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Synthesis and Photochromism of Amorphous Diarylethene Having Styryl Substituents

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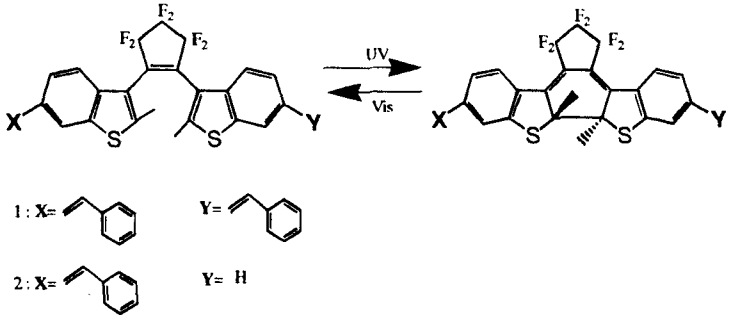
1,2-bis (2-methyl- 1-benzothiophen-3-yl) perfluorocyclopentene derivatives having styryl substituents at 6 and 6′ positions of the benzothiophene rings were synthesized. The mono-substituted derivative was crystal, while the di-substituted one formed amorphous state below the glass transition temperature(Tg) of 60°C. Reversibe photocyclization reactions were observed in the amorphous state.

Keywords: Photochromism; Amorphous; Glass Transition Temperature; Diarylethene

INTRODUCTION

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 materials, diarylethene derivatives have attracted much attention

because of their specific performance, thermal stability in both states and fatigue resistant property.[1,2] The diarylethene exhibits photochemical cyclization and cycloreversion reactions upon UV and visible light irradiations, not only in solution or polymer films but also in crystalline [3] as well as bulk amorphous solid states.[4,5] For the practical applications, the amorphous solid state is most promising because of its optical transparency and capability to form thin film by spin-coating method. In the present paper, synthesis and photochormic behavior of new diarylethene derivatives having styryl substituents are studied.



SCHEME 1

EXPERIMENTAL SECTION

1,2-Bis(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene derivative having styryl substituents at 6 and 6' positions of the benzothiophene rings, **1** and **2** were synthesized according to the reaction route shown in Figure 1. Compounds **1** and **2** were purified

carefully by HPLC and GPC. The molecular structure was confirmed by NMR, Mass spectra and elemental analysis. The closed-ring isomers were isolated by passing UV irradiated hexane solutions containing **1** and **2** through HPLC(silica-gel/hexane:ethyl acetate=96%:4%).

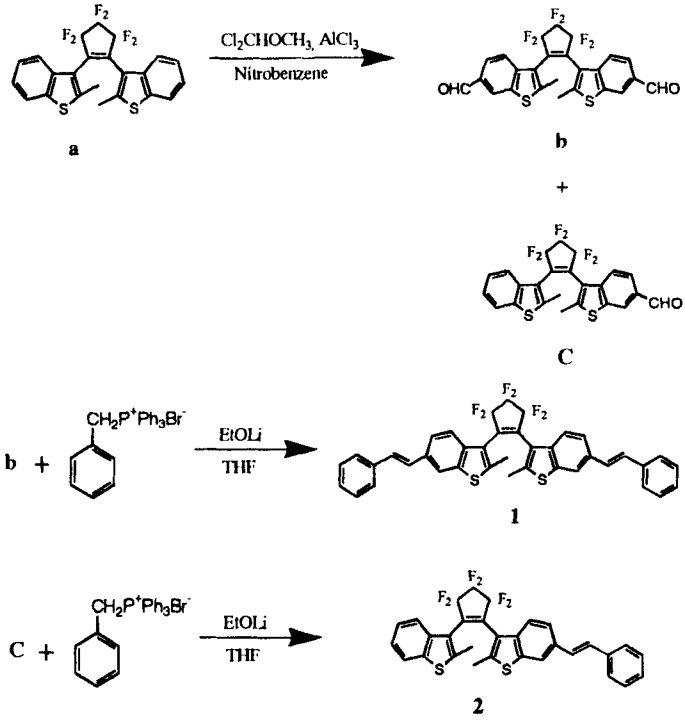


FIGURE 1 Syntheses of compounds **1** and **2**.

