

Photochromic properties of diarylethenes having 2,4-diphenylphenyl substituents in the amorphous and PMMA films

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Abstract

1,2-Bis[5-methyl-2-(2,4-diphenyl)phenyl-4-thiazolyl]perfluorocyclopentene **1a** and 1,2-bis-[2-methyl-5-(2,4-diphenyl)phenyl-3-thienyl]perfluorocyclopentene **2a** were synthesized and their photochromic performance was examined in the bulk amorphous states. Compounds **1a** and **2a** formed stable amorphous bulk solid at room temperature and the glass transition temperatures (T_g s) of them were observed at 77 °C. The conversions in the photostationary states were evaluated to be 88% and 90% in the amorphous films prepared from the closed-ring isomers **1b** and **2b**. The values are higher than that of 1,2-bis[2,4-dimethyl-5-(2,4-diphenyl)phenyl-3-thienyl]perfluorocyclopentene **3** (74%). Photochromic reactions of these compounds were also examined in poly(methyl methacrylate) (PMMA) films. The conversion ratios of **1** and **2** (91% for both compounds) in the PMMA films are also higher than that observed in **3** (80%). The photocyclization quantum yields of **1a**, **2a**, and **3a** are the same, while the photocycloreversion quantum yields of **1b** and **2b** are lower than that of **3b**. The higher conversions of **1** and **2** are attributed to the lower photocycloreversion quantum yields, which were caused by the decrease in the steric hindrance between 4-position of the aryl groups and perfluorocyclopentene ring.

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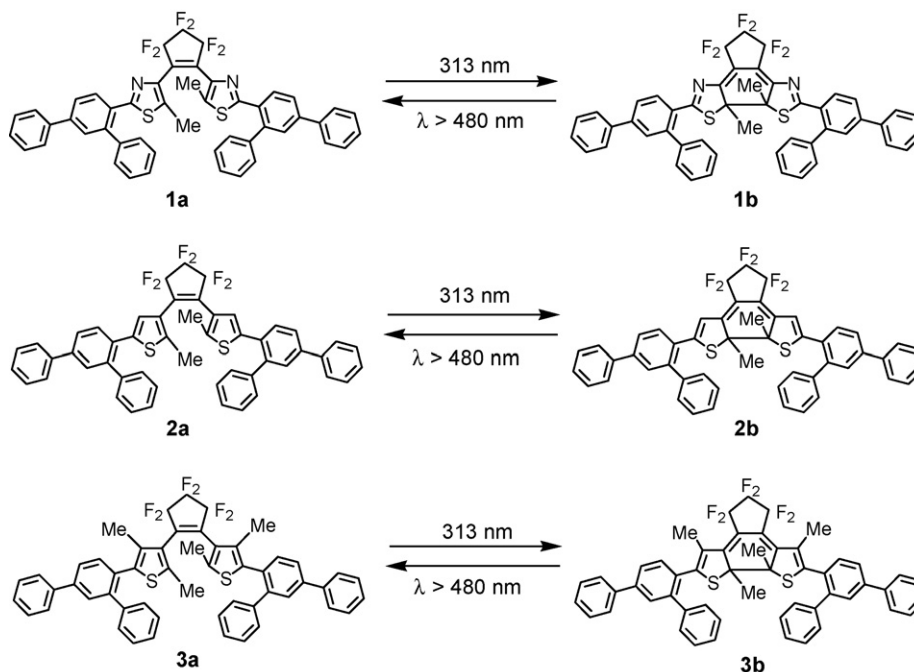
Keywords: Photochromism; Diarylethene; Amorphous film; PMMA film

1. Introduction

Photochromic compounds have attracted much attention because of their potential ability for optical memory media and photo-optical switching devices [1,2]. For the practical applications the photochromic reaction should take place in solid states, such as in polymer matrices, sol–gel glasses or bulk amorphous states [3]. Among them bulk amorphous photochromic materials are the most promising for the practical use because of their optical transparency and capability to form thin films by a spin-coating method [4–17]. In previous papers [14,16], we showed that introduction of 2,4-diphenylphenyl groups to diarylethene derivatives are effective to stabilize the amorphous state. When the diphenylphenyl groups are introduced at both sides of bisbenzothienylethene, the highest T_g of

