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Articles

Refractive Index Changes of Amorphous Diarylethenes Containing 2,4-Diphenylphenyl Substituents

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Photochromic diarylethene derivatives containing 2,4-diphenylphenyl substituents formed stable amorphous solids and showed reversible solid-state photochromism. Refractive indices of the amorphous films changed reversibly with the photochromic reactions as much as $\Delta n = 0.028$ at 817 nm. Changes in both absorption band and static polarizability contributed to the large refractive index modulation.

Introduction

Considerable efforts have been made to develop organic materials which change refractive indices upon photoirradiation. Various photorefractive, as well as photochromic, materials have been reported to serve as the photoresponsive phase-modulating material.[1−8] Photochromic diarylethenes are the most promising candidates for the refractive index modulation materials[9−16] because of their fatigue resistant and thermal irreversible photochromic performance.[17−19] 3D Recording, hologram recording, and waveguide type switching devices based on the refractive index modulation of diarylethenes have been reported.[9−11,20−24] However, the refractive index change of diarylethene-dispersed polymer films is relatively small, with Δn being less than 0.01 at the transparent wavelength range. It is strongly desired to increase the photoinduced refractive index change for the practical applications to optical switches and memories.

The refractive index change is dependent on the volume density of the photoactive molecules in the medium and the photochromic efficiency. The most convenient way to increase the density of the photoactive molecules is to make them form bulk amorphous solids by themselves.[12,25−33] In the past studies, we prepared two amorphous diarylethenes with relatively

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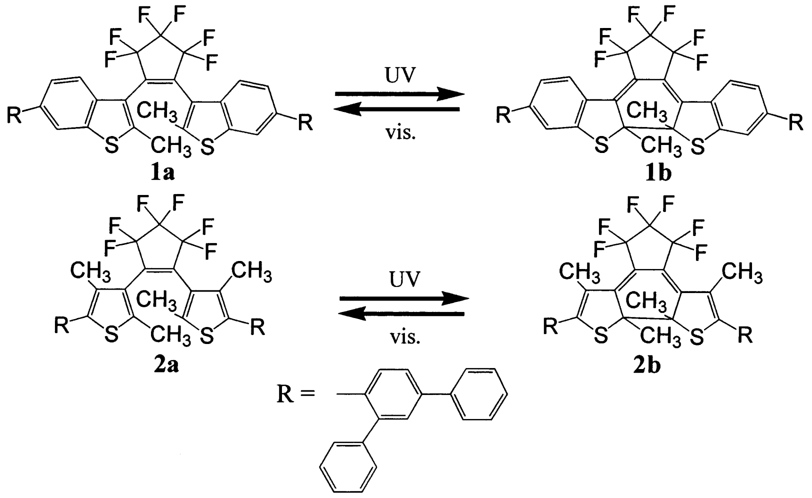
Scheme 1. Molecular structures of compounds 1a, 1b, 2a, and 2b



high thermal stability, 1,2-bis(2-methyl-6-(2,4-diphenylphenyl)-1-benzothiophene-3-yl)perfluorocyclopentene **1a** and 1,2-bis(5-(2,4-diphenylphenyl)-2,4-dimethyl-3-thienyl)perfluorocyclopentene **2a**.[18,30] These molecules contain 2,4-diphenyl−phenyl substituents as shown in Scheme 1, which are effective to stabilize the amorphous state even at higher temperature. In the present paper, optical properties of the amorphous diarylethene films of **1** and **2** are studied and reversible photon-mode refractive index modulation is demonstrated as well as their wavelength dispersions.

