Photochromic Polysiloxanes Substituted with 1,2-Bis(2-methylbenzo[*b*]thiophene-3-yl)hexafluorocyclopentene

Hee-Won Shin and Yong-Rok Kim*

Department of Chemistry, Yonsei University, Seoul 120-749, Korea

Eunkyoung Kim*

Department of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

Abstract: Photochromic diarylethene polymers (**DPs**) in which 1,2-bis(2-methylbenzo[*b*]thiophene-3-yl)hexafluorocyclopentene (BTF6) were covalently grafted onto the polymer main chain as pendant photochromic units were newly synthesized and their photochromic properties were investigated using steady-state and picosecond time-resolved spectroscopies. Polysiloxanes substituted with BTF6 molecules were prepared by sol-gel process using a mixture of tetraethoxysilane (TEOS), a silylated BTF6, and an organically modified silane precursor in the presence of HCl. The polysiloxane film (**DP1**) prepared from ω-methoxy poly(ethylene glycol) 3-(triethoxysilyl) propylcarbamate (MPGSC) as the silane precursor showed a much lower glass transition temperature than that (**DP2**) from heptadecafluorodecyltrimethoxysilane (HDFTMS). The ring-closure quantum yields of **DP1** and **DP2** were determined to be 0.20 and 0.02, respectively. Such a large difference in the quantum yield was attributed to the polymer matrix environment of the free inner volume.

Keywords: photochromism, diarylethene polymer, free inner volume, quantum yield, average lifetime.

Introduction

Photochromism is a photoinduced reversible reaction between two isomers which have different optical responses. Among various photochromic molecular systems, diarylethene derivatives have attracted much attention for their potential application of photonic devices, such as high-density optical data storage media and optical switch, since they exhibit good thermal stability of the isomers and high fatigue resistance for the photochromic reversibility as well as their high photochromic efficiencies and sensitivities.[1-4] To date, a number of diarylethene derivatives have been investigated by several optical methods in solution and solid phases.[5-10] These studies have suggested that the open isomer has two types of conformations in its electronic ground states, such as parallel and antiparallel isomers.[6,7,10] It is generally known that, among the two conformers, only the antiparallel conformer undergoes the ring-closure reaction.[11]

For the purpose of practical application, photochromic reactions in solid-state are preferentially being investigated. In recent years, various methods have been employed to prepare the photochromic thin films; dispersed type of photochromic molecules in polymer matrices,[7,8,12] backbone photochromic polymer consisting of the photochromic molecular units in the main chain,[13] and photochromic molecular crystals.[14] Although the dispersion of photochromic molecules into polymer matrix is the most convenient method, it is still difficult to obtain a homogeneous film which contains a high concentration of photochromic molecules due to aggregation effect among the photochromic molecules.[15] In the case of the backbone type, although it exhibits the high ring-closure quantum yield (0.86), the ring-opening quantum yield is extremely small (0.0015) due to the structural stability of the closed isomers in the backbone photochromic polymer.[13] For the photochromic crystalline films, there are also fabrication difficulties in the preparation of thin crystalline films.[14]

In this study, therefore, we have synthesized new diarylethene polymers (**DPs**) in which the photochromic molecules are covalently grafted onto the polymer backbone as pendant type (Figure 1(b)), and their photochromic reactions are investigated by employing the steady-state and picosecond time-resolved spectroscopies. The pendant type of photochromic molecules which are covalently grafted onto the polymer backbone are expected to have the following

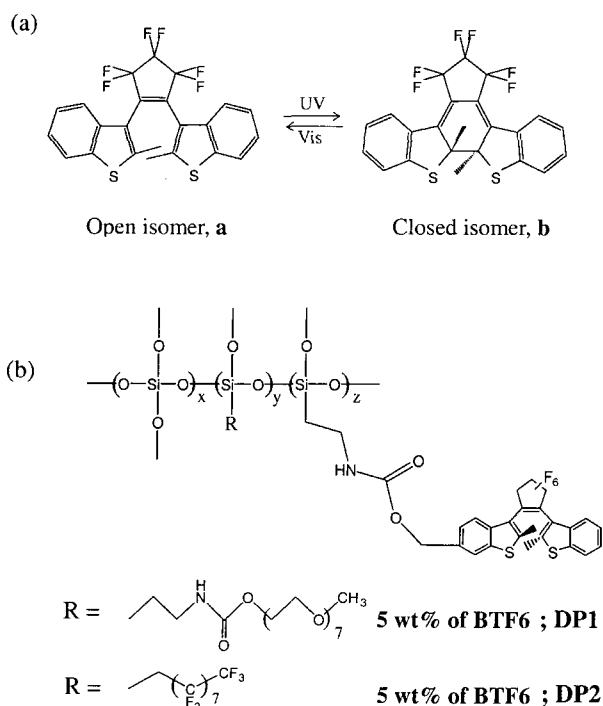*Corresponding Author. E-mail: yrkim@yonsei.ac.kr, eunkim@yonsei.ac.kr

