Fluorescence On/Off Switching in Polymers Bearing Diarylethene and Fluorene in Their Side Chains

Tatsumoto Nakahama, Daichi Kitagawa, Hikaru Sotome, Syoji Ito, Hiroshi Miyasaka, Seiya Kobatake

Citation	The Journal of Physical Chemistry C, 121 (11); 6272-6281
Issue Date	2017-03
Type	Journal Article
Textversion	author
Supporting Information	The Supporting Information is available free of charge on the ACS Publications website at https://doi.org/10.1021/acs.jpcc.6b12819.
Rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in The Journal of Physical Chemistry C, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://doi.org/10.1021/acs.jpcc.6b12819
DOI	10.1021/acs.jpcc.6b12819

Self-Archiving by Author(s)
Placed on: Osaka City University

Fluorescence On/Off Switching in Polymers Bearing Diarylethene and Fluorene in Their Side Chains

Tatsumoto Nakahama,[†] Daichi Kitagawa,[†] Hikaru Sotome,[‡] Syoji Ito,[‡] Hiroshi Miyasaka,*[,‡] and Seiya Kobatake*[,†]

[†]Department of Applied Chemistry, Graduate School of Engineering, Osaka City University,

3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp

[‡]Division of Frontier Materials Science and Center for Promotion of Advanced Interdisciplinary

Research, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531,

Japan.

E-mail: miyasaka@chem.es.osaka-u.ac.jp

ABSTRACT: A diarylethene-fluorene dyad connected by an ester bond (**DE-FL**) and random and alternative copolymers with diarylethene and fluorene moieties in their side chains (**poly(DE1$_x$-co-FL1$_y$)** and **poly(DE1-alt-FL2)**) were synthesized, and their fluorescence on/off switching properties were investigated. All compounds exhibited reversible photochromism and fluorescence on/off switching in a solution upon alternating irradiation with ultraviolet (UV) and visible light. Although the fluorescence intensity of **DE-FL** linearly decreased with increasing photocyclization conversion of the diarylethene, the fluorescence intensity of **poly(DE1$_x$-co-FL1$_y$)** at the same molar fraction of diarylethene/fluorene significantly decreased with photocyclization conversion. Moreover, the fluorescence intensity of the polymers in the photostationary state was much lower than that of **DE-FL**. These results indicate that the fluorescence on/off switching properties of the polymers were improved by introducing diarylethene and fluorene moieties into their side chains. Moreover, it was revealed that the monomer sequences and the molar fractions of the diarylethene and fluorene moieties affected the fluorescence on/off switching properties of the copolymers.

2

Introduction

Organic fluorescent materials have played an important role in various research fields, such as optoelectronics,[1-3] bioimaging,[4] and microanalysis.[5] In particular, fluorescence-switchable molecules are widely studied and have potential applications in sensing materials,[4-7] bioimaging materials for super-resolution microscopy,[8-10] and single-molecule memory materials[11-16] because their fluorescence intensities and/or colors show sensitive changes in response to various external stimuli. Green fluorescent protein, carbocyanine dye, and photochromic molecules have been used as fluorescence-switchable materials.[17] Recently, the fluorescence on/off switching of various photochromic diarylethenes has been reported.[18,19] Diarylethenes undergo thermally irreversible photoisomerization between a colorless open-ring form and a colored closed-ring form upon alternating irradiation with ultraviolet (UV) and visible light; they show excellent performance, with high thermal stabilities, high photocyclization quantum yields, and high fatigue-resistant properties compared to other photochromic compounds.[18,19] Diarylethenes linked to fluorophores exhibit fluorescence on/off switching upon alternating irradiation with UV and visible light. When diarylethenes are in their open-ring forms, the fluorophores exhibit fluorescence. When diarylethenes are converted to their closed-ring forms, the fluorescence is quenched by an energy transfer from the fluorophore moiety to the diarylethene closed-ring form.[20,21] Fluorescence-switchable diarylethenes exhibit properties, such as high fluorescence on/off contrast and rapid switching speed, which are desirable for applications in the field of optoelectronics and bioimaging.[22]

3

When the photocyclization conversion of diarylethenes linked to fluorophores does not reach 100% at the photostationary state (PSS), residual fluorescence occurs, which results in low fluorescence on/off contrast. To improve their fluorescence on/off contrast, molecules bearing one fluorophore and multiple diarylethenes have been reported. Bis(phenylethynyl)anthracene,[23] porphyrin,[24] and perylenediimide[25] linked to multiple diarylethenes has been investigated for their fluorescence on/off switching properties. In particular, Zhu and co-workers reported that a perylenemonoimide dyad modified with triple diarylethenes exhibited a high fluorescence on/off switching speed; its fluorescence on/off contrast is the highest reported to date.[22] Moreover, aggregates such as silica nanoparticles,[26] organic nanoparticles,[27] and polymers[28-31] have been proposed as alternative approaches to improve fluorescence on/off switching properties. Recently, Métivier and co-workers reported that fluorescent photochromic organic nanoparticles prepared by a reprecipitation method exhibited bright red emission, complete on/off contrast with full reversibility, and excellent fatigue resistance.[27]

Among them, Akagi and co-workers reported a series of photoresponsive and full-colored fluorescent conjugated copolymers introduced diarylethene to their side chains,[28] and demonstrated white fluorescence on/off switching by mixing the red, green, and blue fluorescent conjugated polymer nanoparticles in the appropriate ratio.[29] Additionally, super-resolution localization of water-soluble fluorescence photoswicthable polymers was enabled with sub-40 nm spatial resolution in imaging subcellular organelles.[30] Thus, the fluorescence on/off switchable diarylethene polymers are of great interest for the applications described above. However, there is few report on the effect of polymer

4

structures such as a monomer sequence for the fluorescence on/off switching properties, such as the fluorescence on/off contrast and switching speed, although various systems of polymers containing diarylethenes and fluorophores have been proposed for the applications described above. By clarifying this effect, it is expected to lead to the system bearing more efficient fluorescence on/off switching properties even if the same diarylethene and fluorophore moieties are used.