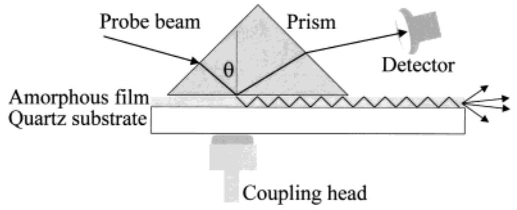
Experimental Section

1a and **2a** were synthesized as has been reported elsewhere.[31,34] These molecules were purified carefully by GPC (chloroform) and HPLC (silica gel/hexane:ethyl acetate = 96:4). The closed-ring isomers **1b** and **2b** were isolated from UV (280 nm > λ > 420 nm) irradiated hexane solutions using HPLC. The amorphous films were prepared by spin-coating toluene solutions of **1b** and **2b** on an optically flat fused quartz plate (n = 1.4570 at 632.8 nm, n = 1.4530 at 817 nm, n = 1.4471 at 1320 nm, and n = 1.4443 at 1553 nm). Residual solvent was removed under reduced pressure at 60 °C for 24 h. Thickness of these films was from 400 to 3000 nm.

Thermal properties of the samples were studied with a differential scanning calorimeter (Pyris 1, Perkin-Elmer). Temperature was calibrated with indium and zinc and heating rate was 10 °C min^{-1}. UV−visible absorption spectra were recorded on a spectrophotometer (U-3500, Hitachi). An ultrahigh-pressure Hg lamp (1 kW, Ushio-1005 D) was used as a light source and the appropriate wavelength of light was selected with optical filters and/or a monochromator. Quantum yields of photochemical reactions in solutions were determined by using 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene as a reference.

Refractive index measurement was carried out using a prism coupler (Metricon, model 2010).[35] Scheme 2 shows the experimental setup of the prism coupler. The refractive index and the thickness were measured with accuracies of ±0.0005 and ±0.3%, respectively. The probe wavelengths in the prism coupler were 632.8, 817, 1320, and 1553 nm. The right-angled prism (Metoricon, 200-P-1) used for optical coupling had refractive indices of 1.9648, 1.9521, 1.9385, and 1.9350 at 632.8, 817, 1320, and 1553 nm, respectively. Coupling profiles as a function of incident angle were analyzed with the 2010 system software. Film thickness was also measured using a surface profiler (Alpha Step 500, Tencor Instruments).

Scheme 2. Prism coupler system for refractive index measurements



Results and Discussion

Photochromic reactions of diarylethenes **1** and **2** were studied in hexane. Figure 1 (a) and (b) show the absorption spectra of the open- and closed-ring isomers of **1** and **2** and also those of the photostationary states (PSS) under irradiation with 313 nm light. The closed-ring isomers **1b** and **2b** showed red-purple and blue colors, in which the absorption maxima were observed at 540 and 561 nm, respectively. Upon irradiation with visible light, the hexane solutions turned colorless and absorption bands in the visible range disappered. Upon irradiation the colorless solutions turned to red-purple (**1b**) and blue (**2b**). The conversions at PSS were

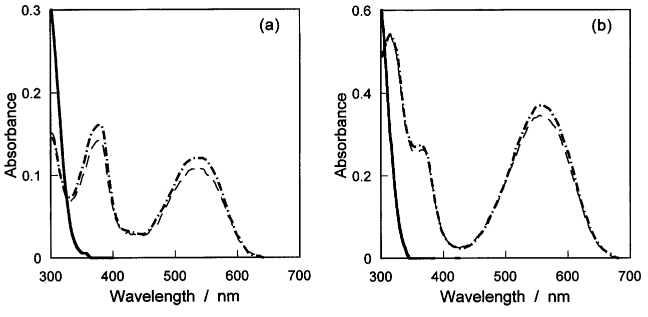


Figure 1. Absorption spectra of compounds **1** (a) and **2** (b) in hexane solutions: dotted line, **1b** and **2b** (initial state); solid line, **1a** and **2a** after bleaching by irradiation with visible light irradiation; broken line: photostationary state under irradiation with 313 nm light.