(a)

Open isomer, **a**   Closed isomer, **b**

(b)

R =   **5 wt% of BTF6 ; DP1**

R =   **5 wt% of BTF6 ; DP2**

Figure 1. (a) Molecular structures of the open and closed isomers of 1,2-bis(2-methylbenzo[*b*]thiophene-3-yl)hexafluorocyclopentene (BTF6). (b) Structural formulae of the diarylethene polymers (**DPs**).

advantages over other solid-state systems; high concentration content of photochromic molecules in the polymer without the aggregation and the formation of concentration gradient, more uniform morphology expected by smaller surface roughness of the polymer film than that of the dispersed one,[15] higher ring-opening quantum yields than the backbone type, and relatively easy preparation process compared with the molecular crystals.

Among various diarylethene derivatives which were previously studied, 1,2-bis(2-methylbenzo[*b*]thiophene-3-yl) hexafluorocyclopentene (BTF6) was chosen as the photochromic molecule for this study due to its high photochromic efficiency and well-characterized properties.[2,7,12,16] The ring-closure quantum yields of BTF6 are reported to be 0.41 and 0.31 in *n*-hexane solution[16] and the dispersed system of poly(ethylene glycol)-grafted polysiloxane solid matrix,[7] respectively. The polymer matrices employed in this study are the modified polysiloxanes with different side chains which affect free inner volume of the matrices.

Experimental

Materials. Tetraethoxysilane (TEOS, Tokyo Kasei) and 3-nitro-α,α,α-trifluorotoluene (Aldrich) were used as received. Tetrahydrofuran (THF) was distilled over metallic sodium. Dimethylformamide (DMF) was distilled over anhydrous

magnesium sulfate under reduced pressure. Poly(ethylene glycol)monomethylether (PEGM, M_n=350, Aldrich) was dried over molecular sieves before its use. ω-Methoxy poly (ethylene glycol) 3-(triethoxysilyl)propylcarbamate (MPGSC) was synthesized from (3-isocyanatopropyl)triethoxysilane (Aldrich) and PEGM using dibutyltin dilaurate (Aldrich) as a catalyst.[17] MPGSC was obtained as a transparent liquid after column chromatography. Heptadecafluorodecyltrimethoxysilane (HDFTMS) was purchased from Shin-Etsu Chemical (TSL-8233). Other chemicals were purchased from Aldrich, Fluka, and TCI. All solvents were purified before their usage. All synthetic reactions were controlled under atmosphere of dry argon unless otherwise specified.

Synthesis of 1-(6′-hydroxymethyl-2′-methylbenzo[*b*] thiophen-3′-yl)-2-(2″-methylbenzo[*b*]thiophen-3″-yl)hexafluorocyclopentene (compound 1). 1,2-Bis(2-methylbenzo [*b*]thiophene-3-yl)hexafluorocyclopentene (BTF6), 1-(6′-acetyl-2′-methylbenzo[*b*]thiophen-3′-yl)-2-(2″-methylbenzo [*b*]thiophen-3″-yl)hexafluorocyclopentene (acetyl-BTF6), and 1-(6′-carboxy-2′-methylbenzo[*b*]thiophen-3′-yl)-2-(2″-methylbenzo[*b*]thiophen-3″-yl)hexafluorocyclopentene (carboxy-BTF6) were synthesized according to the method previously reported.[15,16] A solution of LiAlH₄ (0.074 g, 1.96 mmol) in THF (6 mL) was slowly added to the solution of carboxy-BTF6 (0.69 g, 1.31 mmol) dissolved in THF (24 mL) under argon atmosphere. The solution was further stirred for 2 hrs, and methanol was added into the reaction mixture. The undissolved precipitates were removed by filtration. After evaporation of solvent in a vacuum, column chromatography (*n*-hexane/ethyl acetate = 1:3) gave the compound **1** as a pale yellow powder. Yield : 63%; ¹H NMR (CDCl₃) δ: 2.15 (s, 3H), 2.45 (s, 3H), 3.45 (s, 1H), 4.74 (s, 2H), 7.10-7.87 (m, 7H); IR (KBr) : 3364 cm⁻¹.