127 °C is observed. The conversion ratio from the open- to the closed-ring isomers in the amorphous state is strongly dependent on the structure of the diarylethenes. When the methyl groups at 4-position of the thiophene rings of diarylethene are eliminated, the conversion ratios dramatically increase. The conversion ratios of 1,2-bis[2-methyl-5-[4-*N,N*-bis(4-methylphenyl)amino]phenyl-3-thienyl]perfluorocyclopentene and 1,2-bis[2,4-dimethyl-5-[4-*N,N*-bis(4-methylphenyl)amino]phenyl-3-thienyl]perfluorocyclopentene having bulky diphenylamino groups are reported to be 35% and 77% in the amorphous films, respectively [8,10]. In this study, amorphous diarylethenes **1** and **2** having 2,4-diphenylphenyl group have been synthesized, and their photochromic properties have been compared with that of 1,2-bis[2,4-dimethyl-5-(2,4-diphenyl)phenyl-3-thienyl]perfluorocyclopentene **3** in order to know the effect of the methyl substituents at the 4-position. (Scheme 1) Furthermore, we have investigated the photochromic reactions of these compounds in poly(methyl methacrylate) (PMMA) films.

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Scheme 1.

2. Experimental

2.1. General

HPLC was performed on a Hitachi L-7100 liquid chromatography coupled with a Hitachi L-7400 spectrophotometric detector. ^1H NMR spectra were recorded on a Varian Gemini 200 instrument. Mass spectra were measured with a Shimadzu GCMS-QP5050A gas chromatography-mass spectrometer. Absorption spectra record on a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out using an Ushio 500 W superhigh-pressure mercury lamp or an Ushio 500 W xenon lamp. Monochromatic light was isolated by passing the light through a cutoff filter (UV-27) and monochromator (Ritsu MC-10N). The thickness of the films were measured by Alpha-Step 500. The differential scanning calorimetry (DSC) measurement was carried out using a Perkin Elmer, Pyris 1 apparatus. The measurement was carried out at a heating rate of $5^\circ\text{C}/\text{min}$. Poly(methyl methacrylate) (PMMA) ($M_w = 10,000$) was used as polymer matrix.

2.2. Synthesis

2.2.1. 5-Methyl-2-(2,4-diphenyl)thiazole (4)

To a solution of 5-methylthiazole (1.9 g, 19 mmol), iodo-*m*-terphenyl (2.3 g, 6.5 mmol) [18], $\text{PdCl}_2(\text{PPh}_3)_2$ (1 g, 1.42 mmol), and CuI (150 mg, 0.79 mmol) in dry DMSO (50 mL) was added TBAF (27 mL of 1 M THF solution, 27 mmol) under an argon atmosphere. The resulting solution was degassed via five freeze-pump-thaw cycles and heated in an oil bath (65°C). The solution was stirred at that temperature for 3.5 days, and then distilled water was added. The product was extracted with diethyl ether, dried with MgSO_4 , and con-

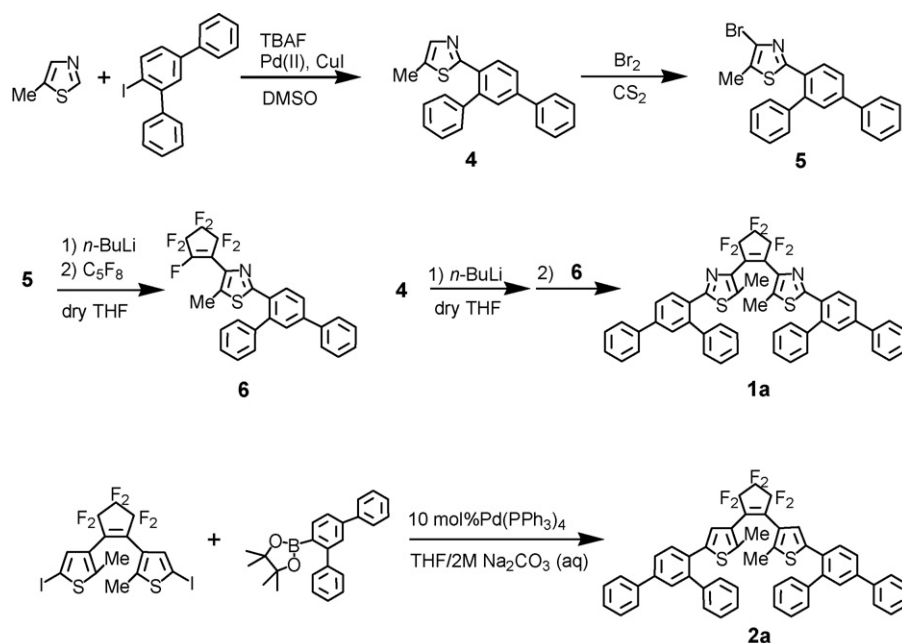
centrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 1:9) to afford to 1.5 g (70%) of **4** as a colorless crystal: mp $128\text{--}129^\circ\text{C}$. ^1H NMR (200 MHz, CDCl_3): $\delta = 2.35$ (d, $J = 1.2$ Hz, 3H), 7.7–7.3 (m, 13H), 8.08 (d, $J = 8.4$ Hz, 1H). MS $m/z = 326$ (M^+). Anal. Calcd. For $\text{C}_{22}\text{H}_{17}\text{NS}$: C 80.70, H 5.23, N 4.28%. Found: C 81.00, H 5.29, N 4.51%.