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Table 1. Optical Properties of Amorphous Diarylethenes 1 and 2

compd	$\lambda_{\max}$ ($\epsilon \times 10^4$) in hexane	conversion at PSS in hexane	$\lambda_{\max}$ in film	conversion at PSS in film[a]
1a	293 nm (5.7)	88%	299 nm	29%
1b	540 nm (2.1)		563 nm	
2a	254 nm (6.0)	94%	262 nm	68%
2b	561 nm (1.0)		570 nm	

[a] The conversion was evaluated from absorbance at $\lambda_{\max}$ in the photostationary state as follows. $\mathrm{Abs}_{(\lambda\max)}$ of the amorphous film of pure closed-ring isomer was first measured followed by complete bleaching with the visible light irradiation. Then $\mathrm{Abs}_{(\lambda\max)}$ was measured again after irradiation with 313 nm. The conversion was evaluated from the ratio of these two $\mathrm{Abs}_{(\lambda\max)}$.

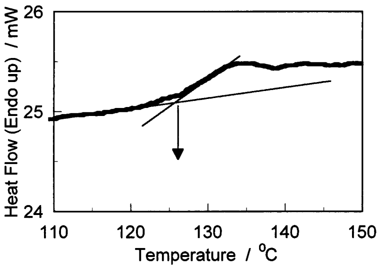

Figure 2. DSC profile of compound **1a** with temperature scanning rate of 10 °C/min. From the threshold temperature of the baseline shift, T_g of 127 °C was evaluated.

evaluated to be 88% (**1**) and 91% (**2**). Absorption peak wavelengths ($\lambda_{\max}$) and absorption coefficients (ϵ) of open- and closed-ring isomers, and the conversion from the open- to the closed-ring isomers at PSS are summarized in Table 1. The quantum yields of photochemical cyclization reaction of **1a** and **2a** were 0.40 and 0.60 while those of cycloreversion reaction of **1b** and **2b** were 0.17 and 0.02, respectively.

Compounds **1** and **2** form stable amorphous solids at room temperature when their toluene solutions are cast on appropriate substrates or those melts were cooled at room temperature. Thermal stability of the amorphous state was studied by DSC measurements. Figure 2 shows the DSC profile of compound **1a**, where a clear shift in the baseline was observed at 120−130 °C. This change in the heat capacity is a characteristic feature of the glass transition. The glass transition temperatures were evaluated as 127 °C for **1a** and 84 °C for **2a** from the onset temperature of the baseline shift. Below the glass transition temperature, molecular motion and migration in the bulk solid are frozen and growth of the crystalline phase is prohibited. Actually, the clear amorphous solids were stable at room temperature for more than 6 months. Thin films, micro-lenses, and even fibers were easily formed by melt-forming or spin-casting methods.

Figure 3 demonstrates a fiber of amorphous solid of compound **2**, which was formed by pulling a viscous melt of compound **2** at about 150 °C. Clear and transparent fiber was easily prepared. Its diameter was about 10 μm and a laser beam was optically coupled at the right end of the fiber. Wavelength of the laser beam was 532 nm for Figure 3(a) and 780 nm for Figure 3(b) and (c). The sample fiber was placed on a test pattern for demonstrating optical transparency of the amorphous photochromic fiber. In all cases, a coupled laser beam was guided in the fiber and the guided laser beam was emitted from the left end of fiber. In Figure 3(c), the fiber was converted to the colored state by irradiation with UV light of 365 nm. Even in the colored state, the beam of 780 nm was guided without significant optical loss. Although the correct value of the optical loss was not evaluated at this stage, we expect that the amorphous diarylethenes would have low optical loss because of their higher optical uniformity than the conventional polymeric optical materials. The polymeric materials tend to exhibit optical anisotropy and inhomogeneity because of partial alignment of the molecular chain in the pulled fiber, microcrystalline phase, and existence of chain ends.