Synthesis of Silylated BTF6 (compound 2). To the mixture containing the compound **1** (105.3 mg, 0.19 mmol), (3-isocyanatopropyl) triethoxysilane (146 μL, 0.57 mmol) and triethylamine (53.7 μL, 0.38 mmol) in 3 mL of THF were slowly added with catalytic amounts of dibutyltin dilaurate.

Scheme I

Compound **1**

Triethylamine
Dibutyltin dilaurate
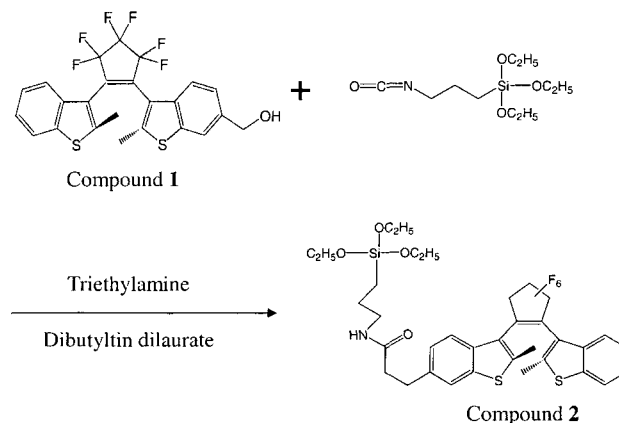
Compound **2**

The mixture solution was stirred at 72 °C under nitrogen atmosphere for 7 hrs. The solvent was removed at a reduced pressure and the compound 2 was recrystallized in *n*-hexane solution in order to produce pale blue crystals. Yield : 81 %; ^{1}H-NMR (CDCl$_3$) δ: 0.63 (t, 2H), 1.24 (t, 9H), 1.66 (p, 2H), 2.27 (s, 3H), 2.40 (s, 3H), 3.17 (q, 2H), 3.82-3.84 (m, 6H), 4.87 (s, 2H), 5.26 (s, 1H), 7.07-7.25 (m, 3H), 7.40-7.65 (m, 4H); IR (KBr) : 1100, 1714, 2875, 3321 cm^{-1}.

Preparation of Photochromic Diarylethene Polymers. The method of preparing sol-gel glasses by acidic hydrolysis of TEOS in ethanol was adopted from the references with a minor modification.[18-20] The molar ratio of TEOS and MPGSC was 4:1. MPGSC (6.31 wt%) and TEOS (7.95 wt%) were added to the solution which contained the following chemicals: 0.15 M HCl (16.3 wt%), ethanol (57.1 wt%), DMF (6.14 wt%), and 3-nitro-α,α,α-trifluorotoluene (6.14 wt%). The homogeneous mixture was stirred for 1 day at room temperature, and the silylated BTF6 (compound 2, 5 wt%) was added to above mixture. The resultant mixture was stirred for 2 days at room temperature and then was further stirred for 1 day at 60 °C. The reaction mixture was cooled to room temperature and concentrated by evaporation under a reduced pressure. Resulting viscous solution was filtered with a membrane of 0.45 μm pore size attached to a teflon syringe, and the solution was coated on 1 × 1 cm^2 quartz plate (Helma) by a spin-coater with the spin rate of 1000-2000 rpm. The coated film was cured at 80 °C for 12 hrs to yield photochromic polysiloxane (**DP1**). Weight content of BTF6 unit in the **DP1** film was 5 wt%.

DP2 was produced from a mixture containing HDFTMS (6.31 wt%) and TEOS (7.95 wt%) using the identical procedure described for **DP1**, and BTF6 content in the **DP2** film was also 5 wt%.

The extent of the curing reaction was determined by IR spectroscopy following the decay of the intensity of the (Si) O-H band at 3300 cm^{-1}. Although the intensity was much decreased after 10 hrs, it was not possible to completely reduce it to zero for both sample (**DP1** and **DP2**) even after 5 days of curing. As the intensity decrease after 12 hrs was

Scheme II

not significant, the curing time was set to 12 hrs.

