Synthesis of Polystyrene and Poly(alkyl methacrylate)s Having Photochromic Dithienylethene Pendant Groups

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ABSTRACT: Polystyrene, poly(ethyl methacrylate), and poly(isopropyl methacrylate) having 1-(2-methoxy-1-benzothiophen-3-yl)-2-{2,4-dimethyl-5-[4-(4-carbonyloxybutyl)phenyl]thiophen-3-yl}perfluorocyclopentenes were synthesized. Photochemical conversion from open-ring to closed-ring forms of the dithienylethenes was 8—18% lower than the conversion of the chromophore mixed in the same matrix. Although no appreciable difference was observed in the photostationary conversion below and above the glass transition temperature (T_g) in polystyrene and poly(ethyl methacrylate), the conversion in poly(isopropyl methacrylate) increased above T_g.

KEY WORDS Photochromism / Dithienylethene / Polystyrene / Poly(ethyl methacrylate) / Poly(isopropyl methacrylate) / Photoconversion / Activation Energy / Glass Transition Temperature /

Various types of photochromic compounds have been so far attempted to apply to optoelectronic devices, such as optical memory and optical switching.[1-14] Among the compounds diarylethenes having heterocyclic aryl groups are the most promising photochromic compounds for the application because of their fatigue resistant and thermally irreversible properties.[1] When we use photochromic compounds for optoelectronic devices, they should be dispersed in polymer matrices by mixing or chemical binding to the polymers.

In the present study, we synthesized polystyrene, poly(ethyl methacrylate), and poly(isopropyl methacrylate) having 1-(2-methoxy-1-benzothiophen-3-yl)-2-{2,4-dimethyl-5-[4-(4-carbonyloxybutyl)phenyl]thiophen-3-yl}perfluorocyclopentenes (DE) in the pendant groups. Photoreactivity below and above T_g, and temperature dependence of photoisomerization rate in coloring and bleaching processes were examined.

EXPERIMENTAL

Materials

Solvents for the reactions were used after distillation. Commercially available reagents were used without further purification. Compounds **1** and **4** were synthesized according to a method described elsewhere.[15]

Synthesis of Dithienylethene 3

4-[4-[4-[2-(2-Methoxy-1-benzothiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentenyl]-3,5-dimethylthien-2-yl]-phenyl]butanol (**2**). Synthesis of primary alcohol by hydroboration–oxidation reaction of olefin was referred to the method of Brown et al.[16] To a stirred anhydrous tetrahydrofuran (THF) solution (11.5 cm³) containing 6.5 cm³ of borane–THF complex (6.5 mmol, 1 M solution) was added a THF solution (7 cm³) containing compound **1** (550 mg, 0.951 mmol) under argon atmosphere, and refluxed for 16 h. The solution was cooled to room temperature, and 4.8 cm³ of ethanol were added. The reaction mixture was oxidized with 6 N sodium

hydroxide aqueous solution (1.6 cm³) and 30% hydrogen peroxide (3.2 cm³) for 1 h at 55°C. The reaction mixture was diluted with ether, saturated with potassium carbonate (2.1 g), and filtered. The filtrate was evaporated and purified by column chromatography on silica gel (ethyl acetate/hexane = 1/7) to give 349 mg of 4-[4-[4-[2-(2-methoxy-1-benzothiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentenyl]-3,5-dimethylthien-2-yl]phenyl]butanol (**2**) in 62% yield.

2: Colorless viscous oil; ^{1}H NMR (CDCl$_3$): $\delta = 1.45$—1.78 (m, 4H, Ar–C–CH$_2$–CH$_2$–C–), 2.02 (s, 3H, Ar–CH$_3$), 2.22 (s, 3H, Ar–CH$_3$), 2.61 (t, $J = 6$ Hz, 2H, Ar–CH$_2$–C–C–C–), 3.65 (t, $J = 6$ Hz, 2H, Ar–C–C–C–CH$_2$–), 3.79 (s, 3H, Ar–OCH$_3$), 7.10—7.38 (m, 6H, Ar–H), 7.59 (d, $J = 8$ Hz, 2H, Ar–H); IR (KBr): 3400 (OH) cm^{-1}; MS (70 eV): m/z 596 (M$^+$).