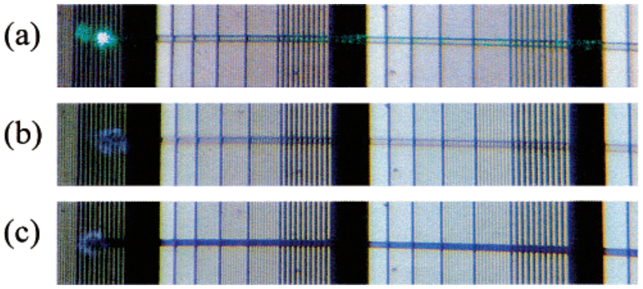

Figure 3. Examples of a fiber of amorphous solid of compound **2** prepared by pulling melt of compound **2a** at about 140 °C. Diameter = ca. 10 μm. (a) 532-nm light was coupled at the right end of the fiber; (b) and (c), 780-nm light was coupled; (c) after UV light irradiation; 780-nm light is observed as white because of an artifact in the CCD camera.

For the optical absorption and refractive index measurements, the sample solution was carefully filtered before spin-coating on a substrate in a clean room (class $<$ 500). Table 1 summarizes the peak wavelengths of optical absorption bands and the conversion ratio of **1** and **2** under irradiation with 313 nm light in the amorphous films. The sample films showed reversible photochromic behavior like that of other diarylethene solutions. The colored films are transparent at the wavelength longer than 690 nm (**1b**) and 710 nm (**2b**). The conversion of **2** in the amorphous film was observed to be as high as 68% and 73% under irradiation with 313 and 300 nm light, respectively. On the other hand, the conversion of diarylethenes **1** was only 29% upon irradiation with 313 nm light. One of the possible origins of this remarkable loss in the photochemical response is intermolecular excited-state energy transfer from **1a*** to **1b** in the mixed amorphous film of **1a** and **1b**. Because the visible absorption band of **1b** overlaps with the fluorescence emission band of **1a**, efficient excited-state energy transfer from **1a** to **1b** is possible and the absorption cross section of **1b** is effectively enhanced by an antenna effect of **1a**.[36] Because **2a** showed no marked fluorescence emission, such effect can be ruled out. Further studies should be done for clarifying intermolecular interaction in the amorphous solid in both the ground state and the excited state.

The refractive indices of amorphous diarylethene films were evaluated by the usual prism coupling method. The reflection intensity profile exhibited a series of coupling dips as typically shown in Figure 4. Each dip corresponds to a guided-wave mode in the amorphous film. Initially the coupling profile of the

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(36) Kawai, T.; Kim, M. S.; Irie, M. *Opt. Mater.* **2002**, *21*, 257.

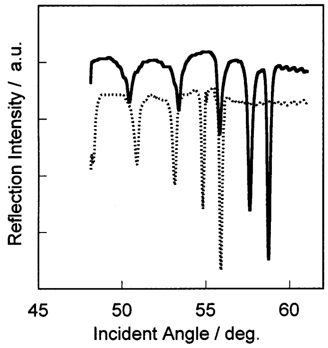

Figure 4. Prism coupling profiles of **2b** film before (solid line) and after (broken line) visible light irradiation. Probe beam was 817 nm in wavelength. 5 coupling modes were observed and estimated refractive indices and thicknesses were $n_{817} = 1.67537$, $n_{817} = 1.6229$, and $T = 2.482\ \mu$m, $T = 2.483\ \mu$m for solid line and broken line, respectively.

amorphous film of **2b** was measured and then the blue film was breached upon irradiation with 633 nm light. As shown in Figure 4, the position of the dips markedly changed upon irradiation with visible light. The composition of this partly bleached film was evaluated to be **2b**/**2a** = 16:84. The resonance condition of the guided-wave mode is typically expressed by eq 1[35]