In this work, we have focused on developing molecules with efficient fluorescent on/off switching properties, such as high speed switching and high fluorescence on/off contrast; we proposed the introduction of diarylethene and fluorene derivatives into the side chains of polymers. First, a diarylethene-fluorene dyad (**DE-FL**) connected by an ester bond was synthesized, as shown in Scheme 1. Next, random and alternative copolymers bearing diarylethene and fluorene derivatives in their side chains (**poly(DE1$_x$-co-FL1$_y$)** and **poly(DE1-alt-FL2)**) were synthesized to investigate the effects of the molar fractions of diarylethene and fluorene and the monomer sequence of the copolymers on their fluorescence on/off switching properties.
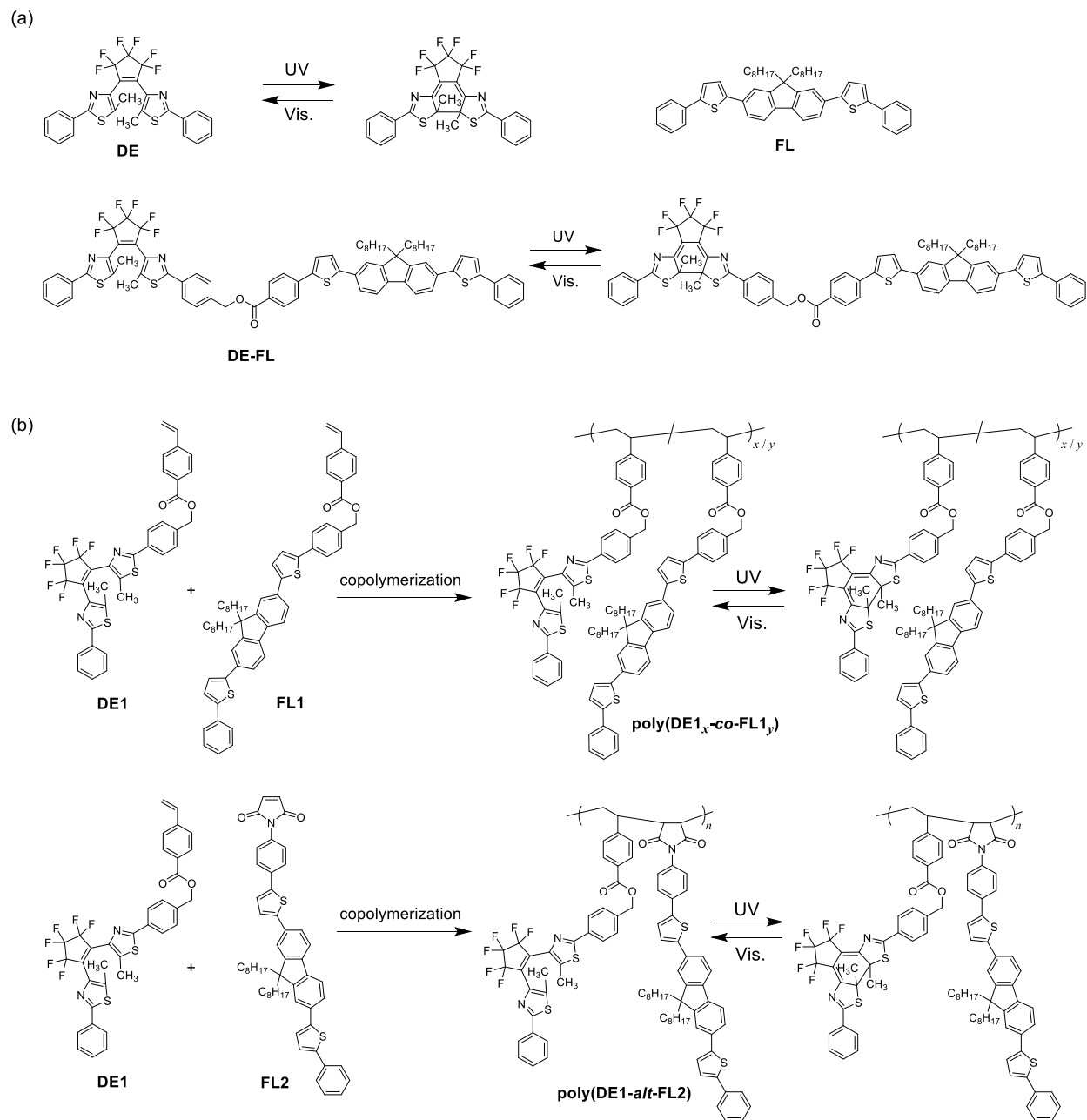
Scheme 1. (a) The molecular structures of diarylethene derivative (**DE**), fluorene derivative (**FL**), and diarylethene-fluorene dyad (**DE-FL**). (b) Synthesis and photochromic reaction of **poly(DE1$_x$-co-FL1$_y$)** and **poly(DE1-alt-FL2)**.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Bruker AV-300N spectrometer at 300 MHz. Deuterated chloroform (CDCl$_3$) was used as the solvent, and tetramethylsilane (TMS) was used as an internal standard. Mass spectra were obtained using a Bruker FT-ICR/solariX mass spectrometer. Gel-permeation chromatography (GPC) was performed using a Tosoh 8000 series GPC system equipped with TSK-gel columns at 40 °C in tetrahydrofuran (THF) as the eluent. Standard polystyrenes were used as the calibration standard. Differential scanning calorimetry (DSC) was performed using a Hitachi DSC7000X instrument at a heating rate of 10 °C min^{-1}. The glass transition temperature (T_g) was determined from an initial inflection point of temperature dependence on DSC. High-performance liquid chromatography (HPLC) was conducted using a Hitachi L-7150/L-2400 HPLC system equipped with a Kanto Chemical Mightysil Si60 column. Recycling preparative HPLC was conducted using a JAI LC-908 equipped with JAIGEL-1H and 2H columns using chloroform as the eluent. Absorption spectra were measured with a JASCO V-560 absorption spectrophotometer. Fluorescence spectra were measured with a Hitachi F-2700 fluorescence spectrophotometer.

Materials. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Toluene and styrene (St) were purified by distillation. All other reagents were commercially available and were used without further purification. For preparing 1,2-bis(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene (**DE**),[32,33] 2,7-bis(5-phenylthiophen-2-yl)-9,9-dioctylfluorene (**FL**),[34] and 1-(5-methyl-2-(4-(4-vinylbenzoyloxymethyl)phenyl)thiazol-4-yl)-2-(5-methyl-2-phenylthiazol-4-

yl)perfluorocyclopentene (**DE1**),[35] a method described in previous papers was used; as for 2-(5-(4-(4-vinylbenzoyloxymethyl)phenyl)thiophen-2-yl)-7-(5-phenylthiophen-2-yl)-9,9-dioctylfluorene (**FL1**), *N*-4-(5-(7-(5-phenylthiophen-2-yl)-9,9-dioctylfluoren-2-yl)thiophen-2-yl)phenylmaleimide (**FL2**), and 1-(5-methyl-2-(4-(5-(7-(5-phenylthiophen-2-yl)-9,9-dioctylfluoren-2-yl)thiophen-2-yl)benzoyloxymethyl)phenylthiazol-4-yl)-2-(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene (**DE-FL**), a description is given in the Supporting Information.

Polymerization. Radical polymerization was conducted in a sealed glass tube under vacuum. Monomer, AIBN, and toluene were placed in a glass tube. The tube was degassed by several freeze-pump-thaw cycles and sealed under vacuum. After polymerization for a prescribed time at 60 °C, the resulting polymers were obtained by precipitation in methanol. The number- and weight-average molecular weights (M_n and M_w) of the polymers were determined by GPC calibrated with standard polystyrenes. The copolymer compositions were determined from the ^{1}H NMR spectra of the copolymers.

Photochemical Reaction. The photocyclization and cycloreversion quantum yields were determined in *n*-hexane relative to **DE**, whose quantum yield has been previously determined ([**DE**] = 1.1×10^{-5} M and [**DE-FL**] = 7.0×10^{-6} M).[36] Photoirradiation was conducted using a 200 W mercury–xenon lamp (Moritex MUV-202) or a 300 W xenon lamp (Asahi Spectra MAX-301) as the light source. Monochromatic light was obtained by passing the light through a monochromator (Jobin Yvon H10 UV). Photocyclization conversions of **DE-FL** and the polymers were determined by ^{1}H NMR spectroscopy and absorption spectroscopic analysis.

Fluorescence Quantum Yield. All measurements performed in solution were conducted with an optical density of approximately 0.1 at the excitation wavelength in 1-cm path length quartz cells at room temperature (298 K). All samples in a solution were deaerated by bubbling with argon gas for 5 min before the measurements. The fluorescence quantum yields (Φ_f) were determined from the integrated intensity in the fluorescence spectrum of a measurement sample relative to that of a reference solution using eq. 1.[37]

$$\Phi_f = \Phi_{f,ref} \times \frac{A_{ref}}{A} \times \frac{I_{ref}}{I} \times \frac{F}{F_{ref}} \times \frac{n^2}{n_{ref}^2}$$

(1)

where A and A_{ref} are the optical densities of the solutions at the excitation wavelength, I and I_{ref} are the excitation light intensities at the excitation wavelength, F and F_{ref} are the integrated intensities of the corrected fluorescence spectra, and n and n_{ref} are the refractive indices of the solvents used for the sample solution and a standard reference solution, respectively. Coumarin 102 ($\Phi_f = 0.76$ in ethanol excited at 390 nm) and Coumarin 153 ($\Phi_f = 0.54$ in ethanol excited at 390 nm) were used as standard references.[38] The Φ_f value was determined as the average of the values obtained using two standard references, and the relative experimental error was estimated to be less than 10%.

Fluorescence Lifetime. Fluorescent dynamics of polymers with fluorene and diarylethene units were measured by means of time-correlated single-photon-counting (TCSPC) method. The experimental setup of our TCSPC system was described in the previous report.[39] Briefly, the output of a Ti:Sapphire laser (Spectra-Physics, Tsunami, 800 nm, 1.8 W, 70 fs, 80 MHz) was divided into two portions. The small portion was detected by a photodiode as a starting signal of TCSPC measurements. The remaining major

portion was converted into the second harmonics (400 nm) using a type I barium borate (BBO) crystal and then used for the excitation of the sample. The repetition rate was reduced to 8 MHz by using an electro-optic modulator (Conoptics, Model 350). The excitation power at the sample position was typically 16 µW (8 MHz). Polarization of the excitation pulses was set to the magic angle with respect to that of the fluorescence detection by using a film polarizer and Babinet-Soleil compensator. A monochromator (Princeton Instruments, Acton SP-2150) was placed before the photomultiplier-tube (Hamamatsu Photonics, R3809U-50) equipped with combination of a pre-amplifier (Hamamatsu Photonics, C5594) and a TCSPC module (PicoQuant, PicoHarp 300). Sample solutions were put in 1-cm quartz cells. Typical response time of the system was ca. 40-ps fwhm, which was determined by the scattering signal of the colloidal solution.