Instruments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 MHz NMR spectrometer. The chemical shifts were determined by using tetramethylsilane (TMS) as an internal reference. Mass spectra were obtained with Shimadzu GC/MS-QP1000 mass spectrometer at 70 eV. Infrared spectra were obtained from Shimadzu IR-435 spectrometer. Surface roughness and thickness of the polymer films were estimated using an α-step (Tencor). The reactions were monitored by thin-layer chromatography with 0.2 mm silica gel plates (Merck). Column chromatography was performed on a silica gel (Merck, 230-400 mesh).

Steady-state absorption and fluorescence spectra were measured with Shimadzu UV-160A spectrophotometer and Hitachi F-4500 spectrophotometer, respectively. A pulsed nitrogen laser (337 nm, Laser Photonics) was utilized as an irradiation source for the photochromic ring-closure. For photochromic reverse reaction (ring-opening), a 520 nm of dye laser (Laser Photonics) pumped by nitrogen laser was used. Neutral density filter was applied to control the irradiation power. A picosecond time correlated single photon counting method was employed to measure the time-resolved fluorescence decay curve.[21] The system was consisted of cavity dumped dual-jet dye laser (Coherent, 700 series) which was synchronously pumped by Nd-YAG laser (Coherent, Antares 76-YAG). The full width at half maximum of the instrumental response function (IRF) was 58 ps. The excitation wavelength of 298 nm was applied to all samples. Fluorescence decay rates were evaluated by an iterative non-linear least squares deconvolution fitting routine. Spectroscopic measurements were conducted under room temperature (20 °C) and ambient conditions.

Results and Discussion

Photochromic conversion quantum yields of **DP1** and **DP2** films were determined by UV-Vis absorption spectra at room temperature. Figure 2 shows the spectral changes induced by ring-closure reactions of **DP1a** and **DP2a** (a and b denote the open and the closed isomers, respectively). Irradiation with a light of 337 nm induced a new absorption band maximized at 520 nm which could be ascribed to the closed isomers in BTF6 unit. Since both open and closed isomers of BTF6 units exhibit an absorbance at UV region, the irradiation of 337 nm causes the photochromic **DPs** to be at the photostationary state.[22]

The insets of Figure 2 indicate the spectral evolutions as a function of irradiation time. The new band around 520 nm disappeared upon exposure to a visible light ($\lambda > 450$ nm) due to the photochromic reverse (ring-opening) reaction. Such characteristics of the absorption bands are similar to those of BTF6 in *n*-hexane solution.[16]

The photochromic quantum yield is defined as the ratio of the number of converted molecules to the number of absorbed
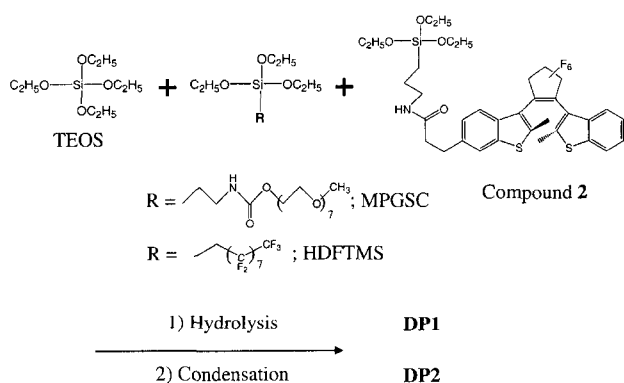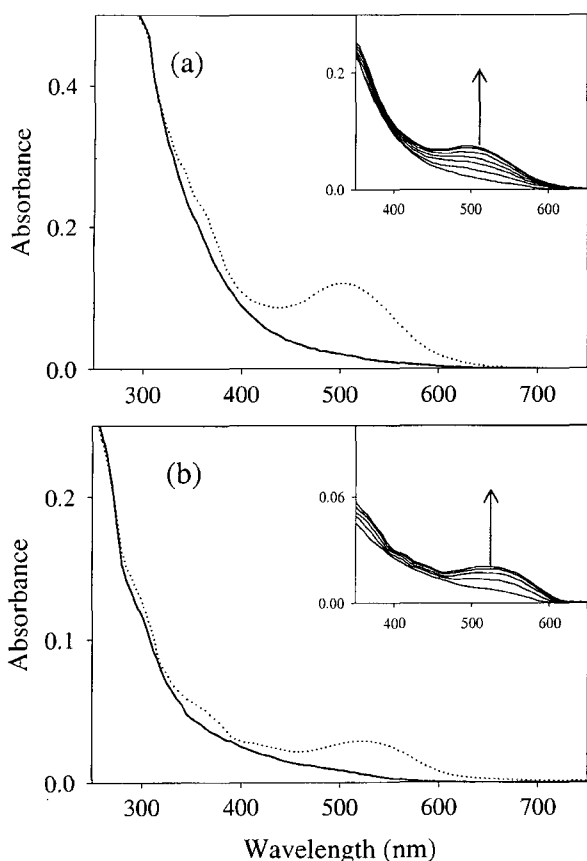
Figure 2. UV-Vis absorption spectra of the open isomers (solid line) and photostationary states (dot line) of (a) **DP1** and (b) **DP2**. Temporal evolutions of the absorption spectra with irradiation of 337 nm at every 20 sec are shown as arrow marks in the insets.