2.2.2. 4-Bromo-5-methyl-2-(2,4-diphenyl)thiazole (5)

Bromine (0.7 g, 4.8 mmol) was added to a stirred solution of **4** (1.6 g, 4.9 mmol) in CS_2 (15 mL). The mixture was stirred at room temperature for 36 h and extracted with ethyl acetate. The organic layer was dried with MgSO_4 and concentrated under reduced pressure. The reduced was purified by column chromatography (ethyl acetate/hexane, 1:9) to afford 400 mg (20%) of **5** as colorless solid: ^1H NMR (200 MHz, CDCl_3): $\delta = 2.25$ (s, 3H), 7.71–7.30 (m, 12H), 8.17 (d, $J = 8.2$ Hz, 1H). MS $m/z = 406$ (M^+). Anal. Calcd. For $\text{C}_{22}\text{H}_{16}\text{BrNS}$: C 65.03, H 3.97, N 3.45%. Found: C 65.17, H 4.05, N 3.71%.

2.2.3. 1-[5-Methyl-2-(2,4-diphenyl)-4-thiazolyl]perfluorocyclopentene (6)

To a stirring solution of **5** (780 mg, 1.9 mmol) in 7.5 mL THF was slowly added dropwise 1.6 M *n*-BuLi in hexane (1.3 mL, 2.00 mmol) at -80°C under an atmosphere of argon. After the mixture had been stirred for 15 min at -80°C , perfluorocyclopentene (0.3 mL, 2.10 mmol) in dry THF (2 mL) was added. The reaction mixture was stirred at -80°C for 1 h, and then distilled water was added. The product was extracted with diethyl ether, dried with MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 1:9) to afford to 400 mg (41%) of **6** as a colorless solid: mp $90\text{--}91^\circ\text{C}$. ^1H NMR (200 MHz, CDCl_3): $\delta = 2.36$ (d,



Scheme 2.

$J = 1.2$ Hz, 3H), 7.74–7.30 (m, 12H), 8.18 (d, $J = 8.4$ Hz, 1H). MS $m/z = 519$ (M^+). Anal. Calcd. For $C_{27}H_{16}F_7NS$: C 62.43, H 3.10, N 2.70%. Found C 60.43, H 3.30, N 2.95%.

2.2.4. 1,2-Bis[5-methyl-2-(2,4-diphenyl)-4-thiazolyl]perfluorocyclopentene (**1a**)

To a stirring solution of **5** (420 mg, 1.03 mmol) in 5 mL THF was slowly added dropwise 1.6 M *n*-BuLi in hexane (0.7 mL, 1.05 mmol) at -80°C under an atmosphere of argon. After the mixture had been stirred for 15 min at -80°C , **6** (360 mg, 0.69 mmol) in dry THF (2 mL) was added. The reaction mixture was stirred at -80°C for 2 h, and then distilled water was added. The product was extracted with diethyl ether, dried with MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 1:9) and GPC and HPLC (ethyl acetate/hexane, 1:9) to afford to 50 mg (9%) of **1a** as a colorless solid: mp 245°C (DSC). ^1H NMR (200 MHz, CDCl_3): $\delta = 1.84$ (s, 6H), 7.7–7.3 (m, 26H), 8.09 (d, $J = 8.2$ Hz, 2H). MS (FAB) $m/z = 826$ (M^+). Anal. Calcd. For $C_{49}H_{32}F_6N_2S_2$: C 71.17, H 3.90, N 3.39%. Found C 70.88, H 3.99, N 3.39%.

2.2.5. Closed-ring isomer (**1b**)

1b was isolated as a purple solid by passing a photostationary solution containing **1a** and **1b** through HPLC (ethyl acetate/hexane, 1/9): ^1H NMR (200 MHz, CDCl_3): $\delta = 1.84$ (s, 6H), 7.7–7.3 (m, 26H), 8.09 (d, $J = 8.2$ Hz, 2H). MS (FAB) $m/z = 826$ (M^+ , 53). Anal. Calcd. For $C_{49}H_{32}F_6N_2S_2$: C 71.17, H 3.90, N 3.39%. Found C 70.95, H 4.10, N 3.49%.