Results and Discussion

 Molecular Design. **DE** and **FL** were employed as the photochromic and fluorophore units of the diarylethene-fluorene dyad and copolymers. **DE** is a diarylethene derivative, and both its open- and closed-ring forms have high thermal stability. **FL** shows blue fluorescence with high Φ_f ($\Phi_f = 0.69$). Because the fluorescence on/off switching in this work is based on the Förster resonance energy transfer (FRET) from the fluorophore to the diarylethene closed-ring form, an overlap between the absorption spectrum of the diarylethene closed-ring form and the fluorescence spectrum of the fluorophore is required to quench the excited energy of the fluorophore with high efficiency. As shown in Figure 1, the fluorescence spectrum of **FL** properly overlaps the absorption spectrum of the closed-ring form of **DE**. Therefore, the fluorescence of **FL** is expected to be quenched when **DE** isomerizes from the open-ring form to the closed-ring form. Contrastingly, when **DE** is in the open-ring form, fluorescence quenching does not occur because the excited state energy level of **DE** is higher than that of **FL**.
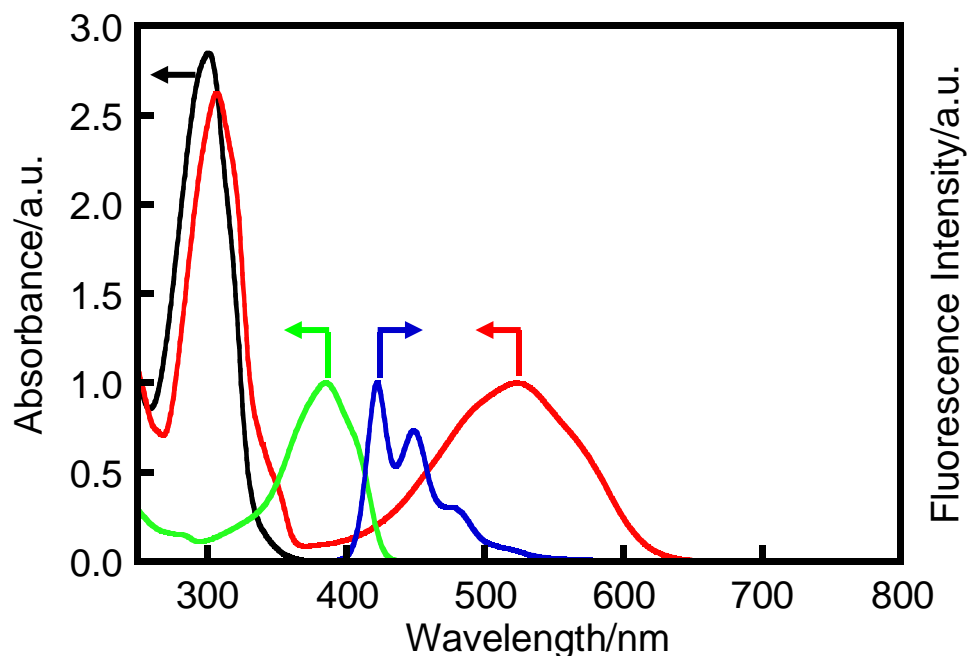
Figure 1. Normalized absorption spectra of the open-ring form (black line) and the photostationary solution upon irradiation with 313 nm light (red line) of **DE** in *n*-hexane, and normalized absorption spectrum (green line) and fluorescence spectrum under excitation at 366 nm (blue line) of **FL** in *n*-hexane.

In **DE-FL**, **DE** is covalently connected with **FL** through an ester spacer. St and maleimide monomers connected with **FL** (**FL1** and **FL2**) were synthesized. Random copolymers bearing **DE** and **FL** in their side chains (**poly(DE1$_x$-*co*-FL1$_y$)**) were synthesized by copolymerization of **DE1** and **FL1** in an arbitrary ratio, where *x* and *y* are the molar fractions of **DE1** and **FL1** in the copolymer, respectively. In addition, alternative copolymers (**poly(DE1-*alt*-FL2)**) were also synthesized by copolymerization of **DE1** and **FL2** with the same molar fractions. Because St and *N*-phenylmaleimide show a charge-transfer complex in the copolymerization process due to their electron-donating and electron-accepting characters, respectively, this copolymerization process leads to alternative copolymers with low monomer reactivity ratios ($r_1 \ll$

0.1 and $r_2 \ll 0.1$).[40] It is expected that the fluorescence on/off switching properties of the polymers will be superior to those of **DE-FL** because a large number of fluorophores are quenched by a single closed-ring diarylethene in the polymer.

Polymerization. Table 1 shows the polymerization conditions, yields, M_n, M_w/M_n, and T_g of the studied polymers. GPC elution curves and ^{1}H NMR spectra of the polymers are shown in Figures S1 and S2, respectively. The compositions of **poly(DE1$_x$-co-FL1$_y$)** were estimated from absorption spectroscopic analysis. It was hypothesized that the absorption spectra of **poly(DE1$_x$-co-FL1$_y$)** are consistent with the summation of a content of **poly(DE1)** and **poly(FL1)** in the composition of **poly(DE1$_x$-co-FL1$_y$)**, as shown in Figure S3. The molar fraction of **FL1** in all **poly(DE1$_x$-co-FL1$_y$)** were determined as shown in Table 1. Next, the composition of alternating copolymers was calculated from ^{1}H NMR spectroscopic analysis. The molar fraction of **FL2** in **poly(DE1-alt-FL2)** and **poly(St-alt-FL2)** was estimated to be 48 and 49%, respectively, by comparing the integral intensities of alkyl, CH_2OCO, and aromatic proton peaks. The composition curve for the copolymerization of **FL1** with **DE1** exhibited a linear relationship, as shown in Figure 2. Therefore, the composition of **FL1** in the copolymers was almost the same as that in the feed. In addition, the yields, M_n, and M_w/M_n of the copolymers were similar. These results indicate that the introduction of **DE** and **FL** to the p-position of St did not affect the polymerization reactivity. The T_g values of **poly(DE1)** and **poly(FL1)** were determined to be 102 °C[35] and 64 °C by DSC, respectively. The lower T_g of **poly(FL1)** is ascribed to the two octyl groups. The T_g values of **poly(DE1$_x$-co-FL1$_y$)** were determined to be 69-96 °C: these values decreased with increasing molar fraction of **FL1** in the

copolymer. Moreover, the compositions of **FL2** in **poly(DE1-*alt*-FL2)** and **poly(St-*alt*-FL2)** were

determined to be ca. 50 mol%. Thus, copolymers consisting of **DE** and **FL** in an arbitrary ratio could be

fabricated.

Table 1. Radical polymerization initiated with AIBN (0.020 M) in toluene for 10 h at 60 °C and characterization of the resulting polymers.

Entry	[DE1] /M	[St] /M	[FL1] /M	[FL2] /M	Yield /%	M_n	M_w/M_n	Molar fraction of FL/mol%[a]	T_g /°C
1[b]	0.37	—	0	—	79	41900	2.24	0	102
2	0.38	—	0.062	—	66	43500	2.28	12[d]	96
3	0.31	—	0.12	—	62	43500	2.19	25[d]	90
4	0.19	—	0.19	—	—[c]	41100	2.77	52[d]	81
5	0.12	—	0.25	—	77	42900	2.40	65[d]	74
6	0.062	—	0.31	—	76	41900	2.92	86[d]	71
7	0.034	—	0.34	—	77	49700	2.71	90[d]	69
8	0	—	0.37	—	64	57200	2.83	100	64
9	0.19	—	—	0.19	85	53400	3.00	48[e]	78
10	—	0.19	—	0.19	79	61100	3.06	49[e]	60

[a] Molar fraction of **FL1** or **FL2** in the polymer.

[b] Ref. 35.

[c] Not determined.

[d] Determined by absorption spectroscopic analysis.

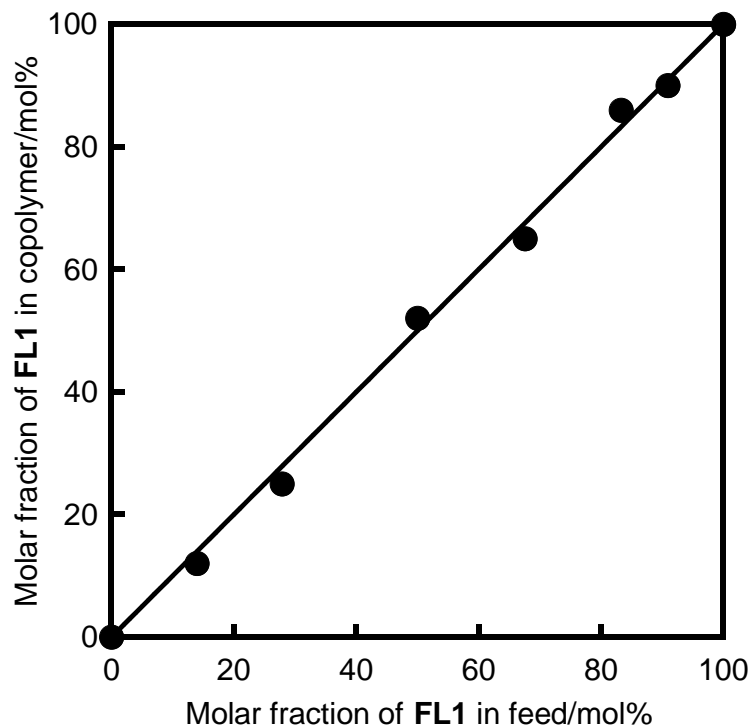[e] Determined by ^{1}H NMR spectroscopic analysis

Figure 2. The composition curve for copolymerization of **FL1** with **DE1** in toluene at 60 °C.