1-(2-Methoxy-1-benzothiophen-3-yl)-2-{2,4-dimethyl-5-[4-(4-methacryloyloxybutyl)phenyl]thien-3-yl}perfluorocyclopentene (**3**). To a stirred sodium hydride (53.4 mg, 1.34 mmol) was added a THF solution (10 cm³) containing compound **2** (166 mg, 0.278 mmol) under argon atmosphere, and stirred for 1 h at room temperature. A THF solution (2 cm³) containing methacrylic anhydride (140 mg, 0.908 mmol) was added to the reaction solution and stirred for 7 h at 50°C. The reaction mixture was cooled to room temperature, acidified with 2 N hydrochloric acid, and extracted with ether. The organic layer was washed with brine, dried over magnesium sulfate, filtered and evaporated. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 1/7) to give 117 mg of 1-(2-methoxy-1-benzothiophen-3-yl)-2-{2,4-dimethyl-5-[4-(4-methacryloyloxybutyl)phenyl]thien-3-yl}perfluorocyclopentene (**3**) in 63% yield.

3: Colorless viscous oil; ^{1}H NMR (CDCl$_3$): $\delta = 1.65$—1.78 (m, 4H, Ar–C–CH$_2$–CH$_2$–C–O), 1.95 (s, 3H, C=C(CH$_3$)–C=O), 2.07 (s, 3H, Ar–CH$_3$), 2.27 (s, 3H, Ar–CH$_3$), 2.66 (m, 2H, Ar–CH$_2$–C–C–C–O), 3.80 (s, 3H, Ar–OCH$_3$), 4.18 (m, 2H, Ar–C–C–C–CH$_2$–O), 5.55 (s, 1H, CH$_2$=C–(C)–C=O), 6.09 (s, 1H, CH$_2$=C(C)–

C=O), 7.10—7.42 (m, 6H, Ar–H), 7.58—7.68 (m, 2H, Ar–H); IR (KBr): 1700 cm^{-1} (C=O); MS (70 eV): m/z 664 (M$^+$); *Anal.* Calcd for $C_{34}H_{30}F_6O_3S_2$: C, 61.44%; H, 4.55%. Found: C, 61.48%; H, 4.69%.

Synthesis of Polymers 5—10

Copolymerization of Dithienylethene 3 with Styrene (5). To a benzene solution (1.5 cm^3) containing compound 3 (20 mg, 0.030 mmol) and styrene (157 mg, 1.51 mmol) was added 2,2′-azobisisobutyronitrile (AIBN) (8.9 mg, 0.054 mmol) and bubbled with nitrogen for 5 min to remove dissolving oxygen. The mixture solution was heated for 2 h at 60—70°C. The reaction mixture was cooled to room temperature and purified by reprecipitation with methanol to give 42.1 mg of 5 in 24% yield.

5: Colorless solid; ^{1}H NMR (CDCl$_3$): $\delta = 0.88$—1.16 (m, –C–C(CH$_3$)–C=O), 1.20—2.00 (m, –CH$_2$–C(Ar)–, Ar–C–CH$_2$CH$_2$–C–, –C–CH(Ar)–, –CH$_2$–C(C)–C=O), 2.06 (s, Ar–CH$_3$), 2.25 (s, Ar–CH$_3$), 3.76 (s, Ar–OCH$_3$), 6.24—6.78 (m, H$_2$, H$_6$ of styrene), 6.87—7.30 (m, H$_3$—H$_5$ of styrene), 7.58—7.66 (m, Ar–H); IR (KBr): 3040 (C–H of Ar), 1730 (C=O), 1605, 1495, 1460 (C=C of Ar), 760 (C–H of Ar), 700 (C=C of Ar) cm^{-1}.

Copolymerization of Dithienylethene 3 with Ethyl Methacrylate (6). Reaction of compound 3 (17.5 mg, 0.0263 mmol) and ethyl methacrylate (151 mg, 1.32 mmol) was performed by the same procedure as for 5. The crude product was purified by reprecipitation with methanol and water to give 21.2 mg of 6 in 13% yield.

6: Colorless solid; ^{1}H NMR (CDCl$_3$): $\delta = 0.68$—1.42 (m, –C–C(CH$_3$)–C=O, –C–(=O)–O–C–CH$_3$), 1.42—1.75 (m, Ar–C–CH$_2$CH$_2$–C–), 1.75—2.00 (m, –CH$_2$–C–(C)–C=O), 2.05 (s, Ar–CH$_3$), 2.20 (s, Ar–CH$_3$), 2.55—2.65 (m, Ar–CH$_2$–C–C–C–), 3.79 (s, Ar–OCH$_3$), 3.85—4.20 (m, –C(=O)–O–CH$_2$–C), 7.10—7.35 (m, Ar–H), 7.55—7.63 (m, Ar–H); IR (KBr): 3000 (C–H of Alkane), 1730 (C=O), 1180—1150 (C–C(=O)–O), 1030 (O–C–C) cm^{-1}.