2.2.6. 1,2-Bis[2-methyl-5-(2,4-diphenylphenyl)-3-thienyl]perfluorocyclopentene (**2a**)

1,2-Bis-(2-methyl-5-iodo-3-thienyl)perfluorocyclopentene (2.0 g, 3.22 mmol) [19], 1-(4,4,5,5-tetramethyl-1,3,2-diox-

borolan-2-yl)-2,4-diphenylbenzene (7.0 g, 10 mmol) [15], and $(\text{PPh}_3)_4\text{Pd}(0)$ (500 mg, 10 mol%) were dissolved in a mixture of THF (25 mL) and aqueous 2 M Na_2CO_3 (16 mL). The solution was refluxed for 24 h under N_2 atmosphere. The product was extracted with diethyl ether, dried with MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography (hexane) and GPC and HPLC (dichloromethane/hexane, 15:85) to afford to 2 g (38%) of **2a** as a colorless solid: mp 169°C (DSC). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 1.74$ (s, 6H), 6.64 (s, 2H), 7.26–7.70 (m, 26H). MS (FAB) $m/z = 824$ (M^+). Anal. Calcd. for $C_{51}H_{34}F_6S_2$: C 74.25, H 4.15%. Found C 73.87, H 4.40%.

2.2.7. Closed-ring isomer (**2b**)

2b was isolated as a purple solid by passing a photostationary solution containing **2a** and **2b** through HPLC (dichloromethane/hexane, 15/85): ^1H NMR (CDCl_3 , 400 MHz): $\delta = 2.00$ (s, 6H), 5.84 (s, 2H), 7.26–7.70 (m, 26H). MS (FAB) $m/z = 824$ (M^+). Anal. Calcd. for $C_{51}H_{34}F_6S_2$: C 74.25, H 4.15%. Found C 73.87, H 4.40%.

3. Results and discussion

1,2-Bis[5-methyl-2-(2,4-diphenylphenyl)-4-thiazolyl]perfluorocyclopentene **1a** and 1,2-bis[2-methyl-5-(2,4-diphenylphenyl)-3-thienyl]perfluorocyclopentene **2a** were synthesized according to Scheme 2. 5-Methyl-2-(2,4-diphenylphenyl)thiazole **4** was prepared by palladium-catalyzed tandem C–H substitution [20] and used for the synthesis of **1a**. **2a** was prepared by the Suzuki coupling reaction at 1,2-bis[2-methyl-5-iodo-3-thienyl]perfluorocyclopentene [19] with 1-(4,4,5,5-tetramethyl-1,3,2-dioxabolan-2-yl)-2,4-diphenylbenzene. Compounds **1a** and **2a** were purified by GPC and HPLC. These structures were confirmed by ^1H NMR, mass spectra, and

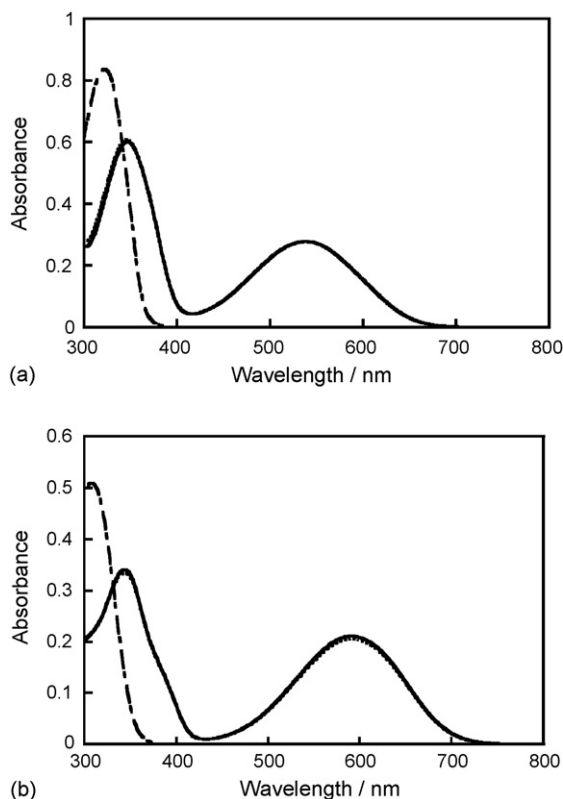


Fig. 1. Absorption spectral changes of (a) **1** (2.04×10^{-6} M) and (b) **2** (1.14×10^{-6} M) in toluene solutions by photoirradiation—dashed line: opening isomer, solid line: closed-ring isomer, and dotted line: in the photostationary state under irradiation with 313 nm light.

elemental analysis. The hexane solutions of **1a** and **2a** were irradiated with UV light and the photoproducts were isolated using HPLC (silica-gel/hexane:ethyl acetate = 93:7 for **1a**, hexane:dichloromethane = 85:15 for **2a**).