Photochromism. The optical properties of **DE-FL** and the polymers are summarized in Tables 2 and 3. Figure 3a–c shows the absorption spectral changes of **DE-FL** in *n*-hexane, **poly(DE1$_{48}$-*co*-FL1$_{52}$)** in THF, and **poly(DE1-*alt*-FL2)** in THF upon irradiation with 313 nm light. The absorption maximum wavelengths (λ_{abs}) were observed at 393, 390, and 390 nm ($\varepsilon = 79900$, 78500, and 78200 M^{-1} cm^{-1}) for **DE-FL**, **poly(DE1$_{48}$-*co*-FL1$_{52}$)**, and **poly(DE1-*alt*-FL2)**, respectively; these correspond to the band for the fluorene moiety. Upon irradiation with 313 nm light, the colorless solution became red, and new absorption bands appeared at 524, 534, and 534 nm for **DE-FL**, **poly(DE1$_{48}$-*co*-FL1$_{52}$)**, and **poly(DE1-*alt*-FL2)**, respectively. The ε values for the closed-ring forms of **DE** in **DE-FL**, **poly(DE1$_{48}$-*co*-FL1$_{52}$)**, and **poly(DE1-*alt*-FL2)** were determined to be 15200, 14300, and 15500 M^{-1} cm^{-1}, respectively. λ_{abs} and

16

ε of **poly(DE1$_x$-*co*-FL1$_y$)** were almost constant regardless of the molar fraction of **FL1** in the copolymer. These spectral changes are ascribed to photoisomerization from the open- to the closed-ring forms. Upon irradiation with visible light (> 500 nm), the solution colors and absorption spectra returned to their initial states. Thus, **DE-FL** and the copolymers exhibited reversible photochromic reactions upon alternating irradiation with UV and visible light. Their photocyclization conversions upon irradiation with 313 nm light were determined to be approximately 88%.

Table 2. Optical properties of **DE**, **FL**, and **DE-FL** in *n*-hexane.

Compound	λ_{abs}/nm (ε/M^{-1} cm^{-1})	Conv. /%	$\Phi_{o \to c}$	$\Phi_{c \to o}$	λ_{flu} /nm	Φ_f	Contrast[a]
DE[b]	524 (14900)[c]	87	0.48	0.018	—	—	—
FL[d]	383 (80100)	—	—	—	423, (449)	0.69	—
DE-FL	393 (79900)[e], 524 (15200)[c]	88	0.25	0.016	436, (464)	0.69	5.6

[a] Contrast is defined as initial fluorescence intensity relative to fluorescence intensity at the PSS.

[b] Ref 32, 33.

[c] λ_{abs} and ε for the closed-ring form of **DE**.

[d] Ref 34.

[e] λ_{abs} and ε for **FL**.

Table 3. Optical properties of the studied polymers in THF.

Polymer	λ_{abs}/nm (ε/M^{-1} cm^{-1})	Conv. /%	λ_{flu} /nm	Φ_f	Contrast[a]
poly(DE1$_{88}$-co-FL1$_{12}$)	391 (78500)[b], 534 (13900)[c]	87	433, (461)	0.16	133
poly(DE1$_{75}$-co-FL1$_{25}$)	391 (80700)[b], 534 (13200)[c]	87	434, (463)	0.13	106
poly(DE1$_{48}$-co-FL1$_{52}$)	390 (78500)[b], 534 (14300)[c]	87	434, (462)	0.15	71
poly(DE1$_{35}$-co-FL1$_{65}$)	390 (78600)[b], 534 (14600)[c]	87	434, (462)	0.20	36
poly(DE1$_{14}$-co-FL1$_{86}$)	389 (78000)[b], 534 (14600)[c]	88	434, (463)	0.37	11
poly(DE1$_{10}$-co-FL1$_{90}$)	389 (80700)[b], 534 (14100)[c]	88	435, (463)	0.42	5.1
poly(FL1)	388 (78800)[b]	—	436, (463)	0.66	—
poly(DE1-alt-FL2)	391 (78200)[b], 534 (15500)[c]	88	436, (464)	0.21	76
poly(St-alt-FL2)	390 (79100)[b]	—	436, (463)	0.69	—

[a] Contrast is defined as initial fluorescence intensity relative to fluorescence intensity at the PSS.

[b] λ_{abs} and ε for the **FL1** or **FL2** unit in the polymers.

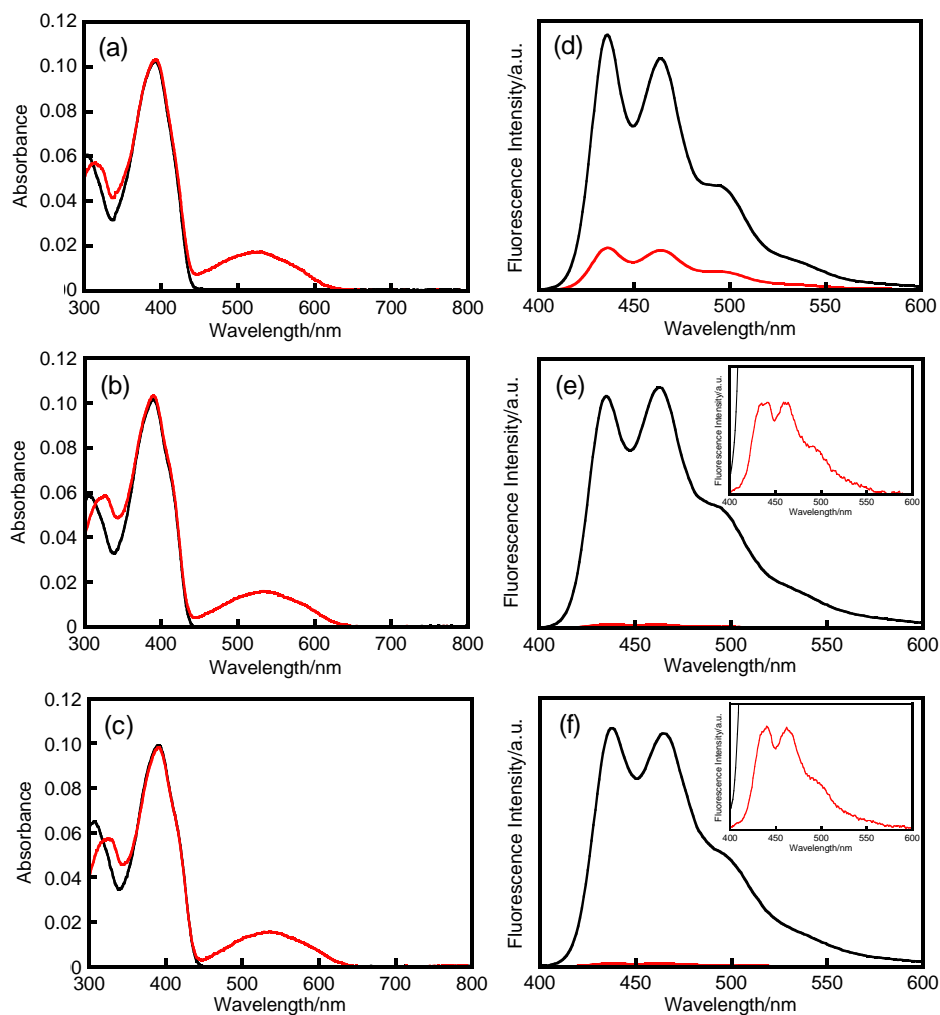[c] λ_{abs} and ε for the closed-ring form of the **DE1** unit in the polymers.

Figure 3. Absorption and fluorescence spectra of **DE-FL** in *n*-hexane (a,d), **poly(DE1₄₈-*co*-FL1₅₂)** in THF (b,e), and **poly(DE1-*alt*-FL2)** in THF (c,f) (1.3×10^{-6} M for **DE** or **DE1** moiety): open-ring form (black line) and photostationary solution upon irradiation with 313 nm light (red line). The fluorescence spectra were recorded upon excitation at 390 nm.

Fluorescence Properties. Figure 3d–f shows the fluorescence spectral changes of **DE-FL** in *n*-hexane, **poly(DE1₄₈-*co*-FL1₅₂)** in THF, and **poly(DE1-*alt*-FL2)** in THF upon excitation at 390 nm. The fluorescence maximum wavelengths (λ_{flu}) of the blue fluorescence for the fluorene moiety were observed at 436, 434, and 436 nm, respectively. λ_{flu} changed only slightly regardless of the molar fraction of **FL1**

in **poly(DE1$_x$-*co*-FL1$_y$)**. The Φ_f of **DE-FL** was determined to be 0.69, which is similar to that of **FL**. The Φ_f values for **poly(DE1$_{48}$-*co*-FL1$_{52}$)** and **poly(DE1-*alt*-FL2)** were determined to be 0.15 and 0.21, respectively; these values are much smaller than those of **DE-FL** and **FL**. The Φ_f values for **poly(DE1$_x$-*co*-FL1$_y$)** decreased from 0.42 to 0.13 with increasing molar fraction of **DE** in the copolymer. The low Φ_f values of **poly(DE1$_x$-*co*-FL1$_y$)** and **poly(DE1-*alt*-FL2)** are due to the presence of the **DE1** unit in the copolymers—this will be discussed in more detail later.