Copolymerization of Dithienylethene 3 with Isopropyl Methacrylate (7). Reaction of compound 3 (20 mg, 0.030 mmol) and isopropyl methacrylate (194 mg, 1.51 mmol) was performed as for 5. The crude product was purified by reprecipitation with methanol and water to give 118.3 mg of 7 in 55% yield.

7: Colorless solid; ^{1}H NMR (CDCl$_3$): $\delta = 0.76$—1.41 (m, –C–C(CH$_3$)–C=O, –C–(=O)–O–C–CH$_3$), 1.62—2.10 (m, Ar–C–CH$_2$CH$_2$–C–, –CH$_2$–C(C)–C=O), 2.05 (s, Ar–CH$_3$), 2.25 (s, Ar–CH$_3$), 2.55—2.71 (m, Ar–CH$_2$–C–C–C–), 3.81 (s, Ar–OCH$_3$), 4.72—4.98 (m, –C(=O)–O–CH–C), 7.15—7.69 (m, Ar–H); IR (KBr): 2980 (C–H of Alkane), 1730 (C=O), 1180—1150 (C–C(=O)–O), 1110 (O–[secondary alkyl]) cm^{-1}.

Polymerization of Styrene (8). To a benzene solution (5 cm^3) containing styrene (1.0 g, 9.6 mmol) was added AIBN (50 mg, 0.30 mmol) and bubbled with nitrogen for 5 min to remove the dissolving oxygen. The mixture solution was heated for 2 h at 60—70°C. The reaction mixture was cooled to room temperature and purified by reprecipitation with methanol to give 0.27 g of 8 in 27% yield.

8: Colorless solid; ^{1}H NMR (CDCl$_3$): $\delta = 1.25$—1.65 (m, –CH$_2$–C(Ar)–), 1.65—2.10 (m, –C–CH(Ar)–), 6.30—6.75 (m, H$_2$, H$_6$ of styrene), 6.90—7.30 (m,

H$_3$—H$_5$ of styrene); IR (KBr): 3040 (C–H of Ar), 1605, 1495, 1460 (C=C of Ar), 760 (C–H of Ar), 700 (C=C of Ar) cm^{-1}.

Polymerization of Ethyl Methacrylate (9). The polymerization of ethyl methacrylate (1.0 g, 8.8 mmol) was performed as for 8. The crude product was purified by reprecipitation with methanol and water to give 41.5 mg of 9 in 42% yield.

9: Colorless solid; ^{1}H NMR (CDCl$_3$): $\delta = 0.82$—1.40 (m, –C–C(CH$_3$)–C=O, –C–(=O)–O–C–CH$_3$), 1.76—2.10 (m, –CH$_2$–C(C)–C=O), 3.98—4.17 (m, –C(=O)–O–CH$_2$–C); IR (KBr): 3000 (C–H of Alkane), 1730 (C=O), 1180—1150 (C–C(=O)–O), 1030 (O–C–C) cm^{-1}.

Polymerization of Isopropyl Methacrylate (10). The polymerization of isopropyl methacrylate (1.0 g, 7.8 mmol) was performed as for 8. The crude product was purified by reprecipitation with methanol and water to give 61.7 mg of 10 in 62% yield.

10: Colorless solid; ^{1}H NMR (CDCl$_3$): $\delta = 0.80$—1.40 (m, –C–C(CH$_3$)–C=O, –C(=O)–O–C–CH$_3$), 1.74—2.12 (m, –CH$_2$–C(C)–C=O), 4.75—5.00 (m, –C(=O)–O–CH–C); IR (KBr): 2980 (C–H of Alkane), 1730 (C=O), 1180—1150 (C–C(=O)–O), 1110 (O–[secondary alkyl]) cm^{-1}.