The absorption spectral changes of **1** and **2** in toluene are shown in Fig. 1a and b. Upon irradiation with 313 nm light, the colorless solutions of **1a** and **2a** turned violet and blue, in which visible absorption bands were observed 537 nm ($\epsilon = 14,000 \text{ M}^{-1} \text{ cm}^{-1}$) and 593 nm ($\epsilon = 18,500 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. The violet and blue colors are due to the closed-ring isomers **1b** and **2b**. When the violet and blue solutions were irradiated with visible light ($\lambda > 480 \text{ nm}$), the spectra readily returned back to the original ones. The conversions in the photostationary state were almost 100% for both solutions. The photocyclization and cycloreversion quantum yields were measured in toluene using furyl fulgide as a Refs. [21,22]. The photocyclization quantum yields (313 nm) of both **1a** and **2a** were determined to be 0.60, which are the same as that of **3a** (0.60) [14]. The bulky 2,4-diphenyl group are anticipated to increase the ratio of the photoactive anti-parallel conformation. The photocycloreversion quantum yields of **1b** and **2b** were determined to be 0.011 and 0.0060, respectively. These values are almost half of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)-perfluorocyclopentene (0.020) [23] and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (0.013) [24], respectively. 2,4-Diphenylphenyl groups are considered to sup-

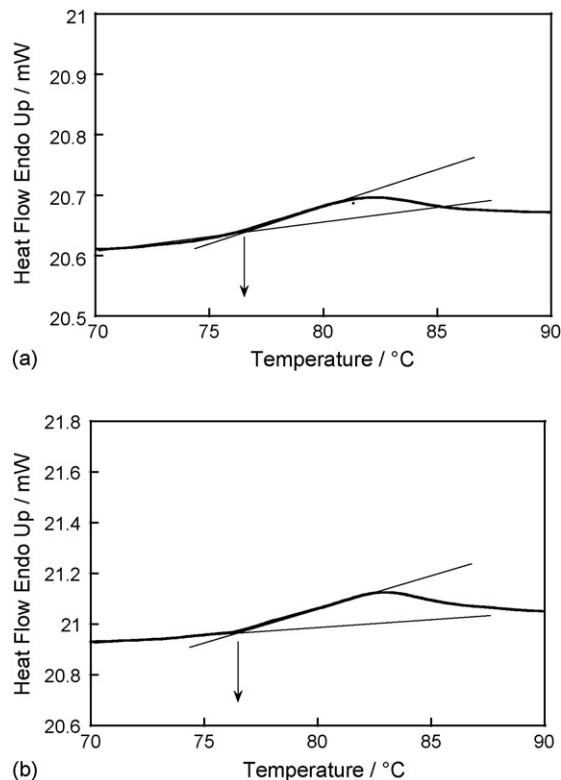
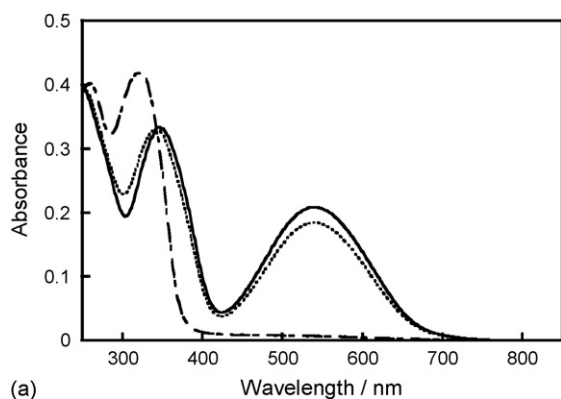


Fig. 2. DSC curve of compounds (a) **1a** (weight=3.4 mg) and (b) **2a** (weight=6.6 mg) with temperature scanning rate = $5 \text{ }^\circ\text{C}/\text{min}$. From the threshold temperature of the baseline shift, T_g s of **1a** and **2a** were evaluated to be $77 \text{ }^\circ\text{C}$.