Fluorescence On/Off Switching. The fluorescence intensity gradually decreased upon irradiation with 313 nm light as shown in Figure 4a. This is ascribed to the energy transfer from the fluorene moiety to the diarylethene closed-ring form. Upon irradiation with visible light, the fluorescence intensity returned to its initial one. These results indicate that **DE-FL** and the copolymers demonstrate fluorescence on/off switching properties upon alternating irradiation with UV and visible light. Figure 4b shows the relative fluorescence intensity (F/F_0) related to the photocyclization conversion of the diarylethene. The F/F_0 value of **DE-FL** linearly decreased with increasing photocyclization conversion of the diarylethene. This result indicates that the fluorescence of the fluorene moiety in **DE-FL** was quenched by one diarylethene moiety in the closed-ring form. However, the residual fluorescence was observed at the PSS, although the fluorescence intensity of **DE-FL** decreased upon irradiation with UV light. The residual fluorescence is ascribed to two factors: one is the fluorescence of **DE-FL** in the open-ring form at the PSS, while the other is the fluorescence of **DE-FL** in the closed-ring form, which did not completely quench the fluorescence of the fluorene moiety. If the fluorescence of the fluorene moiety is completely quenched by

20

the diarylethene closed-ring form, the slope of F/F_0 versus the photocyclization conversion should be −0.01/%$^{-1}$. The slope for **DE-FL** is −0.0093/%$^{-1}$ (r^2 = 0.99), which indicates that about 93% of the fluorescence of the fluorene moiety is quenched by the diarylethene close-ring form. Thus, the strong residual fluorescence and the linear fluorescence decay versus the photocyclization conversion indicate that **DE-FL** does not have efficient fluorescence on/off properties. Moreover, the fluorescence on/off switching properties of **DE-FL** in THF was also investigated as shown in Figure S4. The fluorescence spectra was red-shifted from λ_{flu} = 436 nm in n-hexane to λ_{flu} = 474 nm in THF, which is due to the electron-withdrawing effect of carbonyl group of fluorene moiety. The Φ_f value in THF was determined to be 0.79. Upon irradiation with UV and visible light, the fluorescence on/off switching was observed in THF as well as in n-hexane. The slope of the F/F_0 versus the photocyclization conversion is −0.0099/%$^{-1}$ (r^2 = 0.99), which is slightly larger than that in n-hexane because the overlap integral between the absorption spectrum of the diarylethene closed-ring form and the fluorescence spectrum in THF is larger than that in n-hexane. To investigate the fluorescence on/off switching of **DE-FL** in more detail, the Förster distance (R_0) and FRET efficiency (E) were estimated as follows. The R_0 values of **DE-FL** in n-hexane and THF were determined to be 4.31 and 4.47 nm, respectively, based on the Förster equation.[41] Furthermore, the E values of **DE-FL** in n-hexane and THF were calculated to be 99.0 and 99.2%, respectively, when the distance between diarylethene and fluorene moieties was assumed to be 2.0 nm.[41] These results support that the slope in THF is slightly larger than that in n-hexane.
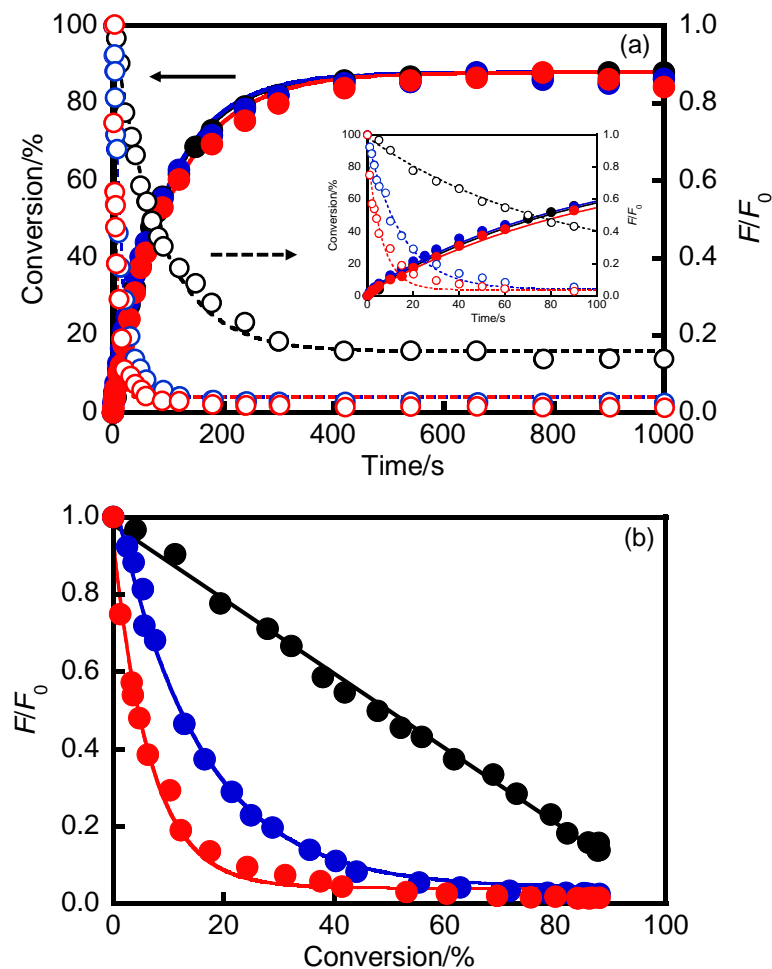
Figure 4. (a) Photocyclization conversion and normalized fluorescence intensity excited at 390 nm relative to irradiation time with 313 nm light (0.24 mW cm^{-2}) of **DE-FL** in *n*-hexane (○ and ●), **poly(DE1$_{48}$-*co*-FL1$_{52}$)** in THF (○ and ●), and **poly(DE1-*alt*-FL2)** in THF (○ and ●). (b) Normalized fluorescence intensity excited at 390 nm relative to the photocyclization conversion of **DE-FL** in *n*-hexane (●), **poly(DE1$_{48}$-*co*-FL1$_{52}$)** in THF (●), and **poly(DE1-*alt*-FL2)** in THF (●).

Upon irradiation with 313 nm light (0.24 mW cm^{-2}) for 60 s, the fluorescence of **poly(DE1$_{48}$-*co*-FL$_{52}$)** was almost quenched although the fluorescence intensity of **DE-FL** in *n*-hexane decreased upon irradiation for 400 s. The photocyclization reaction speed of **DE-FL** and **poly(DE1$_{48}$-*co*-FL$_{52}$)** versus UV irradiation time hardly changed. These results indicate that the fluorescence on/off switching of

22

poly(DE1₄₈-*co*-FL1₅₂) was speedier than that of **DE-FL**. The fluorescence on/off contrast is defined as the value of the initial fluorescence intensity divided by the fluorescence intensity at the PSS. Contrasts for **DE-FL** and **poly(DE1₄₈-*co*-FL1₅₂)** were determined to be 5.6 and 71, respectively. The contrast for **poly(DE₄₈-*co*-FL1₅₂)** is much larger than that for **DE-FL**. Thus, the fluorescence on/off switching property of **poly(DE1₄₈-*co*-FL1₅₂)** is superior to that of **DE-FL**, although **DE** and **FL** in **DE-FL** and **poly(DE1₄₈-*co*-FL1₅₂)** have the same molecular structures and the same molar fractions. As shown in Figure 4b, the F/F_0 value of **poly(DE1₄₈-*co*-FL1₅₂)** largely decreased with increasing photocyclization conversion of the diarylethene. This is because a large number of fluorene moieties are quenched by a single closed-ring diarylethene in the copolymer. These results indicate that the introduction of **DE** and **FL** into the side chains of the polymers improved their fluorescence on/off switching properties.

Moreover, the fluorescence on/off switching of **poly(DE1-*alt*-FL2)** was speedier than that of **poly(DE1₄₈-*co*-FL1₅₂)** although their photocyclization reaction rates hardly changed. The F/F_0 value of **poly(DE1-*alt*-FL2)** significantly decreased with increasing photocyclization conversion of the diarylethene in comparison with that of **poly(DE1₄₈-*co*-FL1₅₂)**. The number of fluorene moieties quenched by a single closed-ring diarylethene of **poly(DE1₄₈-*co*-FL1₅₂)** and **poly(DE1-*alt*-FL2)** is almost the same. Thus, the monomer sequence of the copolymer greatly affects its fluorescence on/off switching properties.

