Synthesis of Amorphous Diarylethenes Having Diphenylethenyl Substituents

Myeong-Suk Kim, Tsuyoshi Kawai, and Masahiro Irie*
Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, and
CREST, Japan Science and Technology Corporation (JST), 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

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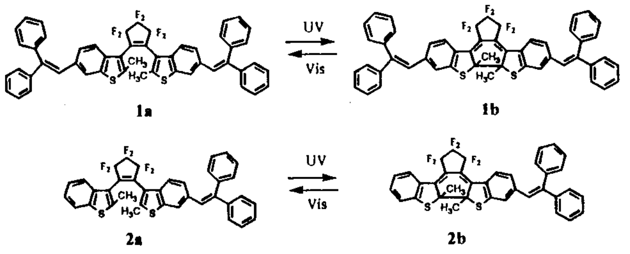
1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene derivatives having diphenylethenyl substituents at 6- and 6'-positions of the benzothiophene rings were synthesized. The mono and disubstituted derivatives formed an amorphous state and the glass transition temperatures were observed at 67 °C and 92 °C, respectively. Reversible photocyclization reactions were observed in the amorphous state.

Photochromic materials have been extensively studied since they are potentially useful for various photonic devices, such as optical memory, photo-optical switching and display. Among a number of photochromic compounds, diarylethene derivatives have attracted much attention because of their specific photochromic performance, thermal stability in both states and fatigue resistant property.[1–3] For the practical applications, the photoreactions should take place in solid states, such as in polymer matrices,[4] bulk crystals[5–8] or an amorphous state.[9,10] The amorphous solid state is the most promising because of its optical transparency and capability to form thin films by a spin-coating method.[11] We report here the synthesis of diarylethenes which exhibit a stable amorphous state and their photochromic behavior in the amorphous state.

1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene derivatives having diphenylethenyl substituents at 6- and 6'-positions of the benzothiophene rings, **1** and **2**, were synthesized by Wittig reaction of the formyl derivatives of the diarylethenes with diphenylethenyl substituents. Compounds **1** and **2** were purified carefully by GPC and HPLC. The molecular structures were determined by ^{1}H NMR, mass spectra and elemental analysis.[12] The closed-ring isomers were isolated from UV irradiated hexane solutions of **1** and **2** using HPLC (silica-gel / hexane: ethyl acetate = 97 : 3). Compounds **1** and **2**, and their closed-ring isomers formed a stable amorphous state when solvent was evaporated from the toluene solution. Amorphous films were prepared by spin coating the toluene solutions of the compounds (typically 1.6×10^{-3} mol/L) on a quartz substrate. The thickness of the films was about 0.1 µm. The films were dried in a vacuum oven at 50 °C for 48 h and their photochromic behavior was examined under vacuum.

Scheme 1.



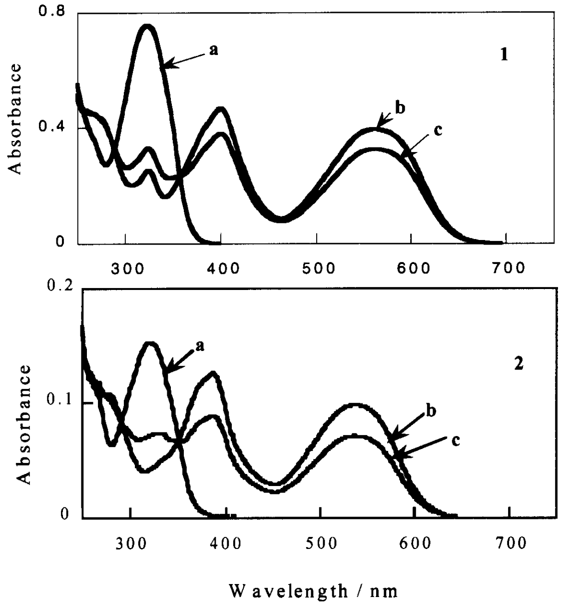


Figure 1. Absorption spectra of **1** (1.3×10^{-5} mol/L) and **2** (4.7×10^{-6} mol/L) in hexane solutions: (a) open-ring isomer, (b) closed-ring isomer, and (c) photostationary state under irradiation with 313 nm light.

The absorption spectral changes of **1** and **2** in hexane are shown in Figures 1(1) and (2), respectively. Upon irradiation with 313 nm light, the strong UV absorption band at 324 nm decreased and new absorption bands appeared at 560 nm and 538 nm, which are ascribed to the closed-ring isomers **1b** and **2b**,[2] respectively. The conversions in the photostationary state were 83% and 72% for the solutions of **1** and **2**, respectively. The photogenerated visible bands disappeared by irradiation with visible light (λ > 450 nm).

Figure 2 shows the absorption spectral changes of **1** and **2** in amorphous thin films. The amorphous film of **1** was prepared from the toluene solution containing the isolated closed-ring isomer **1b**. First, the visible absorption at 580 nm of **1b** was bleached by irradiation with visible light (λ > 450 nm), and then the film was irradiated with UV light (λ = 313 nm). The peak position of the closed-ring isomer **1b** exhibited a considerable red-shift in comparison with that in hexane. Upon 313 nm irradiation, the 325 nm band due to the open-ring isomer **1a** decreased and the 580 nm band due to the closed-ring isomer **1b** increased. The conversion in the photostationary state was evaluated to be 30% for the amorphous film of **1**. The photochemical behavior of the amorphous film of **2** was similar to that of **1**, though the conversion was lower.