Film Preparation

A film sample was prepared by spin-coating toluene solution (0.7—1.1 cm^3) containing 20—50 mg polymers possessing dithienylethene pendant groups, or 20—50 mg of polymers and compound 4 on suprasil glass plates. Film thickness was 0.2—1.5 μm. Absorption coefficients of 4a and 4b were determined as 2.3×10^4 mol^{-1} dm^3 cm^{-1} at 266 nm and 1.2×10^4 mol^{-1} dm^3 cm^{-1} at 567 nm in hexane, respectively.

Measurements

^{1}H NMR spectra were recorded on Varian-Gemin-200 (200 MHz) spectrometer. IR spectra were recorded on a Perkin-Elmer-1600 infrared spectrophotometer. DSC measurements were performed with a Seiko DSC 220C. Film thickness was measured with a Tencor alpha-step 200. Photoirradiation was carried out with a USHIO 1 kW high pressure mercury lamp. Mercury lines of 366 nm were isolated by passing the light through cutoff filters (Toshiba UV-29 and UV-D36C). The light that passed through cutoff filters (Toshiba UV-29 and O-55) was used as visible light ($\lambda > 550$ nm). Absorption spectra were recorded on a spectrophotometer (Hitachi, U-3410). Temperature dependence of the absorption spectra was measured with a multi-channel analyzer (Hamamatsu Photonics, PMA-11) connected to an optical microscope (Nikon Optiphot) and personal computer. Temperature was controlled with a hot-stage (Mettler, FP800).
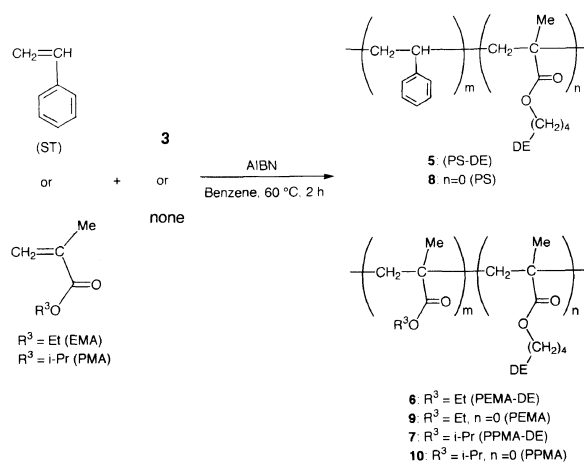
RESULTS AND DISCUSSION

Compound 3 was synthesized as shown in Scheme 1 and polymerized with styrene (ST), ethyl methacrylate (EMA), or isopropyl methacrylate (PMA) in the presence of AIBN as radical initiator in benzene solutions. Polymers 5 (polystyrene (PS)-dithienylethene (DE)), 6 (poly(ethyl methacrylate) (PEMA)-DE), and 7 (poly(-

1: R¹= CH=CH₂ ——— (i) ——→ 2: R²= H
4: R¹= CH₂CH₃   3: R²= C(=O)C(CH₃)=CH₂ ←—— (ii)
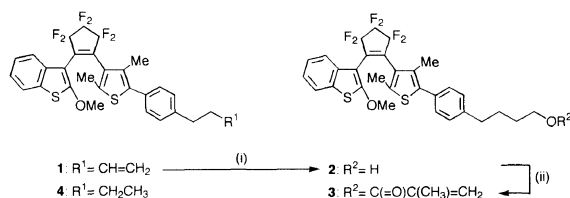
(i) BH₃·THF/THF, refl., 16 h; 6 N-NaOH$_{aq}$, 30% H₂O₂ $_{aq}$, 55°C, 1 h; 62%. (ii) NaH, methacrylic anhydride/THF, 50°C, 7 h; 63%

Scheme 1.

Scheme 2.

Table I. Data of polymers having dithienylethene pendant groups

| No. | Polymer[a] | Composition[b] | | T_g | Molecular weight[c] | |
		m/n		°C	$10^{-3}\,\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
5	PS-DE	19/0.6		88	5.4	1.4
6	PEMA-DE	23/1.0		55	23.4	1.7
7	PPMA-DE	66/1.3		31	8.2	1.7