Figure 5 shows repeating cycles of the photochromic reactions and fluorescence on/off switching of **poly(DE1-*alt*-FL2)** upon alternating irradiation with UV and visible light, which could be repeated 10

times without a significant decrease of the absorbance in their closed-ring form and the fluorescence

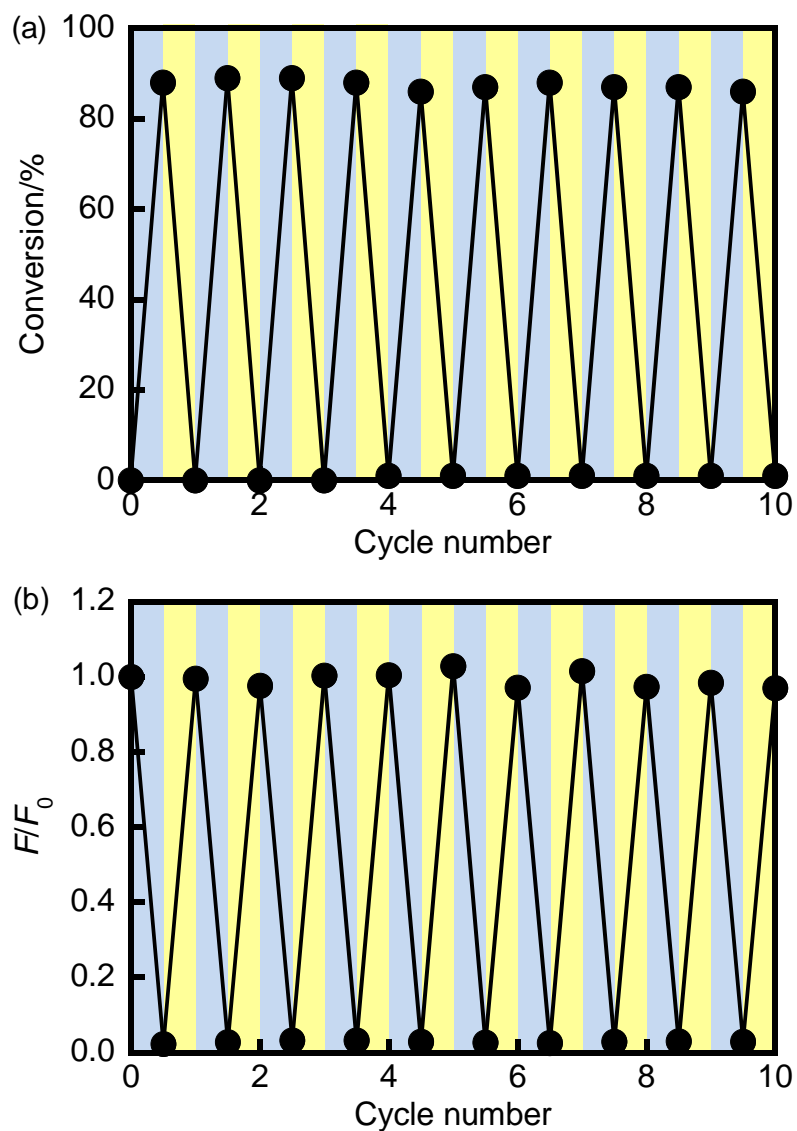intensity in their open-ring form.

Figure 5. Reversible photochromic reactions (a) and fluorescence on/off switching (b) of **poly(DE1-*alt*-FL2)** in THF upon alternating irradiation with 313 nm light for 12 min (0.23 mW cm^{-2}, blue region) (a) and 60 s (0.22 mW cm^{-2}, blue region) (b) and visible light for 3 min (>500 nm, yellow region).

Next, the dependence of the fluorescence on/off switching properties on the molar fraction of **DE1** and **FL1** in **poly(DE1$_x$-*co*-FL1$_y$)** was investigated. Figure S5 shows the absorption and fluorescence spectral changes of **poly(DE1$_x$-*co*-FL1$_y$)** with various molar fractions of **FL1**. The F/F_0 values for **poly(DE1$_x$-*co*-FL1$_y$)** versus the photocyclization conversion are shown in Figure 6. All the copolymers showed fluorescence on/off switching upon irradiation with UV and visible light. The change in the F/F_0 value relative to the photoisomerization conversion decreased with increasing molar fraction of **FL1** in the copolymer. The fluorescence on/off contrast for **poly(DE1$_{10}$-*co*-FL1$_{90}$)** was determined to be 5.1, and 30% of the initial fluorescence was observed as the residual fluorescence even at the PSS. These results are ascribed to the increase in the number of fluorene moieties outside the area where the diarylethene closed-ring form in the copolymer can quench their excited energies. On the other hand, the changes in the F/F_0 value versus the photocyclization conversion increased with decreasing molar fraction of **FL1** in the copolymer. The contrast for **poly(DE1$_{88}$-*co*-FL1$_{12}$)** with the smallest molar fraction of **FL1** in this work was determined to be 133, and the fluorescence of **poly(DE1$_{88}$-*co*-FL1$_{12}$)** was almost quenched at the PSS. **Poly(DE1$_{88}$-*co*-FL1$_{12}$)** showed the most efficient fluorescence on/off switching properties among the **poly(DE1$_x$-*co*-FL1$_y$)** polymers. These results revealed that the fluorescence on/off switching properties of **poly(DE1$_x$-*co*-FL1$_y$)** improved as the molar fraction of **FL1** decreased.
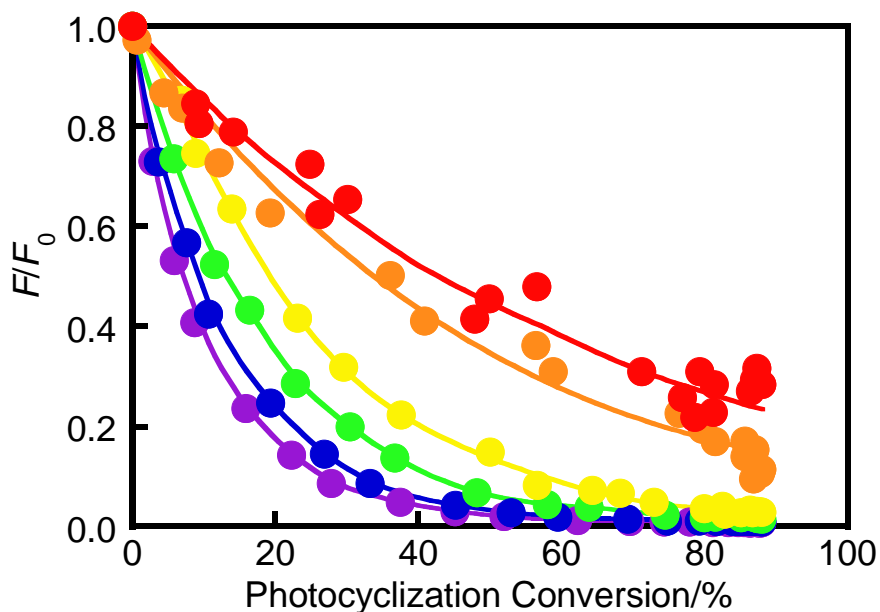
Figure 6. Normalized fluorescence intensity excited at 390 nm as a function of the photocyclization conversion of **poly(DE1₈₈-*co*-FL1₁₂)** (🟣), **poly(DE1₇₅-*co*-FL1₂₅)** (🔵), **poly(DE1₄₈-*co*-FL1₅₂)** (🟢), **poly(DE1₃₅-*co*-FL1₆₅)** (🟡), **poly(DE1₁₄-*co*-FL1₈₆)** (🟠), and **poly(DE1₁₀-*co*-FL1₉₀)** (🔴) in THF (1.3-1.4 × 10⁻⁶ M for fluorene moiety).

Fluorescence Quantum Yield and Fluorescence Lifetime. As mentioned above, the Φ_f values of **poly(DE1$_x$-*co*-FL1$_y$)** and **poly(DE1-*alt*-FL2)** are lower than those of **DE-FL** and **FL**. The absorbance and fluorescence properties of **poly(FL1)** and **poly(St-*alt*-FL2)** in THF were investigated to reveal the reason for the decrease of Φ_f (Figure S6). The Φ_f values of **poly(FL1)** and **poly(St-*alt*-FL2)** were determined to be 0.66 and 0.69, respectively. These values are almost the same as those of **DE-FL** and **FL**. This result reveals that introduction of the fluorene moiety into the side chains of the polymer only slightly affects its fluorescence properties; it also indicates that the lower Φ_f values of **poly(DE1$_x$-*co*-FL1$_y$)** and **poly(DE1-*alt*-FL2)** are not due to intermolecular interactions between the fluorene moieties.

26

Next, the intermolecular interactions between the diarylethene open-ring form and the fluorene moiety were examined. There is a slight overlap between the absorption spectrum of **poly(DE1)** in the open-ring form and the fluorescence spectrum of **poly(FL1)** in THF (Figure S7), which indicates that an energy transfer from the fluorene moiety to the diarylethene open-ring form can occur. Moreover, it is considered that the energy transfer is enhanced in the copolymers because the fluorescence of multiple fluorene moieties is quenched by one diarylethene moiety in the open-ring form. Moreover, because the distance between diarylethene and fluorene moieties is short, other energy transfer process through the exchange interaction such as Dexter mechanism may contribute to some extent. As a result, the Φ_f values of **poly(DE1$_x$-*co*-FL1$_y$)** and **poly(DE1-*alt*-FL2)** decreased due to the increase in the non-radiative energy transfer process by the intermolecular interactions between the diarylethene open-ring form and the fluorene moiety.

