Photochromism of a Dithienylethene Having Diphenylamino Side Groups in the Bulk Amorphous Phase[1]

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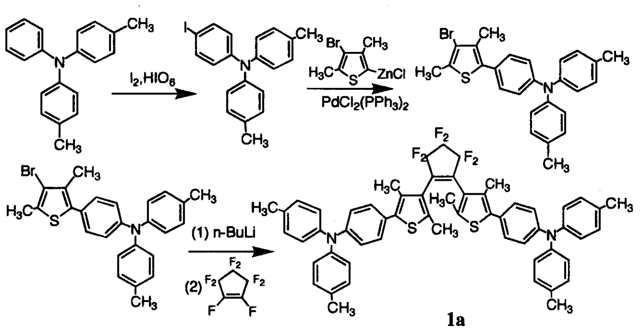
1,2-Bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene was found to form an amorphous state in bulk by introducing diphenylamino substituents at both ends of the molecule. The glass transition temperature was as high as 103 °C. The amorphous film exhibited reversible color and refractive index changes by alternate irradiation with ultraviolet and visible light.

Various types photochromic compounds, such as spirobenzopyrans, azobenzenes, furylfulgides, and diarylethenes, have been so far developed for applications to optoelectronic devices. Among the compounds diarylethenes are the most promising for the applications because of fatigue resistant and thermally irreversible photochromic performance.[2,3] Diarylethenes exhibit photo-reversible changes not only in the optical absorption and fluorescence spectra but also in other optical properties such as refractive index and non-linear optical effect.[4–10] The refractive index change is of special interest because wave-guided optical switches, holographic grating and 3D memories are based on the refractive index change.

For the practical applications photochromic reactions should take place in solid matrices. So far polymers have been used for the solid matrices, but polymer matrices have several defects. In general it is not easy to increase the dye concentration and segregation takes place to some extent after long term storage. The ideal solid matrices are bulk amorphous or crystalline states. Bulk amorphous materials have advantageous characteristics, such as high dye density and low optical scattering, and thin films can be easily prepared from the materials by spin-coating or vacuum deposition methods.[6,11] Optical isotropy of the amorphous state is also favorable for device fabrication. Although several amorphous diarylethenes have been so far reported, the glass transition temperatures are below 80 °C.[6,12–16] For practical use it is preferred to increase T_g above 100 °C. In the present study we report on a new diarylethene which forms an amorphous state in bulk with T_g higher than 100 °C. We also studied the photostimulated reversible change in refractive index in the bulk amorphous state.

A new dithienylethene derivative having diphenylamino groups, 1,2-bis[2,4-dimethyl-5-[4-*N*,*N*-bis(4-methylphenyl)amino]phenyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene, **1a**, was prepared as shown in Scheme 1. The product was purified by GPC and HPLC (silica-gel/hexane) and characterized by the conventional methods.[17] After evaporation of the solvent, **1a** was obtained as colorless amorphous glass. The thin film of **1a** was prepared on a quartz substrate by a spin-coating method from its toluene solution. Optical absorption spectra were measured with a spectrophotometer (Hitachi, U-3500) at room temperature. Thermal property of the sample was studied with a differential scanning calorimeter (Seiko Instruments, DCS6200). The temperature scan rate was typically 5 °C/min. Refractive index of the amorphous sample was measured with a prism-coupler system (Metricon, 2010) utilizing IR-diode laser (817 nm) as a light source.



Scheme 1 Synthesis of **1a**.

Hexane solution of **1a** showed absorption bands at 306 nm (ε_{max} = 48000 $M^{-1}cm^{-1}$) and 333 nm (ε_{max} = 51700 $M^{-1}cm^{-1}$). Upon irradiation with UV light (λ = 366 nm), the colorless hexane solution turned blue, in which absorption peaks were observed at 595 nm and 420 nm. The visible absorption bands disappeared by irradiation with visible light (λ > 480 nm). An isosbestic point was observed at 360 nm. The photochemical colored product was isolated from the UV-irradiated hexane solution by HPLC (silica-gel/hexane). NMR and mass spectra assigned the product to the closed-ring isomer, **1b**.[17] The absorption coefficients are ε_{max} = 20700 $M^{-1}cm^{-1}$ at 595 nm and ε_{max} = 24100 $M^{-1}cm^{-1}$ at 420 nm. The conversion ratio at the photostationary state under irradiation with 313 nm light was estimated to be 99%.

The cyclization and cycloreversion quantum yields in hexane solution were measured using furylfulgide as the reference.[18] The cyclization quantum yield was as large as 0.44, while the cycloreversion quantum yield was very low (0.005). The substitution of electron donating diphenylamino groups is considered to suppress the cycloreversion quantum yield from 0.015 to 0.005.[18] The high conversion in the photostationary state can be explained by the large quantum yield difference between cyclization and cycloreversion reactions.