Table I. Photochromic Ring-Closure and Ring-Opening Quantum Yields (Φ_{pc}) of the Diarylethene Polymers

Samples	BTF6 Content (wt%)	Thickness (μm)	Φ_{pc}	
			^{a}a → b	^{b}b → a
DP1	5	2.1	0.20	0.42
DP2	5	1.6	0.02	0.12

^{a}Irradiation with 337 nm. ^{b}Irradiation with 520 nm.

photons.[7,9,23] The ring-closure and ring-opening quantum yields of **DPs** were determined from the absorbance change by irradiation of the films with 337 and 520 nm light sources, respectively.

The ring-closure quantum yields of the **DPs** in solid film are shown to be smaller than that of BTF6 in solution phase (0.41),[16] which is possibly due to the structural restriction in the molecular space for the conformational change of diarylethene molecules. From Table I, it is noticed that the ring-closure quantum yield of **DP1** (0.20) is one order of magnitude larger than that of **DP2** (0.02) despite of their

similar structures (see Figure 1(b)). Such a large difference in the photochromic efficiency reflects that the environment around the BTF6 units in **DP1** is significantly different from that in **DP2**, and it influences the photochromic quantum yield even in solid matrix phase. In our previous report,[7] the photochromic activity of the dispersed BTF6 in polymer matrix was suggested to be strongly affected by free inner volume of the polymer matrix itself. Among various physical parameters of polymer matrix, the glass transition temperature (T_g) can be correlated with free inner volume of polymer matrix.[24] The volume of free inner space of polymer matrix may increase with decreasing T_g. The T_gs of **DP1** and **DP2** were determined as -48 and 84 °C by DSC, respectively, and a large difference of the T_g values is considered to be induced by the substituents of the side chains. Crosslinking density can be another factor to affect the T_g value. However, due to the identical curing condition for **DP1** and **DP2**, the crosslinking density is not likely to induce such a large difference in the T_g values between them.

It is considered that the polymer matrix of **DP1** provides enough space, in the rubbery state above the T_g, which is necessary for the photochromic conversion that requires rotation of the two benzothiophene rings in BTF6 of **DP1**. On the other hand, in the case of **DP2**, its matrix environment appears to have not enough free inner volume for the photochromic conversion in the glassy state below the T_g of 84 °C, resulting very low ring-closure quantum yield of 0.02. Nakashima et al. also reported the photochromic conversion efficiencies of 1-(2-methylbenzo[b]thien-3-yl)-2-[5-(4-butylphenyl)-2,4-dimethylthien-3-yl]perfluorocyclopentenes covalently grafted onto the networked polysiloxanes as pendant type.[25] Since there was no significant difference in the ring-closure conversion efficiency at the experimental temperature range of 10-75 °C with Nakashima's polymers, of which T_gs were between 24-58 °C, they suggested that
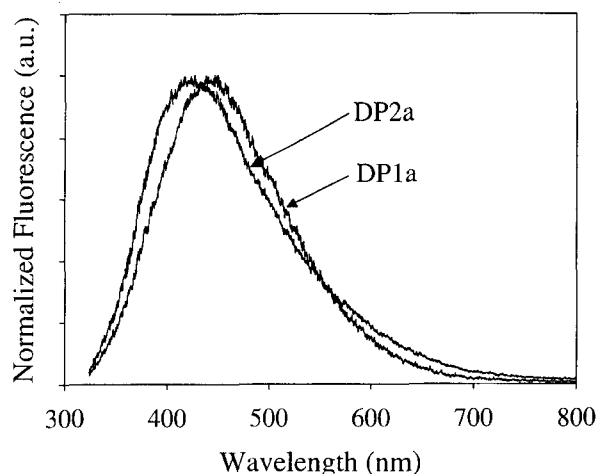