$$2khn \cos\theta - 2\varphi_1 - 2\varphi_2 = 2m\pi \tag{1}$$

where k is the normal component of the wave vector, h is the thickness of the film, and n is the refractive index at the considered wavelength. Variables φ_1 and φ_2 are the phase changes due to the total reflections at the upper film boundary and the lower film boundary, respectively, and depend on the n and refractive index of the substrate. The m parameter is an integer corresponding to the index number of the guided-wave modes. The h and n parameters were numerically calculated by fitting the dip positions with eq 1. For example, the analysis of the coupling profiles shown in Figure 4 resulted in $n_{813} = 1.675(4)$ and $h = 2.48(2)\ \mu$m for the **2b** film and $n_{813} = 1.622(9)$ and $h = 2.48(3)\ \mu$m for the breached film. The changes in the coupling profiles and the dip positions are due to the refractive index change of the film but not due to the thickness change. The film thickness evaluated by the surface profiler was not altered upon photoirradiation.

Coupling profiles of **2b** film 800 nm thick were measured after appropriate periods of visible light irradiation, and the conversion ratio from **2b** to **2a** was evaluated from absorbance at 570 nm. The evaluated refractive indices at 817 nm are plotted in Figure 5 (a) against the ratio in the film. The refractive index almost linearly decreased with the decrease of **2b**. The open squares in Figure 5(a) and (b) indicate refractive indices of the film irradiated with UV light. The refractive index decreased from 1.675 to 1.617 and again increased to 1.645, and it was modulated between 1.617 and 1.645 for several times as shown in Figure 5(b) with alternating irradiations with UV and visible light. The amplitude of refractive index modulation was as large as 0.028 at 817 nm, which is markedly larger than that in dye-dispersed polymer films. Because the light was irradiated though prism and quartz plates, it took several tens of seconds for each coloration and bleaching process. One may achieve a faster switching rate with some lasers of appropriate power and pulse width.

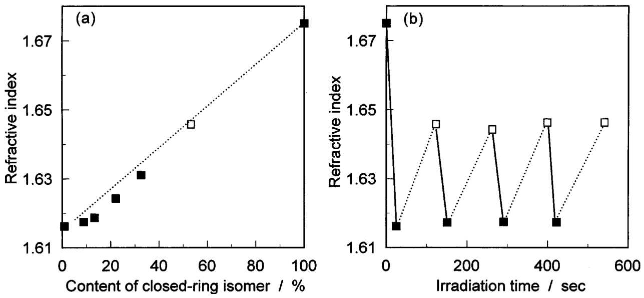

Figure 5. Modulation in refractive index of an amorphous bulk **2b** film by irradiation with UV and visible light. Film thickness = ca. 800 nm. Wavelength = 817 nm. Closed and open circles correspond to after visible and UV light irradiation, respectively. (a) Refractive index as a function of ratio of closed-ring isomer **2b** in the film. (b) Change in refractive index by alternating irradiations with UV and visible light. A Hg lamp of 6 mW was used as an UV light source with an UV-pass filter (UV-D33S, Toshiba). A He–Ne laser of 5 mW was used as the visible light source. The light was irradiated through the prism and quartz substrate.

Table 2. Refractive Index of Amorphous Diarylethenes 1 and 2

	refractive index				estimated	estimated
compd	632.8 nm	817 nm	1320 nm	1553 nm	D value	n_∞ value
1a	1.654	1.637	1.623	1.621	0.436	1.616
1b		1.717	1.687	1.684	0.149	1.677
2a	1.631	1.617	1.604	1.602	0.530	1.597
2b		1.675	1.642	1.640	0.147	1.632

Table 2 summarizes the refractive indices of **1** and **2** at the near-IR region. These refractive index changes are based only on photoisomerization, and no change in refractive index was observed when these films were stored without light irradiation. The wavelength dispersion of refractive index was experimentally analyzed by Sellmeier eq 2[37]