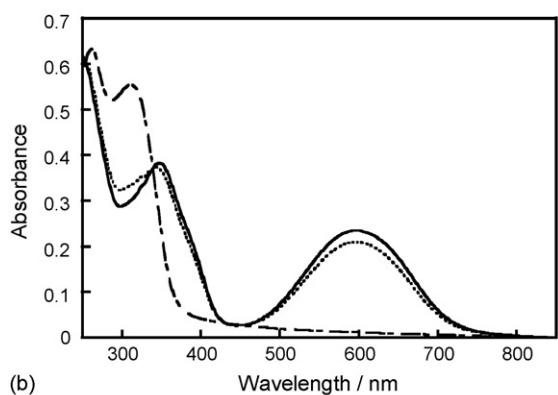
press the photocycloreversion reactions of **1b** and **2b** because of the extension of the π -conjugation chain length. However, the photocycloreversion quantum yield of **3b** was almost the same as that observed in 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (0.015) [25]. This result indicates that the π -conjugated chain system in **3b** is strained by the steric effect between the methyl substituents at the 4-position of thiophene rings and perfluorocyclopentene. This was also confirmed by X-ray crystallography analysis [24,26].

The DSC profiles of **1a** and **2a** are shown in Fig. 2. Both compounds were obtained from hexane solutions as crystals and the melting temperatures were observed at $245 \text{ }^\circ\text{C}$ and $169 \text{ }^\circ\text{C}$, respectively. The crystals were heated above the melting temperatures and then slowly cooled. In the second run, clear shift of the baselines was observed at around $75 \text{ }^\circ\text{C}$. The baseline shift is attributable to the glass to liquid transition. T_g s of **1a** and **2a** were evaluated from the threshold of the shifts to be $77 \text{ }^\circ\text{C}$. Both **1a** and **2a** formed stable amorphous states at room temperature.

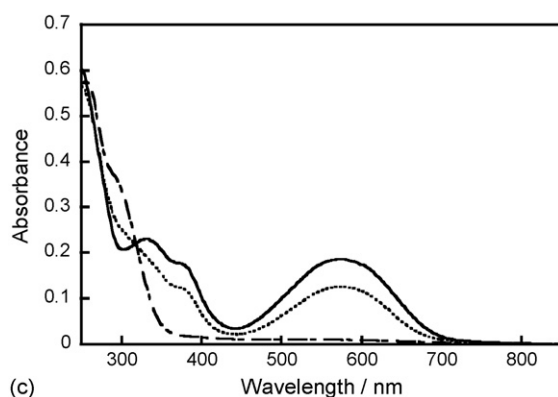
Fig. 3 shows the absorption spectral changes of **1** and **2** in amorphous thin films by photoirradiation. The amorphous films were prepared by casting the chloroform solutions containing the isolated closed-ring isomers **1b** and **2b** on quartz substrates. The films were dried in a vacuum oven at $65 \text{ }^\circ\text{C}$ for 24 h. The thickness of the films were around 500 nm. HPLC analysis indicates that **1b** and **2b** in the amorphous films did not thermally return to **1a** and **2a** under the anneal conditions. The visible absorption peaks of **1b** and **2b** were observed at 540 nm



(a)



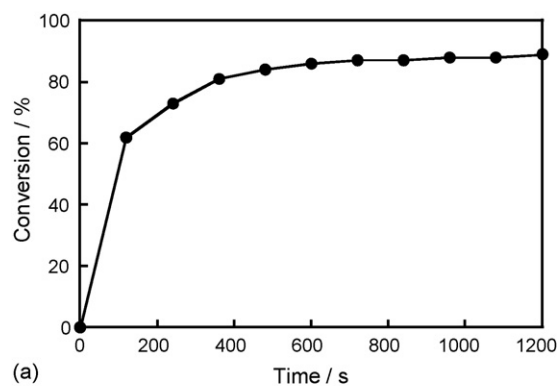
(b)



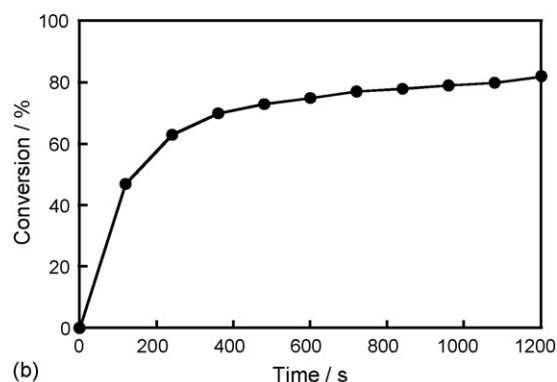
(c)

Fig. 3. Absorption spectral changes of **1** (a), **2** (b), and **3** (c) in bulk amorphous films prepared from the isolated closed-ring isomers—dashed line: open-ring isomer, solid line: closed-ring isomer, and dotted line: in the photostationary state under irradiation with 313 nm light. The films thickness were around 500 nm.

and 597 nm, respectively. Upon irradiation with visible light ($\lambda > 480$ nm), the absorption bands of **1b** and **2b** decreased and new bands appeared at 317 nm and 303 nm, which are ascribed to **1a** and **2a**. Upon irradiation with 313 nm light, the visible absorption bands at 535 nm and 597 nm again appeared. The conversions at the photostationary states under irradiation with 313 nm light were 88% (**1**) and 90% (**2**), respectively. In the case of **3**, the conversion in the photostationary state was determined to be 74% (Fig. 3c). The conversions in the amorphous films of **1** and **2** are much higher than that observed in **3**. This is ascribed to the lower photocycloreversion quantum yields of **1b** and **2b**, as described above.