Figure 3. Steady-state fluorescence spectra of **DP1a** and **DP2a** at the excitation wavelength of 298 nm.

their polysiloxanes matrices had enough space for the photochromic conversion of the diarylethenes even in the glassy state. However, our results of the high ring-closure quantum yield of 0.2 for **DP1** and very low quantum yield of 0.02 for **DP2** indicate that, even they are similar polysiloxanes derivatives, they still have the significant free inner volume difference depending upon the substituents to the polysiloxanes. The steady-state photochromic conversion efficiencies of **DP1** and **DP2** are well correlated to the lifetimes of the corresponding excited states as described below.

Time-resolved fluorescence decay kinetics of the photochromic **DPs** were measured at several detection wavelengths in the fluorescence spectral ranges (Figure 3). Figure 4 presents typical fluorescence decay profiles of **DP1a** and **DP2a** detected at 400 nm after 298 nm excitation. Although the fluorescence decay profiles were well fitted to the triple-exponential function of $A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)+A_3\exp(-t/\tau_3)$ as shown in Table II, the fitted lifetimes and amplitudes can't be simply compared for **DP1** and **DP2**.

In general, the photochromic reactions in polymer films deviate from the first-order-kinetics in the temperature con-
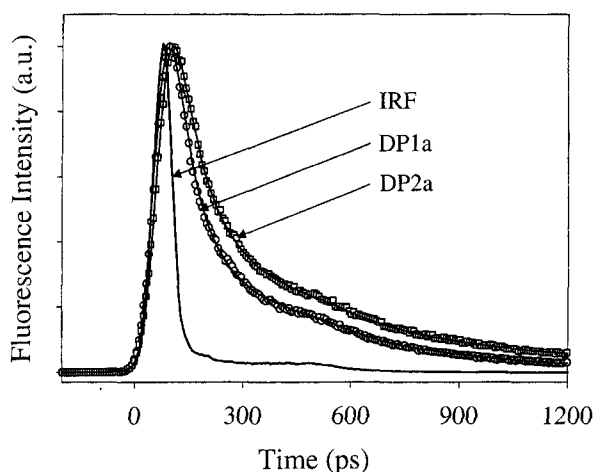
dition below the T_g due to the distribution of the free inner volume size,[26] which is the case of **DP2**. Therefore, the weighted average lifetimes ($<\tau>$) are evaluated just to provide a qualitative support for the ring-closure efficiencies of **DP1** and **DP2**. As listed in Table II, the average lifetime of **DP1a** (101 ps) is significantly faster than that of **DP2a** (176 ps), which can be expected from the higher ring-closure quantum yield of **DP1a** than that of **DP2a**.

Conclusions

We have synthesized new diarylethene polymers in which the pendent photochromic units are covalently grafted onto the polymer main chain. The ring-closure quantum yields of **DP1** and **DP2** were determined to be 0.20 and 0.02, respectively, and the ring-opening quantum yields were 0.42 for **DP1** and 0.12 for **DP2**. The results suggest that the photochromic reaction in polymer matrix strongly depends on the free inner volume of polymer environment which is represented by T_g. The high ring-closure quantum yield of **DP1a** is also reflected on the faster fluorescence average lifetime than the lifetime of **DP2a**.

Figure 4. Time-resolved fluorescence decay profiles of **DP1a** and **DP2a** at the detection wavelength of 400 nm with the 298 nm excitation. The solid lines along data points are the fitted lines. IRF denotes the instrumental response function.

Table II. Fluorescence Lifetimes and Relative Fluorescence Intensities of the Diarylethene Polymers

Samples	λ (nm)	τ_1 (ps)/A_1	τ_2 (ps)/A_2	τ_3 (ps)/A_3	$<\tau>$ (ps)
DP1	400	42/0.79	250/0.19	1024/0.02	101
DP2	400	68/0.69	254/0.26	1271/0.05	176

Triple-exponential function, $I(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)+A_3\exp(-t/\tau_3)$, was assumed for the fluorescence decay. $I(t)$, A, and τ, the time-dependent fluorescence intensity, the relative amplitude and the lifetime, respectively. $<\tau>$ is weighted average lifetime which is defined as $\Sigma A_i\tau_i/\Sigma A_i$. The excitation wavelength for all decays was 298 nm.