In order to further investigate the fluorescence properties of the copolymers, their fluorescence lifetimes were measured (Figure S8). The results are summarized in Table 4. **FL** showed τ of 0.75 ns with a single component. **DE-FL** showed τ of 0.89 ns accompanied with a rise component of 0.20 ns. The component of ca. 0.8 ns is due to the fluorescence of the fluorene moiety. The rise component of ca. 0.2 ns may be due to an energy transfer from the diarylethene open-ring form at the excited state to the fluorene moiety. **DE-FL** at the photostationary state showed the same values as that in the open-ring form, while Φ_f decreased at the PSS. This means that the energy transfer from the fluorene moiety at the excited state to the diarylethene closed-ring form is fast enough not to detect the fluorescent lifetime, and that the

diarylethene closed-ring form efficiently quenches the fluorescence of the fluorene moiety. On the other hand, the studied polymers showed fluorescence lifetimes with multiple components; 0.10 (59%), 0.43 (31%), 1.1 (7%), and 3.6 ns (2%) for **poly(DE1$_{48}$-*co*-FL1$_{52}$)** and 0.091 (61%), 0.44 (27%), 1.2 (10%), and 3.5 ns (2%) for **poly(DE1-*alt*-FL2)** in the open-ring form in THF. Average fluorescence lifetimes (τ_{ave}) were calculated from these values according to $\tau_{ave} = \Sigma\,(\tau \times \%)$; they were determined to be 0.34 ns for **poly(DE1$_{48}$-*co*-FL1$_{52}$)** and 0.29 ns for **poly(DE1-*alt*-FL2)**. The radiative rate constants (k_f) and the non-radiative rate constants (k_{nr}) were calculated from Φ_f according to τ_{ave}: $k_f = \Phi_f/\tau_{ave}$ and $k_{nr} = (1 - \Phi_f)/\tau_{ave}$. The k_f values were calculated to be 0.44×10^9 and 0.71×10^9 s^{-1}, and the k_{nr} values were calculated to be 2.5×10^9 and 2.7×10^9 s^{-1} for **poly(DE1$_{48}$-*co*-FL1$_{52}$)** and **poly(DE1-*alt*-FL2)**, respectively, in the open-ring form in THF. The same method was used to calculate τ_{ave}, k_f, and k_{nr} for **poly(FL1)** and **poly(St-*alt*-FL2)**. Two components for τ in both **poly(FL1)** and **poly(St-*alt*-FL2)** were observed, which may be ascribed to the difference in the conformation in the polymers. The τ_1 values of ca. 0.1 ns for **poly(DE1$_{48}$-*co*-FL1$_{52}$)** and **poly(DE1-*alt*-FL2)** do not exist in **poly(FL1)** and **poly(St-*alt*-FL2)**, which correspond to the energy transfer from the fluorene moiety to the diarylethene open-ring form. This result supports the presence of the intermolecular interactions between the diarylethene open-ring form and the fluorene moiety in **poly(DE1$_{48}$-*co*-FL1$_{52}$)** and **poly(DE1-*alt*-FL2)**. As a result, the apparent k_{nr} values for **poly(DE1$_{48}$-*co*-FL1$_{52}$)** and **poly(DE1-*alt*-FL2)** are much larger than those for **poly(FL1)** and **poly(St-*alt*-FL2)**.

Table 4. Fluorescence lifetimes, fluorescence quantum yields, and radiative and non-radiative rate constants in THF.

Compound	τ_1 /ns	τ_2 /ns	τ_3 /ns	τ_4 /ns	τ_{ave} [a] /ns	χ^2	Φ_f	k_f /ns^{-1}	k_{nr} /ns^{-1}
FL [b]	0.75	—	—	—	—	1.06	0.69	0.92	0.42
DE-FL	0.22 (17%, rise)	0.89 (83%)	—	—	0.70	1.00	0.69	0.98	0.44
poly(DE1₄₈-*co*-FL1₅₂)	0.10 (59%)	0.43 (31%)	1.1 (7%)	3.6 (2%)	0.34	1.06	0.15	0.44	2.49
poly(FL1)	0.32 (16%)	1.1 (84%)	—	—	0.98	1.16	0.66	0.68	0.35
poly(DE1-*alt*-FL2)	0.091 (61%)	0.44 (27%)	1.2 (10%)	3.5 (2%)	0.29	1.07	0.21	0.71	2.68
poly(St-*alt*-FL2)	0.22 (12%)	1.0 (88%)	—	—	0.91	1.14	0.69	0.76	0.34

[a] $\tau_{ave} = \Sigma\,(\tau_i \times \%)$

[b] Ref. 34

CONCLUSION

We synthesized a diarylethene-fluorene dyad connected by an ester bond (**DE-FL**) and random and alternative copolymers bearing **DE** and **FL** in their side chains (**poly(DE1$_x$-*co*-FL1$_y$)** and **poly(DE1-*alt*-FL2)**) to develop materials with highly efficient fluorescence on/off switching properties. Although the fluorescence intensity of **DE-FL** linearly decreased with increasing photocyclization conversion of the diarylethene, the fluorescence intensities of the copolymers significantly decreased with increasing photocyclization conversion of the diarylethene because the fluorescence of many fluorene moieties was quenched by one closed-ring diarylethene moiety. In addition, the fluorescence intensity of **poly(DE1-*alt*-FL2)** significantly decreased with increasing photocyclization conversion of the diarylethene in comparison with that of **poly(DE1$_{48}$-*co*-FL1$_{52}$)**, which revealed that the monomer sequence affects the fluorescence on/off switching properties of the copolymers. Moreover, the fluorescence on/off switching properties, such as the switching speed and contrast, of **poly(DE1$_x$-*co*-FL1$_y$)** were improved by decreasing molar fraction of **FL1** in the copolymer. The Φ_f values of the copolymers were smaller than those of **DE-FL** and **FL**. This is ascribed to the energy transfer from the fluorene moiety to the diarylethene moiety in the open-ring form.

30

ASSOCIATED CONTENT

Supporting Information

Synthetic methods of monomers and Figures S1-S8 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: miyasaka@chem.es.osaka-u.ac.jp (H.M.).

*E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp (S.K.).

Notes

The authors declare no competing financial interest.

31

References

(1)   Yang, X.; Zhou, G.; Wong, W.-Y. Functionalization of Phosphorescent Emitters and Their Host Materials by Main-Group Elements for Phosphorescent Organic Light-Emitting Devices. *Chem*. *Soc*. *Rev*. **2015**, *44*, 8484−8575.

(2)   Scholz, S.; Kondakov, D.; Lüssem, B.; Leo, K. Degradation Mechanisms and Reactions in Organic Light-Emitting Devices. *Chem*. *Rev*. **2015**, *115*, 8449−8503.

(3)   Shizu, K.; Uejima, M.; Nomura, H.; Sato, T.; Tanaka, K.; Kaji, H.; Adachi, C. Enhanced Electroluminescence from a Thermally Activated Delayed-Fluorescence Emitter by Suppressing Nonradiative Decay. *Phys*. *Rev*. *Applied* **2015**, *3*, 014001 (1−7).

(4)   Stender, A. S.; Marchuk, K.; Liu, C.; Sander, S.; Meyer, M. W.; Smith, E. A.; Neupane, B.; Wang, G.; Li, J.; Cheng, J.-X. *et al*. Single Cell Optical Imaging and Spectroscopy. *Chem*. *Rev*. **2013**, *113*, 2469−2527.

(5)   Roeffaers, M. B. J.; Sels, B. F.; Uji-i, H.; De Schryver, F. C. ; Jacobs, P. A. ; De Vos, D. E.; Hofkens, J. Spatially Resolved Observation of Crystal-Face-Dependent Catalysis by Single Turnover Counting. *Nature*, **2006**, *439*, 572−575.

(6)   Pu, S.-Z.; Sun, Q.; Fan, C.-B.; Wang, R.-J.; Li, G. Recent Advances in Diarylethene-Based Multi-Responsive Molecular Switches. *J*. *Mater*. *Chem*. *C* **2016**, *4*, 3075-3093.

(7)   Yang, Z.; Cao, J.; He, Y.; Yang, J. H.; Kim, T.; Peng, X.; Kim, J. S.; Macro-/Micro-Environment-Sensitive Chemosensing and Biological Imaging. *Chem*. *Soc*. *Rev*. **2014**, *43*, 4563−4601.

(8)   Betzig, E.; Patterson, G. H.; Sougrat, R.; Lindwasser, O. W.; Olenych, S.; Bonifacino, J. S.; Davidson, M. W.; Lippincott-Schwartz, J.; Hess, H. F. Imaging Intracellular Fluorescent Proteins at Nanometer Resolution. *Science*, **2006**, *313*, 1642−1645.

