could be ascribed to the cyclization of BTE as described in eq 1. A simulated Sellmeier plot for the red film is shown in Figure 8 and compared with that for the colorless film as a dotted line. Larger Δn_{TE} could be obtained when the wavelength of the monitoring light is shorter. However, in the case of the diarylethene polymer, the strong absorption of monitoring light by the colored film, to proceed backward reaction (ring opening), limits the determination of the refractive index change. Importantly, the refractive index of the BTF6-substituted polymer film could be switched reversibly by using two light sources (UV and He−Ne laser). Furthermore, a refractive index change of 0.0005 with monitoring light of 1300 nm in this study is comparable to that of a BTF6 dispersed polymer film (Δn = 0.0005−0.0003).[13] For full light switching, a refractive index change of 0.0005 was reported to be sufficient as described by Hoshino et al.[13b] Further studies on the effect of the polymer structure on the index change are in progress and will hopefully be applied to an optical switching device or a rewritable recording layer.

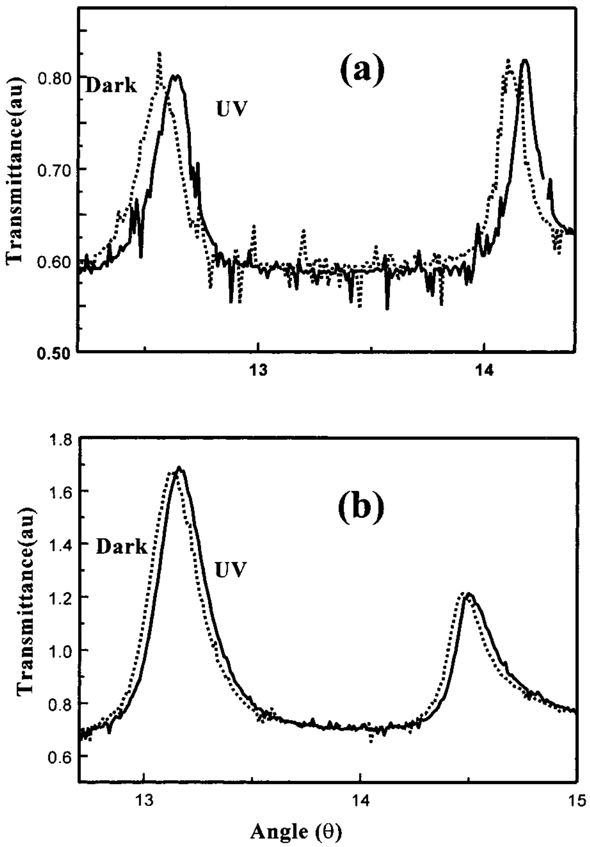


Figure 7. Photoinduced peak shift in the incident angle dependence of transmittance plot (solid line) with a monitoring light of 830 nm (a) and 1550 nm (b). The plot for a He−Ne laser-irradiated film is shown as a dotted line.

Table 1. Photoinduced Refractive Index Change of BTF6 Polymer Film

irradn[a]	monitoring light, nm	angle θ_0, θ_1[b]	n_{TE} (n_{TM})	Δn_{TE}[c]
He−Ne	633	14.053, 12.963	1.5555	
He−Ne	830	14.14, 12.64	1.5459 (1.5468)	
UV	830	14.215, 12.71	1.5467 (1.5476)	0.0008
He−Ne	1300	13.61, 10.26	1.5395 (1.5404)	
UV	1300	13.66, 10.31	1.5400	0.0005
He−Ne	1550	14.47, 13.12	1.5380 (1.5389)	
UV	1550	14.50, 13.16	1.5383	0.0003

[a] UV: irradiation with a 365 nm UV lamp. Photochromic conversion was estimated as 70% compared to that of photostationary state (320 nm irradiation; see text). [b] Angles determined from Figure 4 with a TE polarized light. θ_0 and θ_1 are angles for fundamental mode and first mode, respectively. [c] Photoinduced refractive index change, $\Delta n_{TE} = n_{TE}(\mathrm{UV}) - n_{TE}$ (He−Ne).

In conclusion, we have synthesized a diarylethene polymer, which shows a photochromic refractive index change of 0.0008−0.0003 in the monitoring light of 830−1550 nm. The dispersion property of light in this polymer film was described by the Sellmeier equation, $n_\lambda^2 = n_\infty^2 + D\lambda_0^2/(\lambda^2 - \lambda_0^2)$, in which the n_∞ and D for the polymer film without photocyclization were determined as 1.5356 and 0.18, respectively, while the values after photocyclization by UV irradiation were determined as 1.5368 and 0.042, respectively.

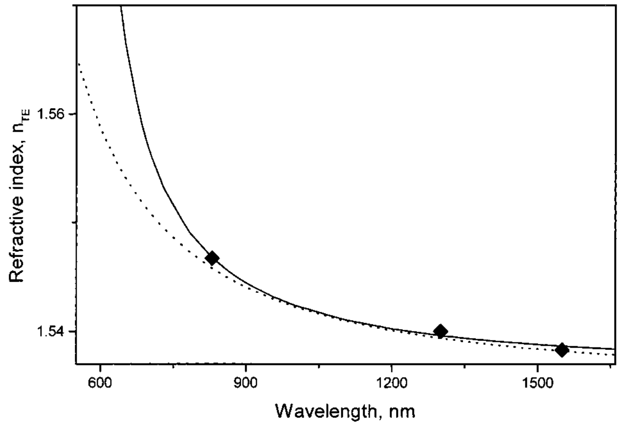


Figure 8. Simulated Sellmeier plot for a red film (solid line) in comparison with that for a colorless film (dotted line).

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