References

(1) M. Irie, and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988).
(2) M. Irie, *Pure Appl. Chem.*, **68**, 1367 (1996).
(3) G. M. Tsivgoulis and J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.*, **34**, 1119 (1995).
(4) S. H. Kawai, S. L. Gilat, and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1011 (1994).
(5) A. T. Bens, D. Frewert, K. Kodatis, C. Kryschi, H.-D. Martin, and H. P. Trommsdorff, *Eur. J. Org. Chem.*, **1998**, 2333 (1998).
(6) H. Miyasaka, T. Nobuto, A. Itaya, N. Tamai, and M. Irie, *Chem. Phys. Lett.*, **269**, 281 (1997).
(7) D.-H. Kwon, H.-W. Shin, E. Kim, D. W. Boo, and Y.-R. Kim, *Chem. Phys. Lett.*, **328**, 234 (2000).
(8) J. C. Owrutsky, H. H. Nelson, A. P. Baronavski, O.-K. Kim, G. M. Tsivgoulis, S. L. Gilat, and J.-M. Lehn, *Chem. Phys. Lett.*, **293**, 555 (1998).
(9) S. Y. Cho, M. Yoo, H.-W. Shin, K.-H. Ahn, Y.-R. Kim, and E. Kim, *Opt. Mater.*, **21**, 279 (2002).
(10) M. Irie, O. Miyatake, and K. Uchida, *J. Am. Chem. Soc.*, **114**, 8715 (1992).

(11) M. Irie, O. Miyatake, K. Uchida, and T. Eriguchi, *J. Am. Chem. Soc.*, **116**, 9894 (1994).

(12) T. Yoshida, K. Arishima, F. Ebisawa, M. Hoshino, K. Sukegawa, A. Ishikawa, T. Kobayashi, M. Hanazawa, and Y. Horikawa, *J. Photochem. Photobiol. A: Chem.*, **95**, 265 (1996).

(13) F. Stellacci, C. Bertarelli, F. Toscano, M. C. Gallazzi, G. Zotti, and G. Zerbi, *Adv. Mater.*, **11**, 292 (1999).

(14) S.-Z. Pu, F.-S Zhang, F. Sun, R.-J. Wang, X.-H. Zhou, and S.-K. Chan, *Tetrahedron Lett.*, **44**, 1011 (2003).

(15) E. Kim, Y.-K. Choi, and M.-H. Lee, *Macromolecules*, **32**, 4855 (1999).

(16) M. Hanazawa, R. Sumiya, Y. Horikawa, and M. Irie, *J. Chem. Soc., Chem. Commun.*, 206 (1992).

(17) M.-H. Lee, S. T. Ko, K. S. Lee, and S. B. Rhee, *Mol. Cryst. Liq. Cryst.*, **294**, 229 (1997).

(18) E. Kim, K. H. Choi, and S. B. Rhee, *Macromolecules*, **31**, 5726 (1998).

(19) K. Matsui and T. Nakazawa, *Bull. Chem. Soc. Jpn.*, **63**, 11 (1990).

(20) K. Matsui, T. Nakazawa, and H. Morisaki, *J. Phys. Chem.*, **95**, 976 (1991).

(21) I.-W. Hwang, H.-H. Choi, B.-K. Cho, M. Lee, and Y.-R. Kim, *Chem. Phys. Lett.*, **325**, 219 (2000).

(22) T. Kawai, N. Fukuda, D. Gröschl, S. Kobatake, and M. Irie. *Jpn. J. Appl. Phys.*, **38**, 1194 (1999).

(23) A. Mejiritski, A. Y. Polykarpov, A. M. Sarker, and D. C. Neckers, *J. Photochem. Photobiol. A: Chem.*, **108**, 289 (1997).

(24) M. P. Stevens, in *Polymer Chemistry*, Oxford Univ. Press, New York, 1999, pp 70-74.

(25) H. Nakashima and M. Irie, *Macromol. Rapid Commun.*, **18**, 625 (1997).

(26) J. G. Victor and J. M. Torkelson, *Macromolecules*, **20**, 2241 (1987).