(9)   Hess, S. T.; Girirajan, T. P. K.; Mason, M. D. Ultra-High Resolution Imaging by Fluorescence Photoactivation Localization Microscopy. *J*. *Biophys*. **2006**, *91*, 4258−4272.

(10) Sengupta, P.; van Engelenburg, S. B.; Lippincott-Schwartz, J.; Superresolution Imaging of Biological Systems Using Photoactivated Localization Microscopy. *J*. *Chem*. *Rev*. **2014**, *114*, 3189−3202.

(11) Fukaminato, T.; Kobatake, S.; Kawai, T.; Irie, M. Three-Dimensional Erasable Optical Memory Using a Photochromic Diarylethene Single Crystal as the Recording Medium. *Proc*. *Jpn*. *Acad*., *Ser*. *B* **2001**, *77*, 30−35.

(12) Corredor, C. C.; Huang, Z. -L.; Belfield, K. D. Two-Photon 3D Optical Data Storage via Fluorescence Modulation of an Efficient Fluorene Dye by a Photochromic Diarylethene.   *Adv*. *Mater*. **2006**, *18*, 2910−2914.

(13) Corredor, C. C.; Huang, Z.-L.; Belfield, K. D.; Morales, A. R. Bondar, M. V. Photochromic Polymer Composites for Two-Photon 3D Optical Data Storage. *Chem*. *Mater*. **2007**, *19*, 5165−5173.

(14) Yun, C.; You, J.; Kim, J.; Huh, J.; Kim, E. Photochromic Fluorescence Switching from Diarylethenes and its Applications. *J. Photochem*. *Photobiol*. *C* **2009**, *10*, 111−129.

(15) Fukaminato, T.; Doi, T.; Tamaoki, N.; Okuno, K.; Ishibashi, Y.; Miyasaka, H.; Irie, M. Single-Molecule Fluorescence Photoswitching of a Diarylethene-Perylenebisimide Dyad: Non-Destructive Fluorescence Readout. *J. Am. Chem*. *Soc*. **2011**, *133*, 4984−4990.

(16) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. Organic Chemistry: a Digital Fluorescent Molecular Photoswitch. *Nature* **2002**, *420*, 759−760.

(17) Fukaminato, T. Single-Molecule Fluorescence Photoswitching: Design and Synthesis of Photoswitchable Fluorescent Molecules. *J. Photochem*. *Photobiol*. *C* **2011**, *12*, 177−208.

(18) Kobatake, S.; Irie, M. Single-Crystalline Photochromism of Diarylethenes. *Bull*. *Chem*. *Soc*. *Jpn*. **2004**, *77*, 195−210.

(19) Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators. *Chem*. *Rev*. **2014**, *114*, 12174−12277.

(20) Giordano, L.; Jovin, T. M.; Irie, M.; Jares-Erijman, E. A. Diheteroarylethenes as Thermally Stable Photoswitchable Acceptors in Photochromic Fluorescence Resonance Energy Transfer (pcfret). *J. Am. Chem. Soc.* **2002**, *124*, 7481−7489.

(21) Métivier, R.; Badré, S.; Méallet-Renault, R.; Yu, P.; Pansu, R. B., Nakatani, K. Fluorescence Photoswitching in Polymer Matrix: Mutual Influence between Photochromic and Fluorescent Molecules by Energy Transfer Processes. *J. Phys. Chem. C* **2009**, *113*, 11916−11926.

(22) Li, C.; Yan, H.; Zhao, L. -X.; Zhang, G. -F.; Hu, Z.; Huang, Z.-L.; Zhu, M.-Q. a Trident Dithienylethene-Perylenemonoimide Dyad with Super Fluorescence Switching Speed and Ratio. *Nature Commun.* **2014**, *5*, 5709 (1−11).

(23) Kawai, T.; Sasaki, T.; Irie, M. A Photoresponsive Laser Dye Containing Photochromic Dithienylethene Units. *Chem. Commun.* **2001**, *8*, 711−712.

(24) He, T.; Tian, H.; Chen, B.; Tu, H.; Müllen, K. Novel Bisthienylethene-Based Photochromic Tetraazaporphyrin with Photoregulating Luminescence. *Adv. Mater.* **2002**, *14*, 918−923.

(25) Tan, W.; Li, X.; Zhang, J.; Tian, H. A Photochromic Diarylethene Dyad Based on Perylene Diimide. *Dyes Pigm.* **2011**, *89*, 260–265.

(26) Fölling, J.; Polyakova, S.; Belov, V.; van Blaaderen, A.; Bossi, M. L.; Hell, S. W. Synthesis and Characterization of Photoswitchable Fluorescent Silica Nanoparticles. *Small*, **2008**, *4*, 134−142.

35

(27) Su, J.; Fukaminato, T.; Placial, J. -P.; Onodera, T.; Suzuki, R.; Oikawa, H.; Brosseau, A.; Brisset, F.; Pansu, R.; Nakatani, K.; Métivier, R. Giant Amplification of Photoswitching by a Few Photons in Fluorescent Photochromic Organic Nanoparticles. *Angew. Chem. Int. Ed.* **2016**, *55*, 1−6.

(28) Watanabe, K.; Hayasaka, H.; Miyashita, T.; Ueda, K.; Akagi, K. Dynamic Control of Full-Colored Emission and Quenching of Photoresponsive Conjugated Polymers by Photostimuli. *Adv. Funct. Mater.* **2015**, *25*, 2794−2806.

(29) Bu, J.; Watanabe, K.; Hayasaka, H.; Akagi, K. Photochemically Colour-Tuneable White Fluorescence Illuminants Consisting of Conjugated Polymer Nanospheres. *Nature Commun.* **2014**, *5*, 3799 (1-7).

(30) Li, C.; Hu, Z.; Aldred, M. P.; Zhao, L. -X.; Yan, H.; Zhang, G. -F.; Huang, Z. -L.; Li, A. D. Q.; Zhu, M. -Q. Water-Soluble Polymeric Photoswitching Dyads Impart SuperResolution Lysosome Highlighters. *Macromolecules* **2014**, *47*, 8594−8601.

(31) Hayasaka, H.; Tamura, K.; Akagi, K. Dynamic Switching of Linearly Polarized Emission in Liquid-Crystallinity-Embedded Photoresponsive Conjugated Polymers. *Macromolecules* **2008**, *41*, 2341−2346.

(32) Uchida, K.; Ishikawa, T.; Takeshita, M.; Irie, M. Thermally Irreversible Photochromic Systems. Reversible Photocyclization of 1,2-Bis(thiazolyl)perfluorocyclopentenes *Tetrahedron* **1998**, *54*, 6627−6638.

(33) Takami, S.; Kobatake, S.; Kawai, T.; Irie, M. Extraordinarily High Thermal Stability of the Closed-Ring Isomer of 1,2-Bis(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene. *Chem*. *Lett*. **2003**, *32*, 892−893.

(34) Nakahama, T.; Kitagawa, D.; Sotome, H.; Ito, S.; Miyasaka, H.; Kobatake, S. Optical Properties and Solvatofluorochromism of Fluorene Derivatives Bearing *S,S*-Dioxidized Thiophene.*Photochem. Photobiol. Sci.* **2016**, *15*, 1254−1263.

(35) Nishi, H.; Namari, T.; Kobatake, S. Photochromic Polymers Bearing Various Diarylethene Chromophores as the Pendant: Synthesis, Optical Properties, and Multicolor Photochromism. *J. Mater*. *Chem*. **2011**, *21*, 17249−17258.

(36) Yokoyama, Y.; Kurita, Y. Synthesis and Photoreaction of Photochromic Fulgides. *J. Synth*. *Org. Chem*. *Jpn*. **1991**, *49*, 364−372.

(37) Parker, C. A.; Rees, W. T. Correction of Fluorescence Spectra and Measurement of Fluorescence Quantum Efficiency. *Analyst* **1960**, *85*, 587−600.

(38) Rurack, K.; Spieles, M. Fluorescence Quantum Yields of a Series of Red and Near-Infrared Dyes Emitting at 600-1000 nm. *Anal*. *Chem*. **2011**, *83*, 1232−1242.

(39) Nagasawa, Y.; Itoh, T.; Yasuda, M.; Ishibashi, Y.; Ito, S.; Miyasaka, H. Ultrafast Charge Transfer Process of 9,9'-Bianthryl in Imidazolium Ionic Liquids. *J. Phys*. *Chem*. *B* **2008**, *112*, 15758−15765.

(40) Mohamed, A. A.; Jebrael, F. H.; Elsabee, M. Z. Copolymerization of Styrene with *N*-Arylmaleimides. *Macromolecules* **1986**, *19*, 32−37.

(41) Medintz, I.; Hildebrandt, N. FRET–Förster resonance energy transfer from theory to applications; Wiley-Interscience: New York, 2013; pp 25−31.

Graphical Abstract