[a] PS, PEMA, PPMA, and DE denote polystyrene, poly(ethyl methacrylate), poly(isopropyl methacrylate), and dithienylethene, respectively, as shown in Scheme 2. [b] Determined by ¹H NMR. [c] Determined by gel-permeation chromatography using polystyrene as the standard.
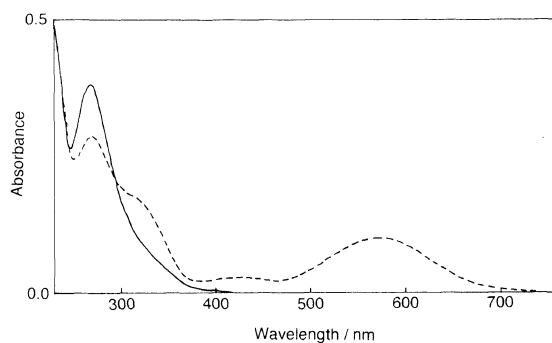

Figure 1. Absorption spectra of film **13Ca** (——) and in the photostationary state (– – –) under irradiation with 366 nm light.
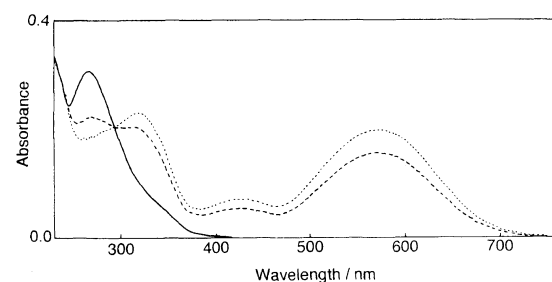

Figure 2. Absorption spectra of film **13Da** (——), **13Db** (·····), and in the photostationary state (– – –) under irradiation with 366 nm light.

isopropyl methacrylate) (PPMA)-DE) were obtained by copolymerization as shown in Scheme 2. Table I shows composition, T_g, number-average molecular weight ($\bar{M}_n$), polydispersity ($\bar{M}_w/\bar{M}_n$) of the polymers **5—7**. Polymers **8** (PS), **9** (PEMA), and **10** (PPMA) were also synthesized from the monomers ST, EMA, and PMA, respectively, by the similar manner as shown in Scheme 2.

Film samples **11C—13C** prepared from polymers **5—7**, respectively, showed normal photochromic reactions. Figure 1 shows typical absorption spectral change of **13C** by irradiation with 366 nm light. Upon irradiation with 366 nm light, the colorless open-ring form **a** was converted to the purple-blue closed-ring form **b**, and the purple-blue color disappeared by irradiation with visible ($\lambda > 550$ nm) light. Similar spectral change was observed for **11C** and **12C**.

The conversion of **11C—13C** from the open-ring to the closed-ring form in the photostationary state by irradiation with 366 nm light was estimated from the spectral data of the film samples **11D—13D**, in which the closed-ring form isomer of **4** was mixed in polymers **8—10**, respectively. Figure 2 shows the absorption spectra for **13Da**, **13Db**, and in the photostationary state by irradiation with 366 nm light. Similar spectral changes were observed for samples **11D** and **12D**. Conversion of **13D** from the open-ring to the closed-ring form at the photostationary state was determined to be 79% by

comparing absorbance at 573 nm of the closed-ring form **13Db** with photostationary absorbance. Conversion of **13C** was calculated to be 67% based on eq 1:

$$\text{Conv}(C) = \text{Conv}(D)\,\frac{\text{Abs}(C)'_{574}}{\text{Abs}(C)_{340}}\,\frac{\text{Abs}(D)_{340}}{\text{Abs}(D)'_{573}} \qquad (1)$$
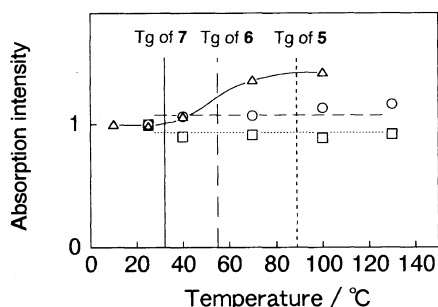
where Conv(C) and Conv(D) are the conversion (%) of DEs chemically bounded to PPMA, **13C**, and DEs mixed in the polymer, **13D**, respectively. Abs(C)'$_{574}$ and Abs(C)$_{340}$ are absorbance at λ_{max} of the closed-ring form in the photostationary state under irradiation with 366 nm light, and the absorbance at 340 nm of the open-ring form, respectively. Abs(D)'$_{573}$ and Abs(D)$_{340}$ denote absorbance at 573 nm of the photostationary state and at 340 nm of the open-ring form DEs mixed in the same polymer matrix. Table II summarizes the conversions of six polymer samples, **11C—13D**, in the photostationary state together with DE content in the polymers.