(a)



(b)

Fig. 4. Time dependence of conversions from **1a** to **1b** in amorphous films prepared from **1b**: (a) immediately after bleaching **1b**; upon irradiation with 313 nm light and (b) after 2 days storage at room temperature after bleaching **1b**; upon irradiation with 313 nm light.

It should be noted that the conversions in the amorphous films are lower than those observed in solutions. To clarify the cause of decrease in the conversions, the amorphous films of **1b**, **2b**, and **3b** were irradiated with 313 nm light. The absorption spectra of **1b** and **2b** in the amorphous films did not change by photoirradiation with 313 nm light for several hours. On the other hand, the absorption maximum of **3b** was decreased to around 74% upon irradiation with 313 nm light for several hours. This indicates that **3b** returned to **3a** under the same conditions. The low conversion of **3** in amorphous films is ascribed to the cycloreversion reaction of **3b**.

Next, the conversions of **1a**, **2a**, and **3a** upon irradiation with 313 nm light were also measured in the amorphous films prepared from the isolated open-ring isomers. Figure S1 shows the absorption spectral changes of **1a**, **2a** and **3a** in the amorphous films. The conversion ratios at the photostationary states under irradiation with 313 nm light are 75% (**1**), 65% (**2**), and 55% (**3**), which are lower than these observed in the amorphous films prepared from **1b**, **2b**, and **3b**. The decrease in the conversions is ascribed to existence of photoinactive parallel conformations in the amorphous film which are prepared from the open-ring isomers. The slightly higher conversion (75%) of **1** is attributed to the difference of ϵ values of **1a** and **1b** at 313 nm.

The time dependence of the conversion in the amorphous film prepared from **1b** upon irradiation with 313 nm light was also examined. Fig. 4a shows the time-course of the conversion under the same condition as Fig. 3a. After 1200 s (20 min) irra-

diation, the conversion ratios from **1a** to **1b** reached 88%. On the other hand, when we examine the photobleached film **1a** prepared from **1b**, which were stored for 2 days in the dark at room temperature, the conversion in the photostationary state under irradiation with 313 nm light slightly decreased to 80% after 20 min irradiation, as shown in Fig. 4b. The photostationary state film was again stored in the dark for several hours and then the conversion was measured. The conversion gradually recovered to the value (88%). The conversion of **1** did not exceed the value (88%) in the photostationary state. It should be noted that the conversion change was observed only for **1**. This result suggests that a small amount of anti-parallel conformers changed to photoinactive anti-parallel conformers in the amorphous film during the above storage in the dark, and the conformers returned to the photoactive anti-parallel conformers after several hours. The conversion change of **1** is attributed to the decrease in the steric hindrance between 4-position of the aryl groups and perfluorocyclopentene ring.

In general, solid state thin films containing a photochromic compound are used for memory media. When photochromic compounds are dispersed in solid polymer matrices, the reactivities are considered to change from those observed in solution. The unfavorable behavior is attributed to the distribution of the free volume size in the matrices. PMMA polymer films containing 0.6 wt% of **1b**, **2b**, and **3b** were prepared by casting toluene solutions on glass substrates. The films were dried in a vacuum oven at 90 °C for 24 h. The thickness of the films were around 4 μm. Fig. 5 shows the photochromic reactions in the PMMA films. Upon irradiation with 313 nm light, the PMMA films of **1**, **2** and **3** turned red and blue, which are due to the formation of **1b**, **2b** and **3b**. Table 1 summarizes the optical data of compounds **1**, **2**, and **3**. These absorption maxima of **1b** and **2b** in PMMA films show hypsochromic shifts in comparison with those of amorphous films, despite the absorption maximum of **3b** is almost the same in both films. The conversions in the photostationary states of **1** and **2** were evaluated to be 91%, respectively. The values are slightly higher than that of **3** (80%). Furthermore, the conversions observed in the PMMA films prepared from **1a**, **2a**, and **3a** were evaluated to be 70%, 60%, and 50%, respectively (Figure S2). The photochromic performances are similar to that observed in the amorphous films. Photochromic reactions of **1** and **2** efficiently undergo in both amorphous and PMMA films up to high conversions.