Compound **1** formed stable amorphous state, while compound **2** turned crystal after storage at room temperature. We described here photochromic reactions in the amorphous film of compound **1**.

Amorphous films were prepared by the spin coating the

dichloroethane solution of compound **1** (typically 0.69mg/26μl) onto a quartz substrate. The thickness of the films was typically 0.1μm. The films were dried in a vacuum oven at 50°C for 3h.

RESULTS AND DISCUSSION

Photochromic Reaction

Figure 2(a) shows the absorption spectral change of **1** in hexane. The open-ring isomer exhibits a strong band at around 297nm. Upon irradiation with 313nm light, a new band appeared at 550nm, which is ascribed to the closed-ring isomer, along with the decrease of 297nm band. The solid line indicates the photostationary state. Figure 2(b)

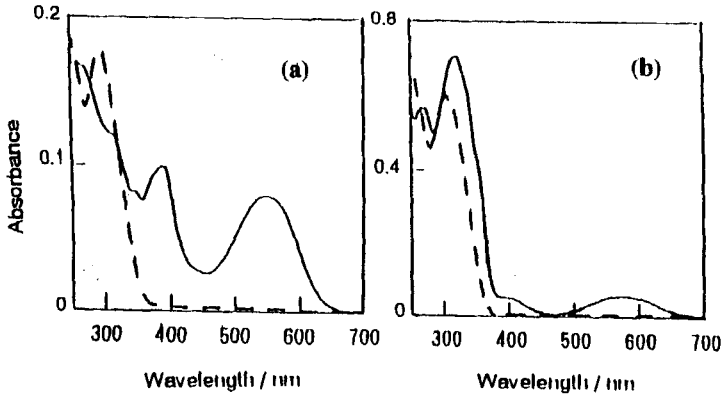


FIGURE 2 Absorption spectra of **1** in (a) hexane solution and in (b) amorphous film (---) before and (—) after irradiation with 313nm light.

shows the absorption spectral change of **1** in the amorphous film, which was prepared by the spin coating method. Upon UV light irradiation,

absorption band of the closed-ring isomer appeared around 570nm which was slightly longer than that in hexane solution.[5] Upon irradiation with visible light, the absorption band at 570nm disappeared. Reversible photochromic reactions of **1** in the amorphous state was confirmed.

DSC Measurement

Figure 3 shows the DSC profile of compound **1**. The difference in the heat capacities above 70°C and below 55°C indicates freezing of molecular motion. Tg was determined from the threshold of heat flow to be about 60°C. It should be noted that **1** investigated here has a cis- and a trans-styryl substituents in each molecule. A stereo-isomer of two trans-styryl substituents showed Tg at around 30°C. The amorphous film was highly stable and preserved the amorphous state for more than 5 month at room temperature. Compound **2** formed crystal with Tm of 150°C.

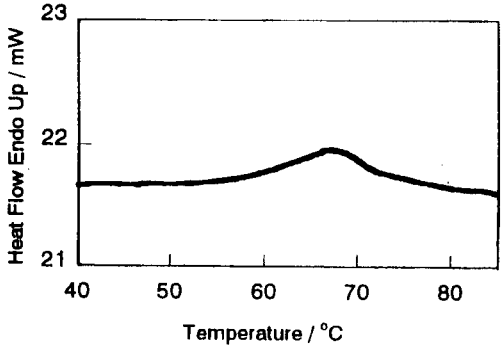


FIGURE 3 DSC profile of compound **1**.
(temperature scan rate=10°C/min, weight=7.7mg)

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