Figure 3 shows the normalized absorption intensities at λ_{max} below and above T_g of **11C—13C** in the photostationary state. No appreciable difference in the

Table II. Conversion of polymers containing dithienylethenes

Sample[a]	Materials	λ_{max} nm	DE Content mol%	Conv.[d] %
11C	PS-DE	576	3.1[b]	61
11D	4 in PS	576	4.8[c]	69
12C	PEMA-DE	572	4.3[b]	64
12D	4 in PEMA	574	2.6[c]	82
13C	PPMA-DE	574	1.9[b]	67
13D	4 in PPMA	573	3.2[c]	79

[a] C denotes dithienylethene chemically bounded to polymer, D denotes dithienylethene mixed in polymer. [b] Determined by ^{1}H NMR. [c] Feed ratio of polymer and dithienylethene when film was prepared. [d] Measured at 25°C.

Figure 4. Absorption intensity changes of polymer film samples, 11C (□), 12C (○), and 13C (△) at λ_{max} by irradiation with 366 nm light at 40°C.

Figure 3. Normalized absorption intensities at λ_{max} of photogenerated colored forms of 11C (···□···), 12C (—○—), and 13C (—△—) below and above the glass transition temperature in the photostationary state under irradiation with 366nm light. Intensity at the lowest measuring temperatures was normalized to 1.

Figure 5. Absorption intensity changes of polymer film samples, 11C (□), 12C (○), and 13C (△) at λ_{max} by irradiation with visible ($\lambda > 550$ nm) light at 40°C.

absorption intensities for 11C and 12C was observed. However, absorption intensity above T_g for 13C was larger than the value below T_g. This indicates that the free volume above T_g in 13C is more widespread than the one below T_g and rotation of the thienyl groups are allowed above T_g. Such free volume change which affects the photoisomerization reaction was not observed for PS and PEMA.

Figures 4 and 5 show the absorption intensity change at λ_{max} for 11C—13C by irradiation with 366 nm and visible ($\lambda > 550$ nm) light at 40°C, respectively. In coloring and bleaching, no appreciable difference was observed among the three samples.
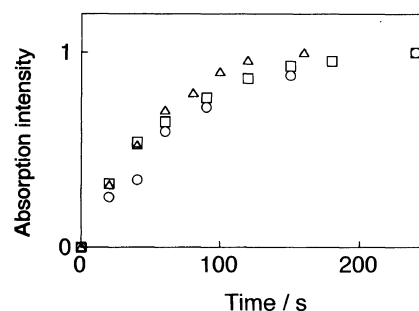
The reversible photoisomerization reaction in Scheme 2 is expressed by eq 2, where A and B denote the open-ring and the closed-ring forms of DE, respectively. $\Phi_{A \to B}$ and $\Phi_{B \to A}$ are quantum yields for the photoisomerization reactions from A to B (coloring) and B to A (bleaching), respectively.

$$A \underset{\Phi_{B \to A}}{\overset{\Phi_{A \to B}}{\rightleftharpoons}} B \qquad (2)$$
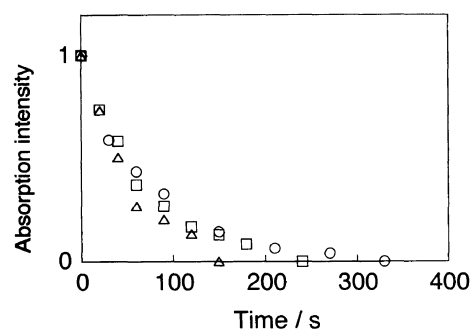
When the open-ring isomer with initial concentration $C_A(0)$ is irradiated with 366 nm light, the formation kinetics of the closed-ring isomer is given as,

$$\ln \frac{Abs(\infty) - Abs(0)}{Abs(\infty) - Abs(t)} = 2.303 \times 10^3 I_0 \varepsilon_A \Phi_{A \to B} \frac{C_0}{C_B(\infty)} t \qquad (3)$$
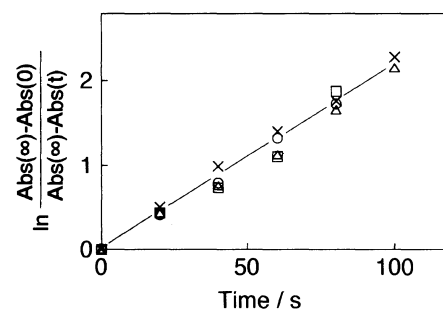
where Abs(t) is the absorbance at λ_{max} of B at time t, I_0