The amorphous films of **1a** and **1b** showed similar photochromic behavior. The **1a** film was colorless and showed the absorption peaks at 304 nm and 334 nm. Upon irradiation with UV light (λ = 313 nm) the film turned blue and the absorption peaks were observed at 432 nm and 606 nm, which are same as the peaks of the **1b** film. The absorption peak wavelengths of the bulk films were slightly longer than those in solution. The conversion ratio at the photostationary states of **1a** and bleached **1b** films under irradiation with 313 nm light were 35% and 48%, respectively. The bleached amorphous film prepared from **1b** exhibited higher conversion ratio in the photostationary state than that of the film prepared from **1a**. The open-ring isomers of diarylethenes have two conformations, parallel and anti-parallel conformations, and the photochemical cyclization reaction takes place only from the anti-parallel conformation. Although interconversion between the two conformers is allowed in solution, the interconversion is strongly suppressed in the amorphous film. When **1a** is produced by visible light irradiation from **1b** in the amorphous film, the photogenerated **1a** is considered to be in the photoactive anti-parallel conformation and hardly interconverts to the photo-inactive parallel conformation. This is the reason why the conversion in the photostationary state of the film prepared from **1b** is higher than that of the film from **1a**. The low conversion in the film prepared from **1a** is that a part of molecules are in the photo-inactive parallel conformation.

Thermal property was studied by DSC as shown in Figure 1. Upon heating, **1a** showed a clear endothermal peak at 113.7 °C , and clear shift in the base line was observed at around this peak, which is typical for the glass-to-liquid transition. The endothermal peak can be assigned to the intermolecular interaction in the glass state. Based on the threshold temperature, the glass transition temperature, T_g, was determined to be 103 °C. Thermal behavior of **1b** was also investigated and clear glass transition behavior was observed above 120 °C and T_g was determined to be 124 °C, as shown in Figure 1(b). Formation of **1a** indicates that the exothermal peak at about 178 °C corresponds to the thermal cycloreversion reaction. The higher T_g of **1b** is attributed to the planer molecular structure of **1b**.

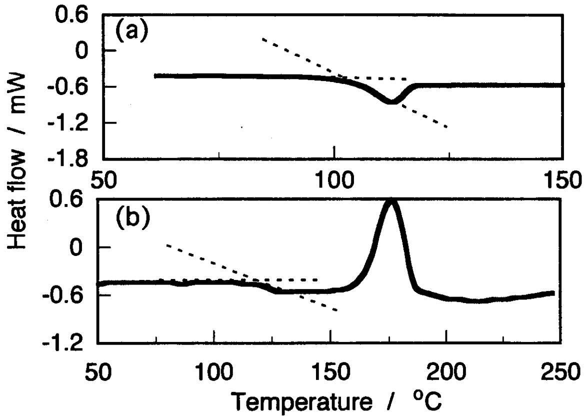


Figure 1. DCS curves of (a) **1a** and (b) **1b**.

The change in the refractive index of **1** was also studied by a prism coupling method.[14] At the monitoring wavelength of 817 nm both **1a** and **1b** have no optical absorption. The refractive index changes upon UV (λ = 313 nm) and visible (λ > 480 nm) light irradiations are shown in Figure 2. The refractive index of **1a** film was 1.619 and increased to 1.635 upon irradiation with UV light. The refractive index of film of **1b** decreased from 1.659 to 1.624 upon irradiation with visible light. These changes in the refractive index clearly indicate that the closed-ring isomer **1b** has higher polarizability than that of the open-ring isomer **1a**. The difference between the refractive indices of **1a** and **1b** was 0.040, which is similar to the value of our previous result on amorphous film.[13] It should also be noted that the refractive index of the bleached **1b** film was slightly higher than that of **1a** film. This difference suggests that the structure of **1a** molecule in the **1a** film is different from that in the bleached **1b** film and, therefore, density is slightly different. The refractive index in the photostationary state of the **1b** film was found to be about 0.015 larger than the bleached **1b** film, which is 43 % of the refraction index change of **1b** film. This ratio is roughly in accordance with the conversion ratio at the photostationary state, 48%, suggesting a linear relationship between composition and refractive index.

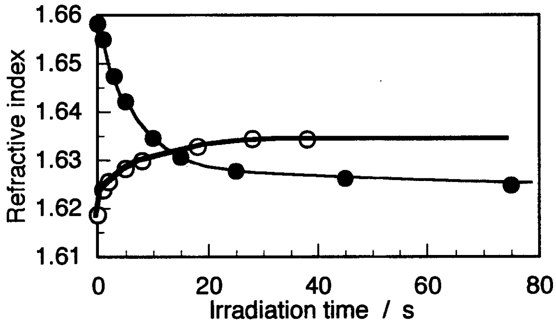


Figure 2. Changes in refractive index of (a) **1a** and (b) **1b** films upon irradiation with UV and visible light, respectively. (25 °C, wavelength = 817 nm).

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17 **1a**: ^{1}H NMR($CDCl_3$): δ = 2.07(s, 3H), 2.10(s, 3H), 2.32(m, 18H), 6.9–7.3(m, 24H). MS *m/z* = 938(M^+). **1b**: ^{1}HNMR ($CDCl_3$); δ = 2.21(s, 6H), 2.32(m, 18H), 6.9–7.3(m, 24H). Anal. Found: C,73.30;H, 5.53; N, 2.89%. Calcd. for $C_{57}H_{48}F_6N_2S_2$: C, 72.90; H, 5.15; F, 12.14; N, 2.98; S, 6.83%. MS *m/z* (M^+) = 938.
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