$$n_\lambda^2 = n_\infty^2 + D\lambda_o^2/(\lambda^2 - \lambda_o^2) \tag{2}$$

where D is a constant value related to the oscillator strength and density of the molecule in the film, λ is the wavelength of a monitoring light, and n_λ is refractive index at λ. The term λ_o is the wavelength of absorption peaks, 29, 563, 262, and 570 nm for **1a**, **1b**, **2a**, and **2b**, respectively, and n_∞ is the refractive index at the longest wavelength limit. As shown in Figure 6, square of n_λ of **1a**, **1b**, **2a**, and **2b** films linearly increased with increase in $\lambda_o^2/(\lambda^2 - \lambda_o^2)$. The parameters D and n_∞ in eq 2 were evaluated from the slopes and intercepts of the regression lines shown in Figure 6. The results are summarized in Table 2. Figure 7 shows estimated and measured dispersion of refractive indices of **1a**, **1b**, **2a**, and **2b**. The fact that the measured data of the refractive indices is well reproduced indicates that the dispersion of refractive index of the amorphous diarylethene films can be expressed by the Sellmeier equation.

The origin of the refractive index difference between the closed- and the open-ring forms is explained by the two terms in the Sellmeier equation. Because the closed-ring isomers have the optical absorption to 500–600 nm, the molecular polarizability at wavelength longer than

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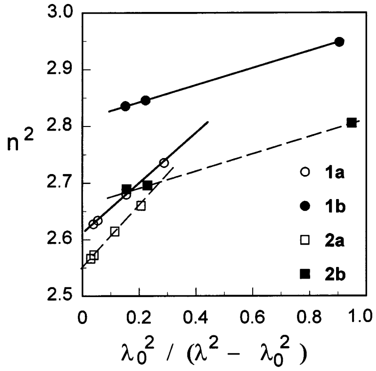

Figure 6. Plots of n^2 of amorphous films of **1a** (open circle), **1b** (closed circle), **2a** (open square), and **2b** (closed circle) against $\lambda_0^2/(\lambda^2 - \lambda_0^2)$ and their regression lines.

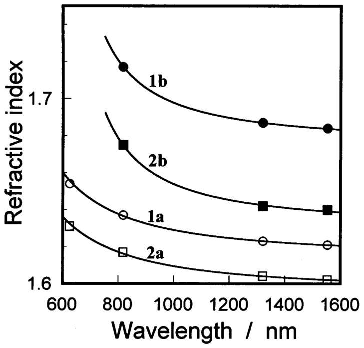

Figure 7. Measured (marks) and estimated (lines) dispersion of refractive indices of amorphous films of **1a** (open circle), **1b** (closed circle), **2a** (open square), and **2b** (closed circle).

the absorption band should be larger than that of the open-ring isomer. The dispersion effect is expressed in the second term of eq 2 and is dominant in the shorter wavelength range. As summarized in Table 2, n_∞ values of the closed-ring isomer are considerably larger than those of the open-ring isomers. As n_∞ is an ideal value of the refractive index at low frequency limit, this difference means that the static polarizability of the closed-ring isomer is considerably larger than that of the open-ring isomer. Whereas the π-conjugation system in the open-ring form of diarylethene is limited to the heterocyclic aryl groups, the π-conjugation system extends throughout the molecule in the closed-ring isomer. The larger π-conjugation length is an origin of the larger static polarizability of the closed-ring isomers. As a related matter, one of the authors has reported that the dielectric constant of the bulk diarylethene solid at low frequency is modulated with the photochromic reaction.[12]

Summary

The diarylethenes **1** and **2**, which have 2,4-diphenylphenyl substituents, formed stable amorphous solids, which exhibit fairly high photoresponsibility. Because the amorphous solid was composed only of photoactive diarylethene, a large amplitude of refractive index modulation upon photoirradiations was observed. Especially, compound **2** exhibited a reversible refractive index modulation as large as 0.028 at 817 nm by alternative irradiation with UV and visible light. From an analysis based on the Sellmeier equation, the origin of the refractive index change was attributed to the difference in both the dispersion effects and the static polarizabilities in both photoisomers. Because of their transparency at near-IR range even in the colored form, the refractive index modulation has nondestructive capability as the active materials of optical switching and memory devices.

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