Figure 6. Irradiation time dependence of the left hand side of eq 3 in the coloring process of polymer film sample 13C at 25°C (□), 40°C (○), 70°C (△), and 100°C (×).

is the irradiation light intensity, ε_A is molar extinction coefficient of A at the irradiation wavelength of 366 nm, C_0 is the total concentration ($C_A(t) + C_B(t)$), and $C_B(\infty)$ is the equilibrium concentration of B.[15]

Absorption changes at 572—576 nm, where the closed-ring isomer has absorption maximum, in film samples of polymers by irradiation with 366 nm light were measured at 10—130°C. Typical plots according to eq 3 for 13C measured at 25—100°C are shown in Figure 6. The left hand side of eq 3 increases linearly with time in the initial stage. The initial coloring rate did not depend on temperature. The coloring has no activation energy.

When the closed-ring isomer with initial concentration $C_B'(0)$ is irradiated with visible ($\lambda > 550$ nm) light, the kinetics of the bleaching process is expressed by eq 4:

$$\ln \frac{Abs'(0)}{Abs'(t)} = 2.303 \times 10^3 I_0 \varepsilon_B' \Phi_{B \to A} t \qquad (4)$$

where Abs'(0) and Abs'(t) denote absorbance at λ_{max} for

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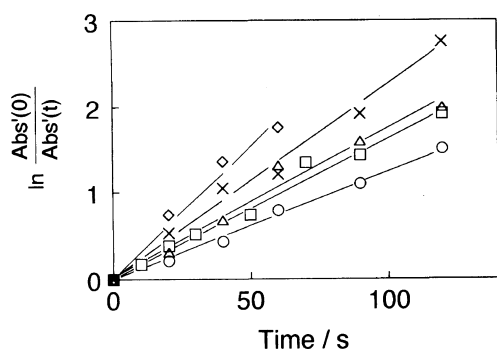
Figure 7. Irradiation time dependence of the left hand side of eq 4 in the bleaching process of polymer film sample **13C** at 10°C (□), 25°C (○), 40°C (△), 70°C (×), and 100°C (◇).

B before and under irradiation with visible ($\lambda > 550$ nm) light, respectively, and ε'_B is the molar extinction coefficient at λ_{max} for B.[15]

Absorption changes at 572—576 nm for the above three polymer samples by irradiation with visible ($\lambda > 550$ nm) light were measured at 10—130°C. Plots according to eq 4 linearly increased with time. Figure 7 shows typical plots for **13C** measured at 10—100°C. The bleaching rate increases with temperature.

Conversion in the photostationary state is expressed as follows

$$\text{Conv}(C) = \frac{\varepsilon_A \Phi_{A \to B}}{\varepsilon_A \Phi_{A \to B} + \varepsilon_B \Phi_{B \to A}} \times 100 \qquad (5)$$

where ε_B is molar extinction coefficient of B at the irradiation wavelength of 366 nm. When the bleaching quantum yield increases with temperature, the conversion should decrease. However, the conversion of **13C** increased with temperature above T_g as shown in Figure 3. This anomalous behavior is explained as follows. In polymer films, DE has two conformations, non-reactive parallel and reactive anti-parallel, and the mutual transformation between them is prohibited below T_g. The cyclization quantum yields in the initial stage as shown in Figure 6 reflect the reactivity of DEs in the anti-parallel conformation, while in the photostationary state above

T_g the transformation efficiency from the parallel to the anti-parallel conformation also contributes to the quantum yields. The ultimate conversion in the photostationary state is expected to increase when DEs in the non-reactive parallel conformation transform to the reactive anti-parallel conformation. The activation energy of bleaching in PPMA was lowest ($1.5\,\text{kcal mol}^{-1}$) among the three samples (PS, $3.4\,\text{kcal mol}^{-1}$; PEMA, $2.4\,\text{kcal mol}^{-1}$). Both low activation energy and efficient transformation in the two conformations are considered to cause photostationary conversion to increase above T_g in PPMA. In PS and PEMA increase in bleaching quantum yields is considered to be cancelled out by conformational transformation, and appreciable temperature dependence of the photostationary conversion above T_g was not observed.

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