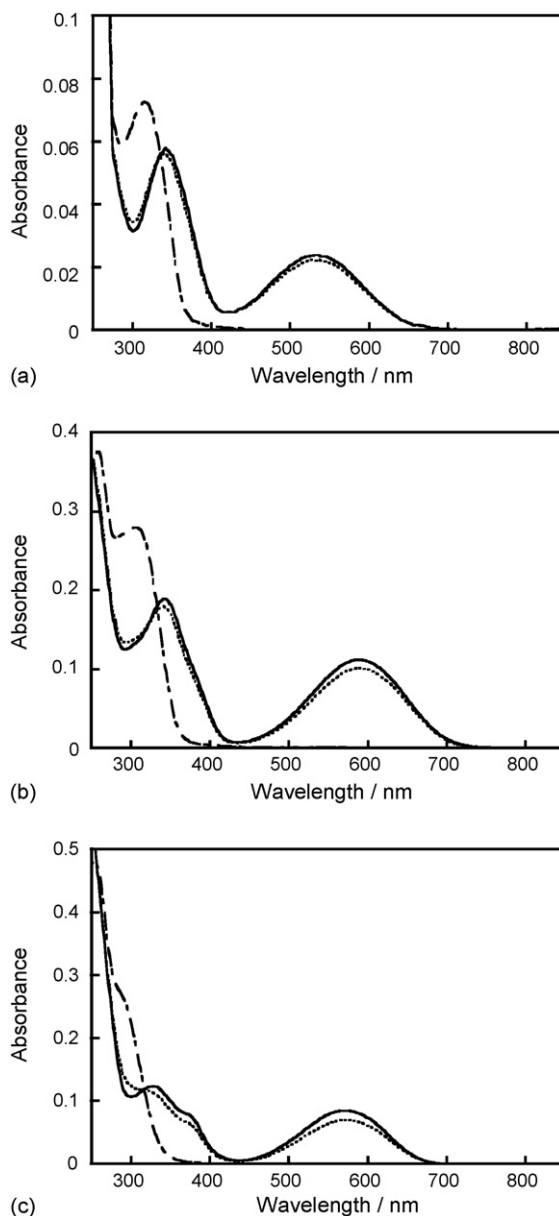


Fig. 5. Absorption spectral changes of PMMA films containing (a) **1**, (b) **2** and (c) **3** (0.6 wt%)—dashed line: open-ring isomer, solid line: closed-ring isomer, and dotted line: in the photostationary state under irradiation with 313 nm light. The films thickness were around 4.0 μm.

Table 1
Properties of diarylethenes **1**, **2** and **3** having 2,4-diphenylphenyl substituents in solution, amorphous and PMMA films

Compound	λ_{\max} (nm) (ϵ , $M^{-1} \text{cm}^{-1}$) in solution	Φ in solution	Conversion in solution (%)	λ_{\max} (nm) ^a in amorphous film	Conversion ^a in amorphous film (%)	λ_{\max} (nm) ^b in PMMA film	Conversion ^b in PMMA film (%)
1a	323 nm (41,000)	$\Phi_{ab} = 0.60$ (313 nm)	99	320	88	315	92
1b	537 nm (14,000)	$\Phi_{ba} = 0.011$ (537 nm)		539		533	
2a	308 nm (44,800)	$\Phi_{ab} = 0.60$ (313 nm)	99	305	90	311	91
2b	593 nm (18,500)	$\Phi_{ba} = 0.0060$ (593 nm)		597		591	
3a	254 nm (60,000) [14]	$\Phi_{ab} = 0.60$ (313 nm) [14]	97 [14]	262	74	–	80
3b	561 nm (10,000) [14]	$\Phi_{ab} = 0.020$ (561 nm) [14]		573		571	

^a This indicates the value of Fig. 3.

^b This indicates the value of Fig. 5.

4. Conclusions

Compounds **1** and **2** formed stable amorphous states at room temperature and underwent efficient photochromic reactions in amorphous films as well as in solutions. The conversions at the photostationary state in amorphous films **1** and **2** were evaluated to be around 90%, which are higher than that of **3**. This is ascribed to the steric effect between 4-position of aryl groups and perfluorocyclopentene ring in the closed-ring isomer **3b**. The photochromic reactions of **1**, **2**, and **3** in the PMMA films also efficiently underwent as well as in the amorphous films. The high conversions in the amorphous films of **1** and **2** are advantages for the practical use.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2006.10.024.

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