The conversion from **1a** to **1b** in the amorphous film pre-

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pared from the solution of the open-ring isomer **1a** was much lower, around 10%. In the film half of the molecules are in the photochemically inactive parallel conformation.[13] This is the reason of the low conversion. When the amorphous film was prepared from the solution of the closed-ring isomer **1b** as shown in Figure 2, all molecules are in the photoactive anti-parallel conformation. The increase in the conversion is ascribed to the high content of the photoactive conformers.

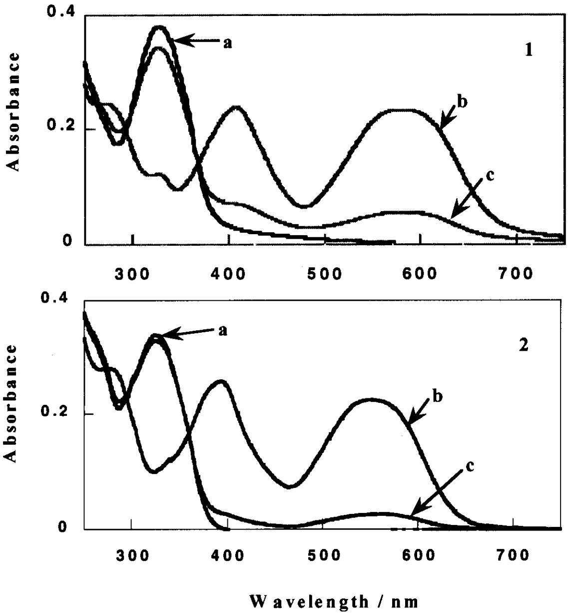

Figure 2. Absorption spectra of **1** and **2** in amorphous films: (a) open-ring isomer, (b) closed-ring isomer, and (c) photostationary state under irradiation with 313 nm light.

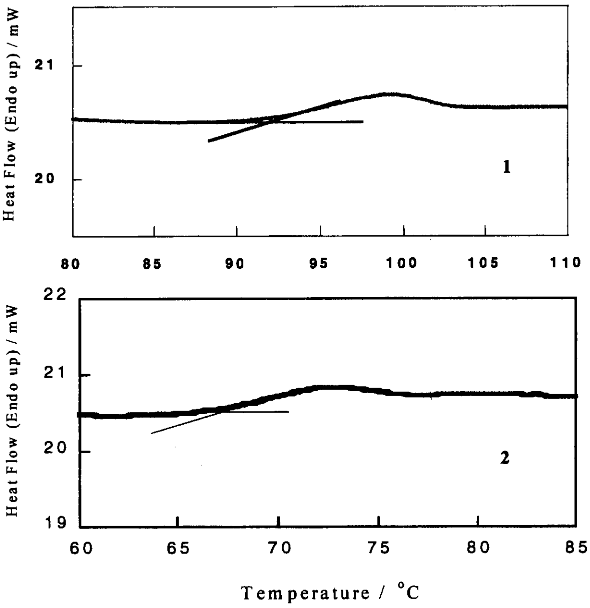

Figure 3. DSC curves of compounds **1** and **2**. **1**: temperature scan rate=10 °C/min, weight=5.2 mg; **2**: temperature scan rate=10 °C/min, weight=8.2 mg.

The DSC profiles of **1** and **2** are shown in Figure 3. Compounds **1** and **2** were obtained from the hexane solutions as crystals and their melting temperatures were 208 °C and 193 °C, respectively. The crystals were heated above the melting temperatures and then slowly cooled. In the second run, clear shifts of the baselines were observed at around 90 °C and 70 °C for **l** and **2**, respectively. The baseline shifts were attributable to the glass to liquid transition. T_g's of the samples **1** and **2** were evaluated from the shifts to be 92 °C and 67 °C, respectively. T_g of **1** is high enough for the practical applications to the optical memory and switching devices.

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12 **1a**: mp 208 °C; ^{1}H-NMR (400 MHz, acetone-d_6, 20 °C) δ = 2.27 (s, 3.5H), 2.53 (s, 2.5H), 6.90–8.30 (m, 28H), Found: C, 74.60; H, 4.34%. Calcd for $C_{51}H_{34}F_6S_2$: C, 74.25; H, 4.15%. **1b**: ^{1}H-NMR (400 MHz, acetone-d_6, 20 °C) δ = 1.94 (s, 6H), 6.90–8.30 (m, 28H). **2a**: mp 193 °C ; ^{1}H-NMR (400 MHz, acetone-d_6, 20 °C) δ = 2.32 (s, 1.83H), 2.30 (s, 1.83H), 2.54 (s, 1.17H), 2.57 (s, 1.17H), 6.91–7.86 (m, 18H), Found: C, 68.78; H, 3.88%. Calcd for $C_{37}H_{24}F_6S_2$: C, 68.72; H, 3.74%. **2b**: ^{1}H-NMR (400 MHz, acetone-d_6, 20 °C) δ = 1.99 (s, 6H), 6.91–7.86 (m, 18H).
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